

Covalently Linked Dyads and Triads of Phthalocyanines and Porphyrins

Ateyatallah Aljuhani

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Declaration

The research described in this thesis is, to the best of my knowledge, original except where due reference is made.

Ateyatallah Aljuhani.

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Abstract

The phthalocyanines are a family of intensively coloured compounds, with some important properties and are classified as important materials for many applications. Structurally, a phthalocyanine is similar to a porphyrin. In chapter one, a brief introduction of their synthesis, properties, and applications is given along with some examples of phthalocyanine dimers. The preparation of new functionalised phthalocyanine and porphyrin compounds has been the subject of intense research over the last three decades in order to develop new commercial applications. Numbers of phthalocyanine and porphyrin dimers and oligomers have been generated using a variety of linkages. The first aim of this project to synthesise a chromophore (a zinc phthalocyanine) linked to the *meso*-position of the porphyrin core via a flexible spacer. The synthesis of such models presents several challenges due to very long synthetic routes and tedious separation using currently available methods. To achieve this a range of reactions was explored with the aim of attaching a 1,6-hexanediol linker at the peripheral position of the phthalocyanine. The second aim was to prepare a dimer of phthalocyanine material with enforced communication between the phthalocyanines. This dimer was eventually achieved by oxidative Eglinton coupling of the corresponding monomeric phthalocyanine ethyne. The third aim was to synthesise a dinitrobenzene-bridged bis-macrocyclic system such as between a phthalocyanine and porphyrin in order to investigate chemistry which could be applicable to a variety of metallo- and free-base porphyrins and phthalocyanines. The fourth aim was synthesis of a trimeric porphyrin with flexible linkages and different metal centres (to allow further selective complexation). All the results of this synthesis are presented together in chapter 2, and the detailed experimental and characterisation appears in chapter 3.

Abbreviations

λ	wavelength
Å	Angström
°C	Degree Celsius
d	Doublet
DCM	Dichloromethane
dd	Doublet of doublets
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DBN	1,5-Diazabicyclo(4.3.0)non-5-ene
DMAE	dimethylethanolamine
Et	Ethyl
Et ₂ O	Diethyl ether
h	Hour
Hz	Hertz
IR	Infrared
<i>J</i>	Coupling constant in Hertz
K ₂ CO ₃	Potassium carbonate
LC	Liquid crystal
M	Molar
m	Multiplet
M.p	Melting point
M ⁺	Molecular ion peak.
MALDI-MS	Matrix associated laser desorption ionization mass spectrometry.

Me	Methyl
MEM	2-Methoxyethoxymethyl
min	Minute
mmol	Millimole
MPc	Metal Phthalocyanine.
NLO	Nonlinear Optical
NMR	Nuclear Magnetic Resonance Spectroscopy
Pc	Phthalocyanine.
PcH ₂	Metal-free phthalocyanine.
PET	Petroleum ether
Ph	Phenyl
PN	1,2-Dicyanobenzene or (1,2-Phthalodinitrile).
ppm	Parts per million
rt	Room temperature
s	Singlet
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TPP	Tetraphenylporphyrin
MsCl	Methanesulfonyl chloride
UV-Vis	Ultra violet-Visible
δ	chemical shift in parts per million (ppm)
ε	molar extinction coefficient

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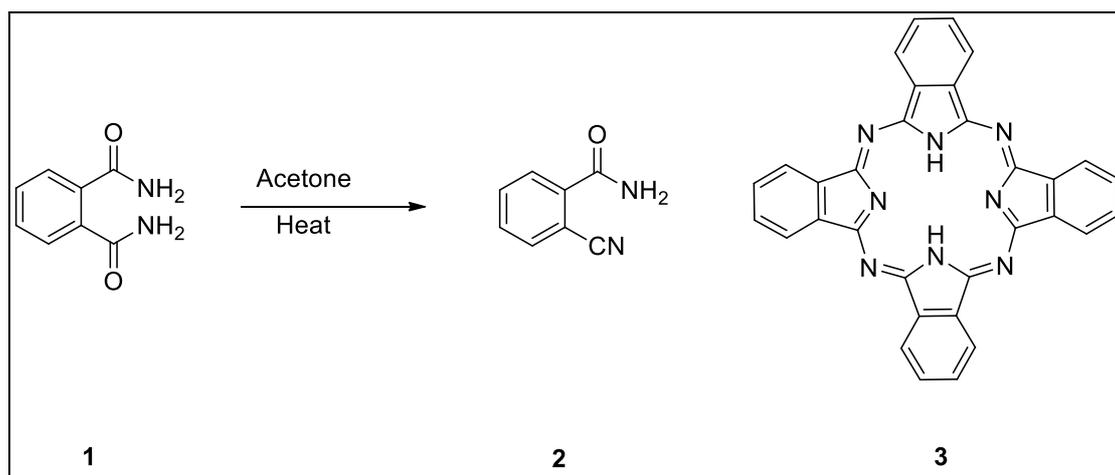
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CHAPTER 1

Introduction to Phthalocyanines

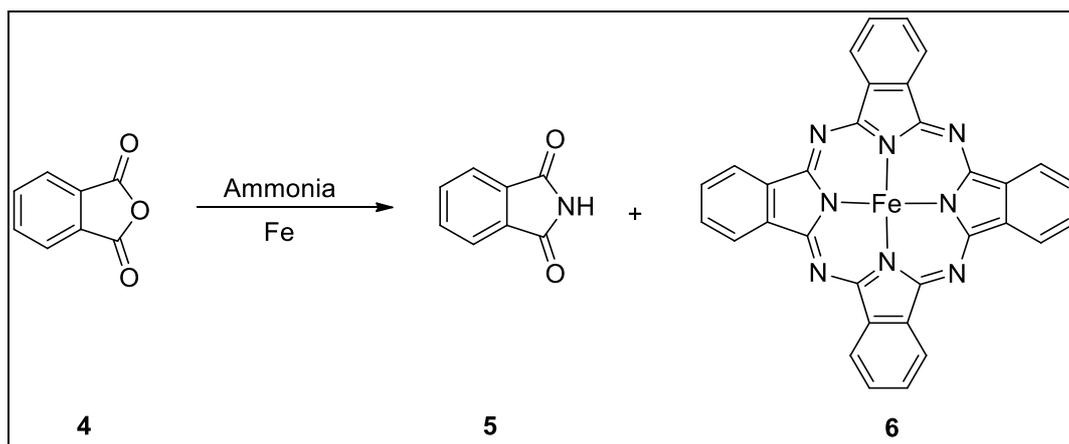
1.1 History of Phthalocyanines

Phthalocyanines (Pcs) are man-made macrocyclic molecules. The first metal-free phthalocyanine **3** was accidentally discovered by Braun and Tcherniac in 1907 as a by-product during the preparation of ortho-cyanobenzamide **2** from phthalamide **1** in acetone (Scheme 1).¹ However, no attention was given to the discovery at that time. Later, in 1927, De Diesbach and Von der Weid were the next to report the preparation of a phthalocyanine. It was discovered during the cyanation of ortho-dibromobenzene with copper(I) cyanide in an attempt to make a phthalonitrile.² A blue product was obtained, which was identified as copper phthalocyanine.²



Scheme 1: First synthesis of metal-free phthalocyanine.

At Scottish Dyes Limited, the third observation of a phthalocyanine **6** was made in 1928. The observation was made by chance during the preparation of phthalimide **5** from phthalic anhydride **4** and ammonia (Scheme 2).³ The product mixture contained traces of a dark blue compound, which was later shown to be iron phthalocyanine.³ The blue product was a direct result of the iron vessel used in the production process.³



Scheme 2: Synthesis of iron phthalocyanine.

This phthalocyanine compound was investigated meticulously by Linstead.⁴ He was the first to use the term phthalocyanine,⁴ deriving the name from the Greek words naphtha (rock oil) and cyanine (blue). In subsequent years, using a variety of analytical techniques, the structure of phthalocyanine as well as procedures for obtaining several metal and metal-free phthalocyanines (Pcs) were clarified.⁵ Robertson later confirmed Linstead's structure by using X-ray crystallography, showing that the Pc molecule is planar rather than three-dimensional.⁶

1.2 Structure of Phthalocyanines

Phthalocyanine **3** belongs to the tetrapyrrole macrocycle class, with the structure containing an alternating nitrogen atom-carbon atom ring. This class includes porphyrins **7** and porphyrazines **8**.⁷

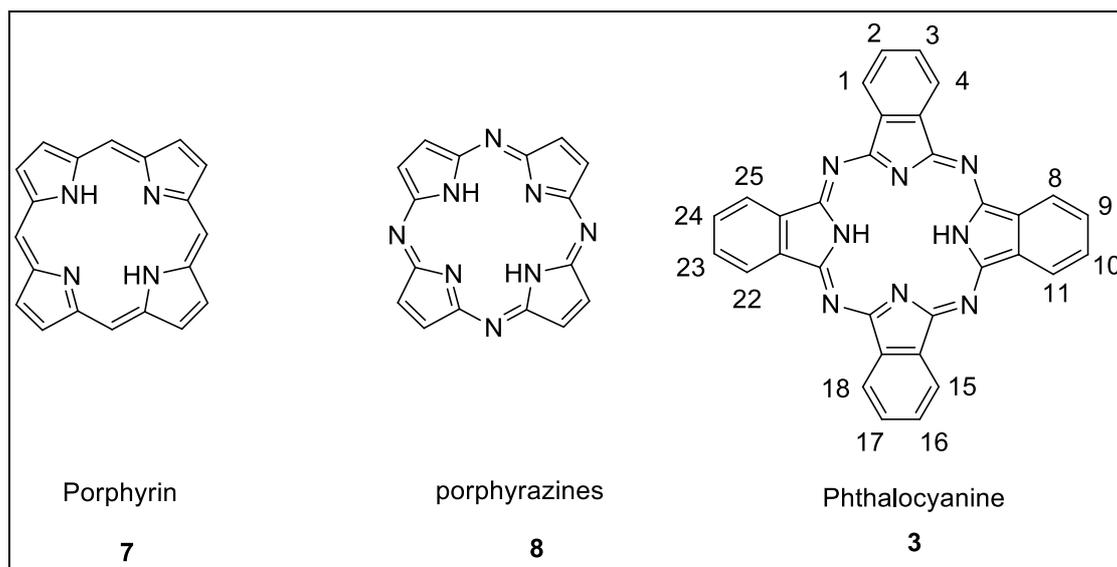


Figure 1: Molecular structures of tetrapyrrole macrocycles.

Phthalocyanines **3** are made up of four isoindoline units linked together at the 1,3- positions by aza bridges. Pcs possess high optical absorption, along with synthetic flexibility as well as thermal stability. The molecule has a conjugated, 18 π -electron aromatic planar structure. This π system, which is delocalized over alternate carbon and nitrogen atoms, provides the unique chemical and physical properties attributed to Pcs. Pcs become an important class of materials for second and third-order nonlinear optics because of their versatility, exceptionally high thermal stability, architectural flexibility, ease of processing and fabrication.⁸ Phthalocyanines are found to exhibit a variety of efficient nonlinear optical effects,^{9,10} this large nonlinearity originates^{9,10} from their extensively delocalised two dimensional 18 π -electron distribution¹¹ and they can contain low-lying energy states due to metal-to-ligand and ligand-to-metal charge transfer.¹² In addition, there are 16 possible sites of substitution on the fused benzene rings, which allow incorporation of different substituents on the *peripheral* or *non-peripheral* positions. The positions 1,4,8,11,15,18,22,25 are call *non-peripheral* while 2,3,9,10,16,17,23 and 24 are known as *peripheral* or β -position¹³ in the ring as outlined in Figure 1.

Pcs can host different elements in the central cavity, with more than 70 different metals having been incorporated in the phthalocyanine core,¹⁴ forming metallo-phthalocyanines (MPcs). The presence of a metal atom in the Pc central core allows for axial ligation. Axial substitution in Pc complexes generally increases solubility, reduces molecular aggregation and evokes relevant changes to the electronic structure of the molecule by altering the π -electron distribution attributed to the dipole moment of the central metal–axial ligand bond.¹⁵ The coordination of the Pc ligand with metal and metalloid elements results in an alteration of molecular conformation and several conformations are known.¹⁶ The most common conformations are planar, ruffled, waved, domed, and skew domed. Pcs metallated with heavy metals show a domed conformation.^{16,17} The essentially planar conformation of Pcs can also be distorted by substituents alone, through conformational stress.¹⁸

1.3 Absorption spectra of phthalocyanines

The absorption spectra are one of the essential techniques for the identification of phthalocyanines. There are five main absorption bands specified to the phthalocyanine structure. They are referred to as Q, B (or Soret), N, L and C bands.¹⁹ The lowest energy absorption, the Q bands, originates from a π - π^* transition.²⁰ The purity and intensity of phthalocyanines' colour arises from an isolated and intense band (Q-band) at the red end of the visible spectrum of light, between 650 and 720 nm approximately. A second band (B-band) appears as a broad band between 300 and 400 nm, being generally less intense (Figure 2). The N, C, and L bands which appear at higher energy than the Soret band are not often used in the analysis of phthalocyanine structures.¹⁹ In the spectra of metal phthalocyanine solutions, the intense Q-band arises from doubly degenerate π - π^* transition between the A_{1g} (a^2_{1u}) ground state to the first excited singlet state, which has E_u ($a^1_{1u}e^1_g$) symmetry. The second allowed π - π^* transition (B-band) is caused by a transition between either an a_{2u} or a

b_{2u} orbital to the e_g orbital (LUMO).²¹ In the case of metal free phthalocyanines all states are non-degenerate, due to the reduced D_{2h} molecular symmetry. The Q-band is polarised in either the x or y direction and is therefore split into two bands.²²

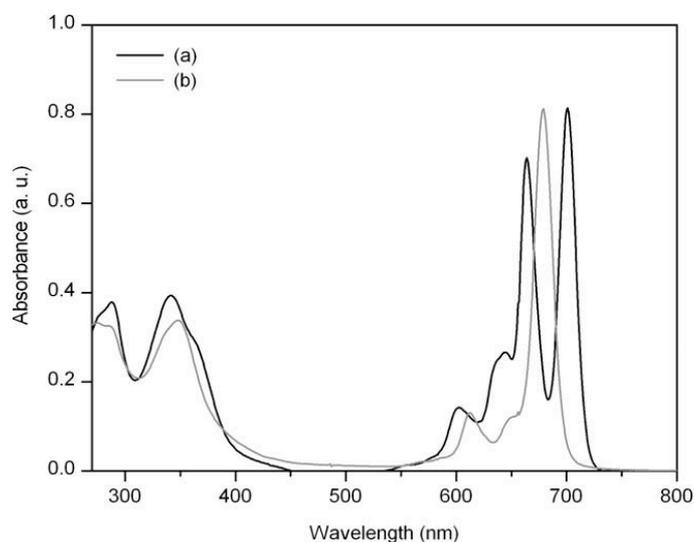


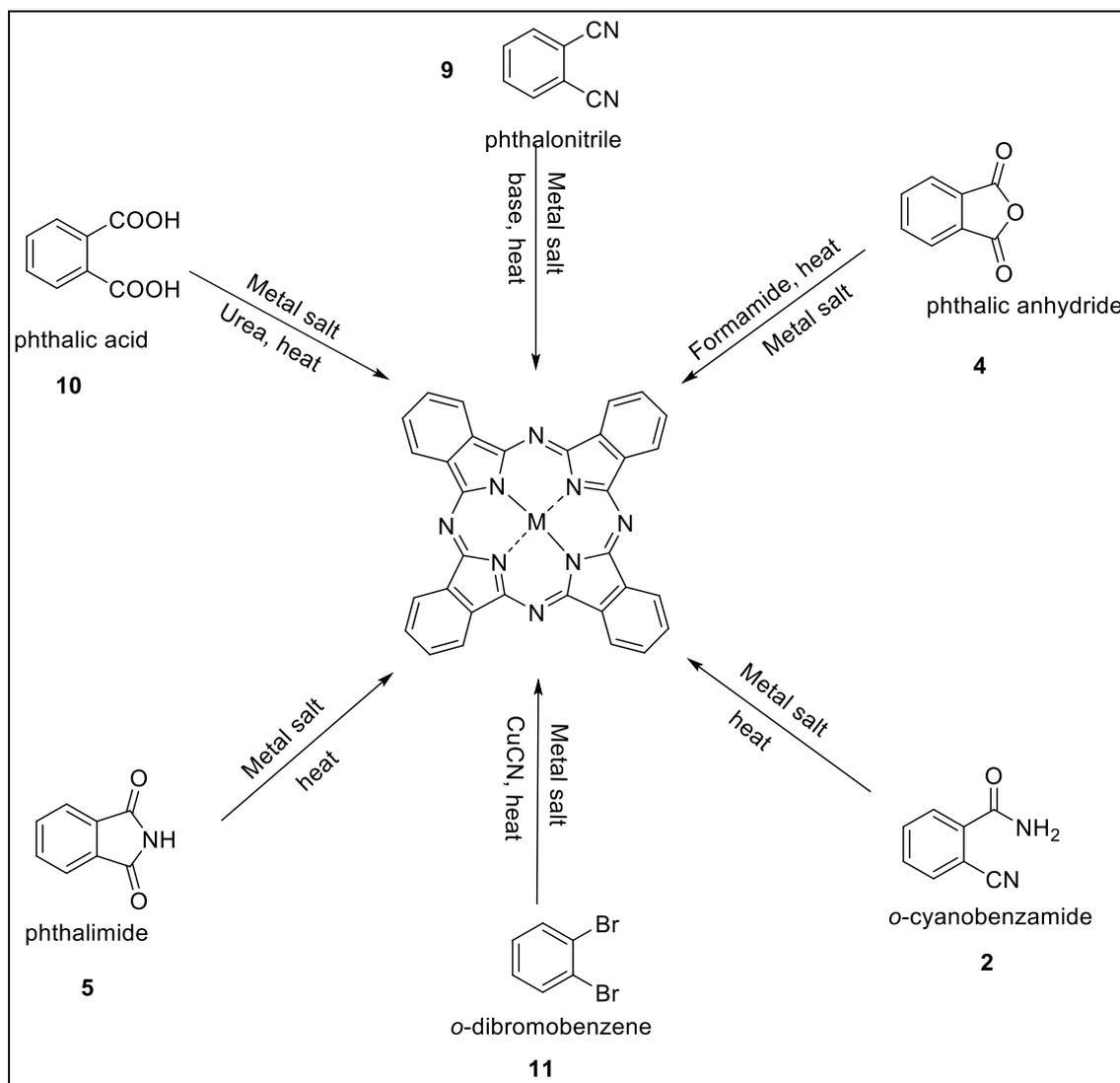
Figure 2: Typical UV-vis spectra for a phthalocyanine as (a) a free-base and (b) a metal complex.²³

1.4 Synthesis of Phthalocyanines

In general, phthalocyanines are prepared by cyclisation of four 1,2-disubstituted benzene units. There are two main methods to synthesise Pcs via tetramerisation. The first one is synthesis via tetramerisation of a single precursor to prepare the symmetrical Pcs. The second path is synthesis via tetramerisation of two or more precursors. These two paths will be discussed in this introduction.

1.4.1 Synthesis via Tetramerisation of a Single Precursor

A variety of derivatives of *ortho*-substituted benzene can serve as precursors in the synthesis of Pc macrocycles (Scheme 3). The precursors include phthalic anhydride, phthalic acid, phthalonitrile, phthalimide, diiminoisoindoline, *o*-cyanobenzamide, *o*-dibromobenzene and cyclohex-1-ene-1,2-dicarboxylic anhydride, among others. Phthalonitriles are popular for laboratory syntheses due to better yields, while phthalic anhydride is used in mass production, as it is relatively cheap.²⁴ Preparing Pcs via phthalonitriles mostly requires heating with a metal template in a high boiling point solvent such as pentanol. The advantage of phthalonitrile as a precursor is that it readily gives good yields of Pc complexes with most metals except mercury and silver, while other precursors such as phthalimide and other phthalic acid derivatives often give unreliable results.²⁵



Scheme 3: Synthetic routes to metallophthalocyanines (MPcs) from various precursors.

Unsubstituted metal-free Pcs (H_2Pc) can be prepared using the Linstead method.²⁶ Here the reaction of a phthalonitrile with lithium, sodium or magnesium alkoxide in a high boiling alcoholic solvent forms an alkali metal Pc. The Pc can then be demetallated by adding a dilute acid to obtain H_2Pc . The latter can also be converted into MPcs by refluxing in the presence of metal salts.²⁷ The Tomoda method, a simple and direct route to the synthesis of Pcs by heating phthalonitrile with catalytic amount of DBU or DBN in the presence of a metal salt, was reported in the 1980s.^{28,29} This route provides a good yield in the case of H_2Pc of up to 70%, and 80% for metallated Pcs. Strong organic bases such as DBU and DBN

(Figure 3) generally promote the formation of Pcs in higher yields, while weaker ones such as TEA and pyridine do not favour the formation of Pcs.

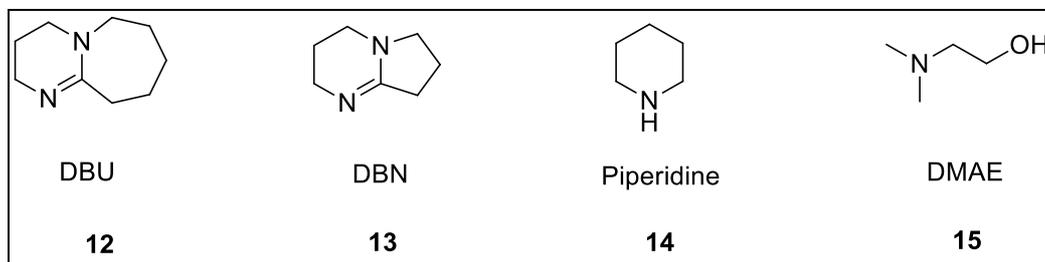
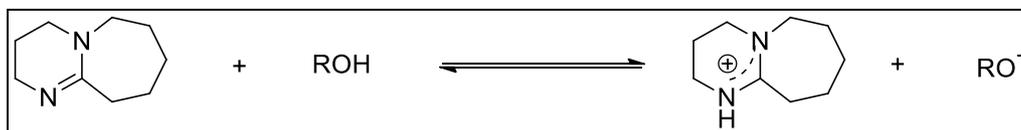


Figure 3: Structures of common organic bases used in Pc synthesis

Tomoda *et al.* proposed that the strong base is a proton acceptor, generating an alkoxide in the process (Scheme 4).²⁸ The resulting alkoxide then acts both as the nucleophile and reducing agent.³⁰ The alkoxide reacts with cyano group of a phthalonitrile, forming an alkoxyisindoline intermediate, which rapidly tetramerises and cyclises to form a Pc.

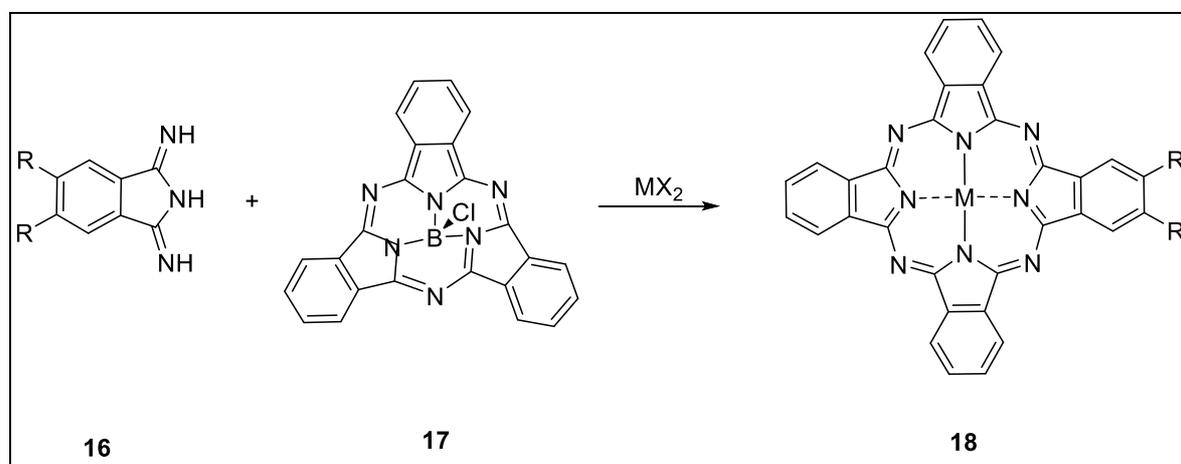


Scheme 4: Formation of alkoxide anion (RO⁻) in preparation of Pcs.²⁶

1.4.2 Synthesis via tetramerisation of two or more precursors

The unsubstituted and many of the substituted Pcs reported in the literature are symmetrical compounds. However, the inherent symmetry is a limitation for many purposes.³² The synthesis of Pcs with different substituents can lead to interesting properties and applications as well. Some of these properties are improving the solubility and reactivity at the same time.^{31,33-35} Many of the products from the reaction of two or more different phthalonitriles

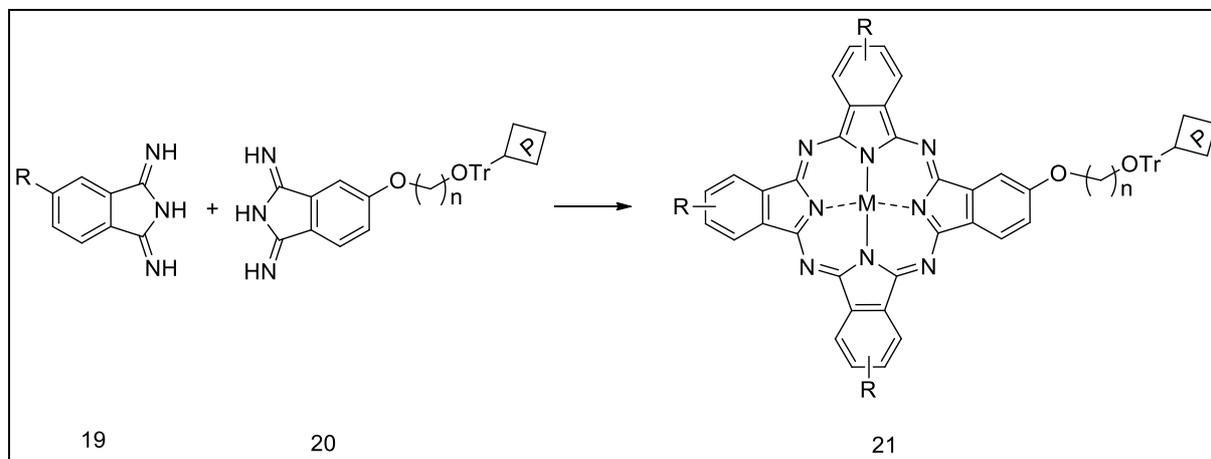
are present as a statistical mixture of Pcs. However, if the precursors are themselves symmetrical, then product ratios may change significantly. Various protocols for the tetramerisation of two or more phthalonitriles have been reported in the past. In the late 1980s, Kobayashi and co-workers reported the synthesis of unsymmetrical Pcs (A_3B -type), through ring expansion of a subphthalocyanine in the presence of succinamide or diiminoisoindoline derivatives (Scheme 5).³⁶ The only disadvantage of this method, in many cases, is the fragmentation of the subphthalocyanine ring followed by statistical ring closure to form a mixture of all possible Pcs.^{37,38} The reactant's properties and reaction conditions play an important role in the ring expansion. In other words, the best yield could be gained when a metal template is used and by selectively choosing the substituents on the precursors. For example, subphthalocyanines without substituents or with electron-withdrawing groups, and diiminoisoindoline derivatives with electron donating groups resulted in better yields.^{39,40}



Scheme 5: Selective synthesis of A_3B -type Pc.³⁸

In 1982, Leznoff and co-workers developed an alternative approach to synthesis A_3B -type Pc derivatives using polymeric support as shown in Scheme 6.⁴¹ In this approach a mono-functionalised diiminoisoindoline precursor **20** bound to solid polymer (P) reacts with another diiminoisoindoline derivative **19**.⁴¹⁻⁴³ The unreacted diiminoisoindoline derivatives

19 and the soluble A₄-type Pc are washed off and the desired Pc is cleaved under mild conditions. However, this is limited to easy on-off properties of the precursor bound to the solid support.



Scheme 6: Synthesis of A₃B-type Pc on polymer support.⁴¹

As mentioned earlier the substituted Pcs resulting from two or more phthalonitriles can be synthesised by statistical condensation methods⁴⁴⁻⁴⁸ of substituted phthalonitriles using appropriate ratio, followed by chromatographic separation of the wanted products. This may be achieved via Tomoda synthesis, just as those obtained from single phthalonitriles. The optimisation of reactant ratios and reaction conditions in this method may lead to a reasonable yield of the target compound, however, the reaction still gives six (Figure 4) different substituted Pcs, not including constitutional isomers.³⁶ The formation of one or two of the major isomers can be improved by the modification of the properties of substituents on the phthalonitriles and optimisation of the reaction conditions. For example in case of formation of A₃B type, the use of one of the phthalonitriles in excess is one such modification that may be favourable. In other cases, half Pcs have been used in the preparation of A₂B₂ Pcs.⁴⁹ The disadvantage of this method is that the separation of constitutional isomers is often difficult, and involves tedious chromatographic procedures.⁵⁰⁻⁵³

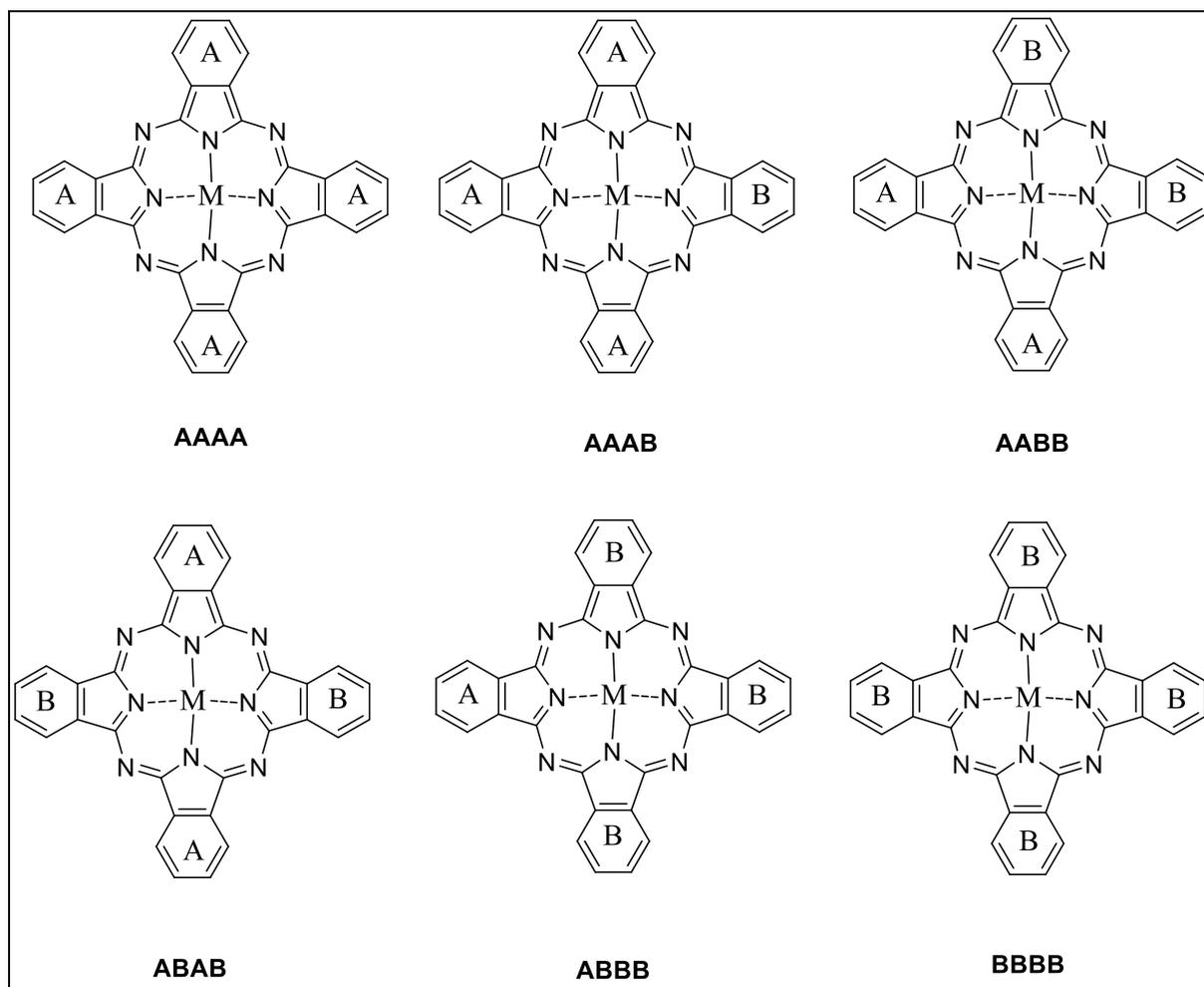


Figure 4: Six differently substituted Pcs formed during mixed condensation of two differently substituted precursors, A and B.³⁶

1.5 Some examples of phthalocyanine dimers

1.5.1 Introduction

During the last two decades, a large amount of phthalocyanine synthetic chemistry research has been undertaken, with special attention on the preparation and the study of a wide variety of phthalocyanine dimers. Basically, the type of linkage between the macrocyclic units plays an important role in classifying the type of dimers. There are different types of dimers such as

covalently linked cofacial dimers, conjugated homo and heterodimers, self-assembled dimeric capsules, linear dimers, or lanthanoid and actinoid sandwich dimers.⁵⁴ These types usually find applications as polynuclear multi-electron transfer catalysts,^{55,56} due to their electrocatalytic properties.⁵⁷ As with mononuclear phthalocyanines, the challenge of dimer preparation is with the synthesis of the appropriately substituted precursors.

1.5.2 Covalently linked cofacial dimers

The synthesis of binuclear “clamshell” metal-free and metallated Pcs was reported by Leznoff and co-worker in 1984. These binuclear Pcs were linked together through a stable five atom bridge.⁵⁸ The soluble binuclear Pc was prepared by the generation of bis(alkyloxy)phthalonitriles from symmetrical diols. Therefore, the treatment of 4-nitrophthalonitrile with 2,2-dimethyl-1,3-propanediol give the 1,3-bis-(dicyanophenoxy)-2,2-dimethylpropane. Afterwards, the conversion of yielded product into its isoindoline analogue was followed by condensation with an excess of the second type of isoindoline to give 1,3-bis(9,16,23-trineopentophthalocyaninoxy)-2,2-dimethylpropane (Figure 5).

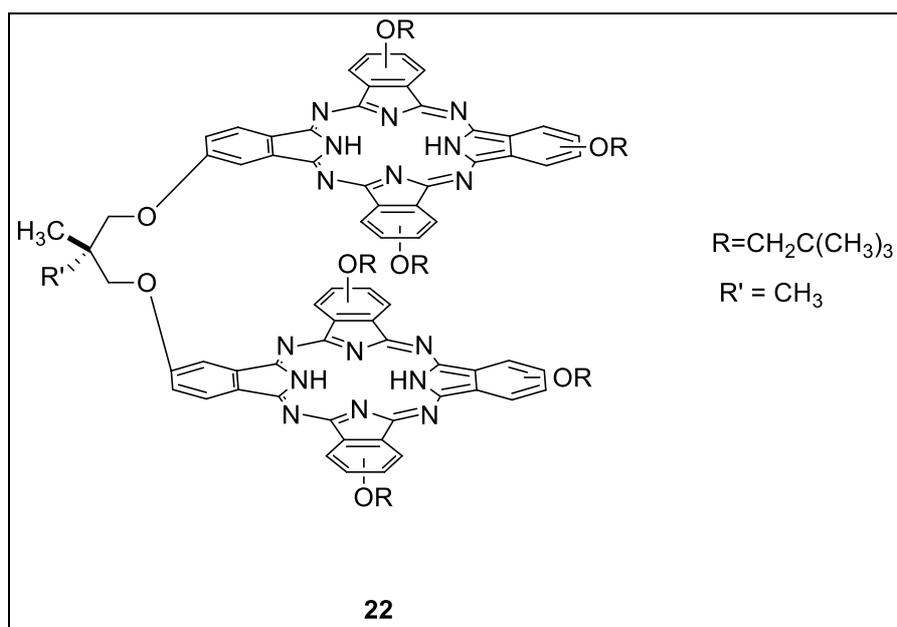


Figure 5: Leznoff's binuclear “clamshell” metal-free Pcs.⁵⁸

As completion of the previous work they managed to synthesise a total series of phthalocyanine dimers linked together by different lengthed chains.⁵⁹⁻⁶¹ Later, in 1987, Leznoff *et al.* described the preparation of cofacial binuclear phthalocyanine linked by triatomic bridge on a rigid naphthalene unit.⁶² They prepared it by a mixed coupling reaction between 4-iodophthalonitrile and 1,8-diiodonaphthalene in the presence of nickel powder to give 1,8-*bis*(3,4-dicyanophenyl)naphthalene. In the same procedure to what they did in the previous work they then converted it into its isoindoline analogue and subsequent mixed condensation gave 1,8-*bis*-2'-(9',16', 23'-trineopentoxypthalocyaninyl) naphthalene (Figure 6). These syntheses were the first examples of covalently linked cofacial dimers.

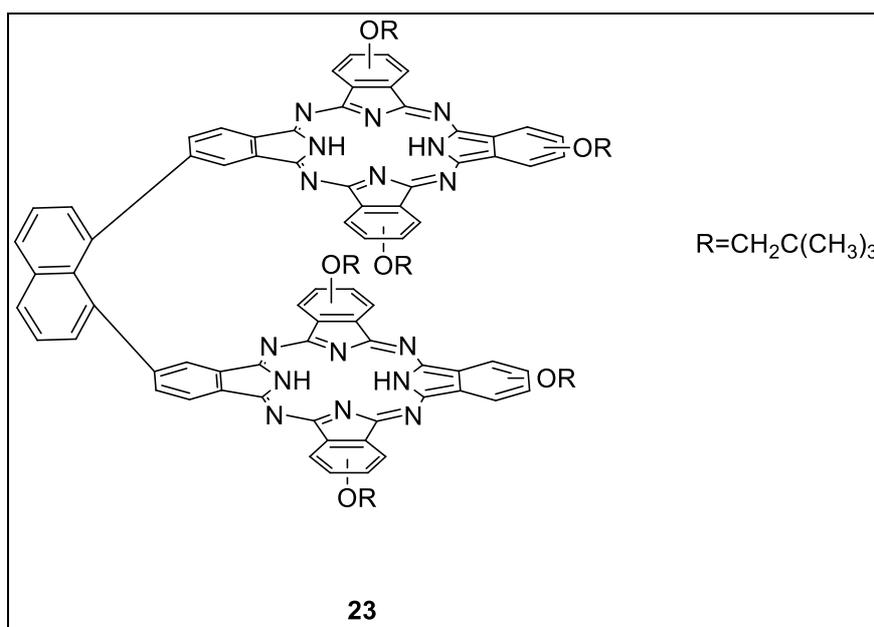
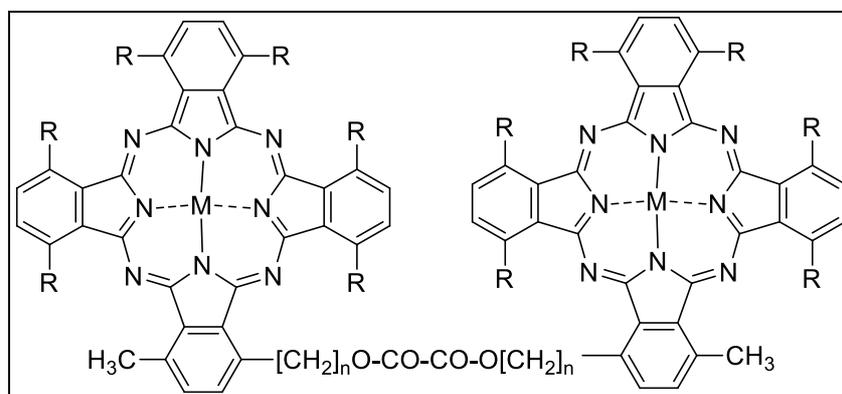


Figure 6: Pcs linked together by a naphthalene spacer.⁶³

At UEA, in 1996, Bryant *et al.* described the synthesis of series of 1-(hydroxyalkyloxy)-4-methyl-8,11,15,18,22,25-hexakis(octyl)phthalocyanine.⁵⁸ The compounds displayed liquid crystalline properties.⁶³ Also, the same materials have been used as precursors for the preparation of di- and tri-nuclear phthalocyanines linked by oxalyl ester groups (Figure 7).

They report that all the multinuclear Pcs except one showed liquid crystal behaviour. Such compounds were also deposited as spin coated films which may find application within gas sensing devices.⁶⁴



M	N	R
H ₂	3	C ₈ H ₁₇
H ₂	4	C ₈ H ₁₇
H ₂	5	C ₈ H ₁₇
H ₂	6	C ₈ H ₁₇
H ₂	8	C ₈ H ₁₇
Cu	5	C ₈ H ₁₇

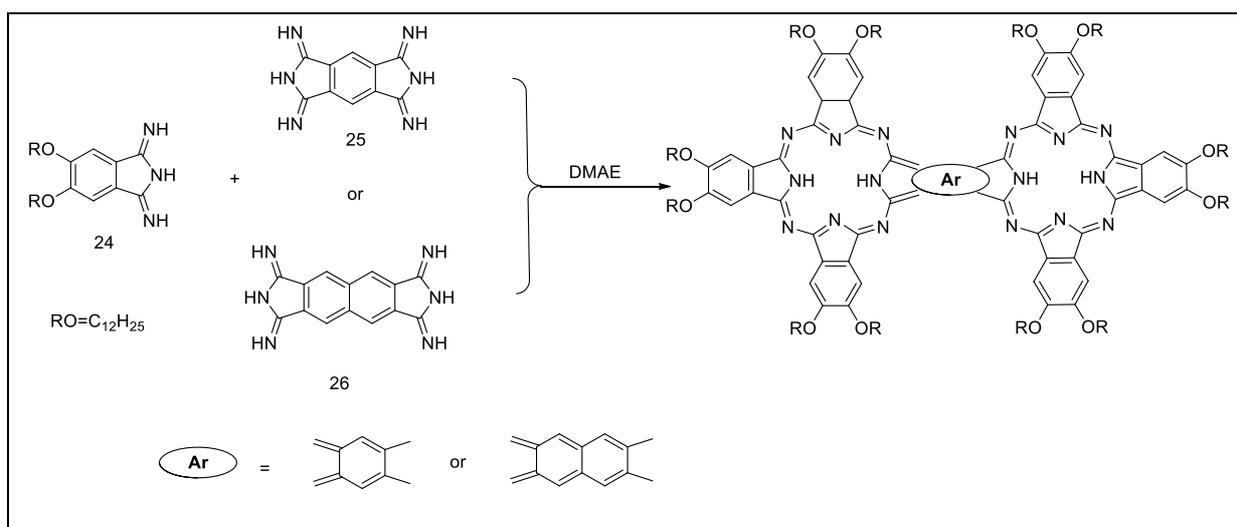
Figure 7: Bryant's phthalocyanine dimers exhibiting liquid crystal behaviour.⁶⁴

1.5.3 Conjugated homo and heterodimers

1.5.3.1 Homodimers sharing a common aromatic ring

The first example of covalently linked symmetrical binuclear Pcs was reported by Van de Mark *et al.* In this example the symmetrical binuclear Pcs are covalently linked by sharing a

benzene or naphthalene ring.⁶⁵ The synthesis required preparation of didodecyloxyphthalonitrile⁶⁶ in three stages. The first stage was the alkylation of catechol followed by dibromination and a Rosenmund-Von Braun cyanation reaction.⁶⁷ After preparation of the second precursors **25** and **26**,⁶⁵ the final step involved the synthesis of symmetrical binuclear Pcs by mixed condensation of the derivatives **25** or **26** with the diiminoisoindoline **24** derived from didodecyloxyphthalonitrile to give the binuclear Pc as illustrated in Scheme 7:



Scheme 7: Binuclear Pcs covalently linked by sharing a benzene or naphthalene ring.⁶⁵

1.5.3.2 Homodimers and heterodimers linked by alkynyl spacers

Covalently linked binuclear Pcs are attracting attention because of the interesting effects arising from the further extension of the π conjugation.⁶⁸ In 2000, Cook and Heeney reported an example of conjugated planar homodimer.⁶⁹

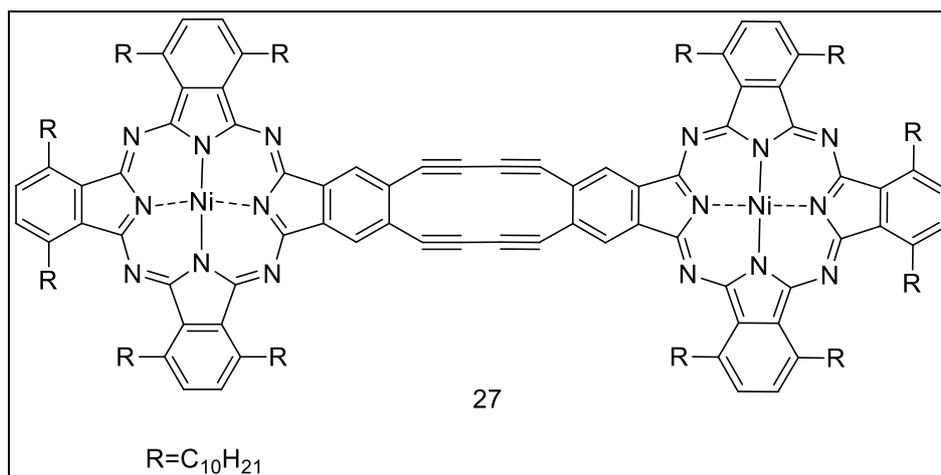


Figure 8: Heeney's diphthalocyaninyl-dehydro[12]annulene.⁶⁹

An oxidative coupling of dialkynylphthalocyanine⁶⁸ was used to synthesise this diphthalocyaninyl-dehydro[12]annulene shown in Figure 8. A report that such annulenes are polymerisable at the diyne unit^{70,71} indicates that phthalocyanino-dehydroannulenes could act as useful precursors for the syntheses of novel phthalocyanine network polymers but no further reports have emerged.

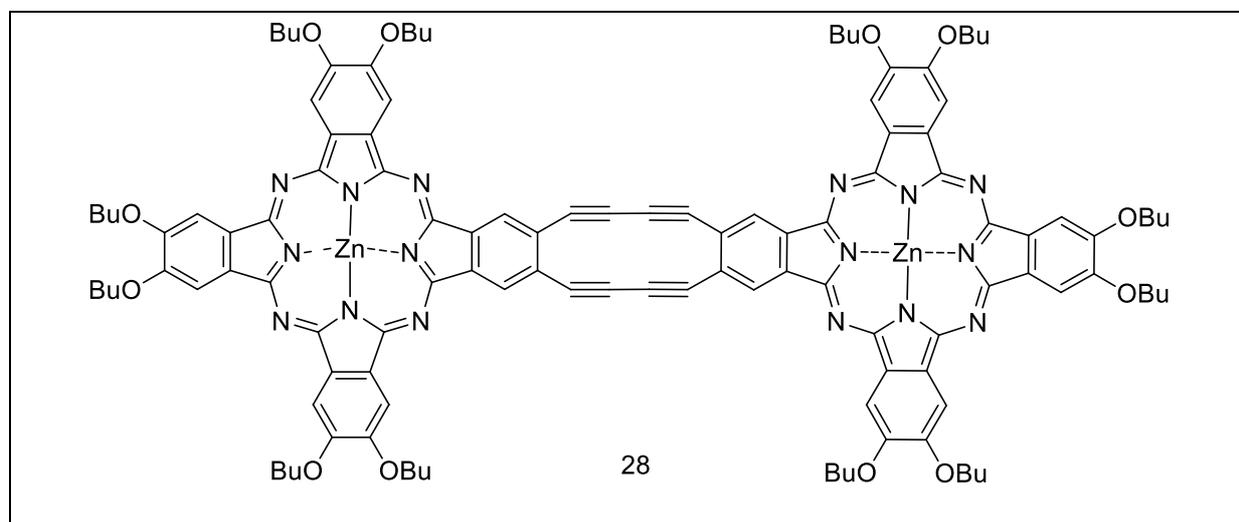


Figure 9: Torres' diphtalocyanino-dehydro[12]annulene.⁷²

Similar preparation of cyclooligomeric phthalocyanines with a dehydroannulene core was reported by Torres *et al.*⁷² (Figure 9). The dimer and trimer were prepared via oxidative coupling mediated by copper from the unsymmetrical diethynyl substituted phthalocyanines.

1.5.3.3 Homodimers linked by metals

The dimerisation of a phthalocyanine analogue containing two pyridine units was reported by Kobayashi and co-worker.⁷³ The two macrocycles are linked to each other by two pyridine-Pd-pyridine bridges as illustrated in Figure 10.

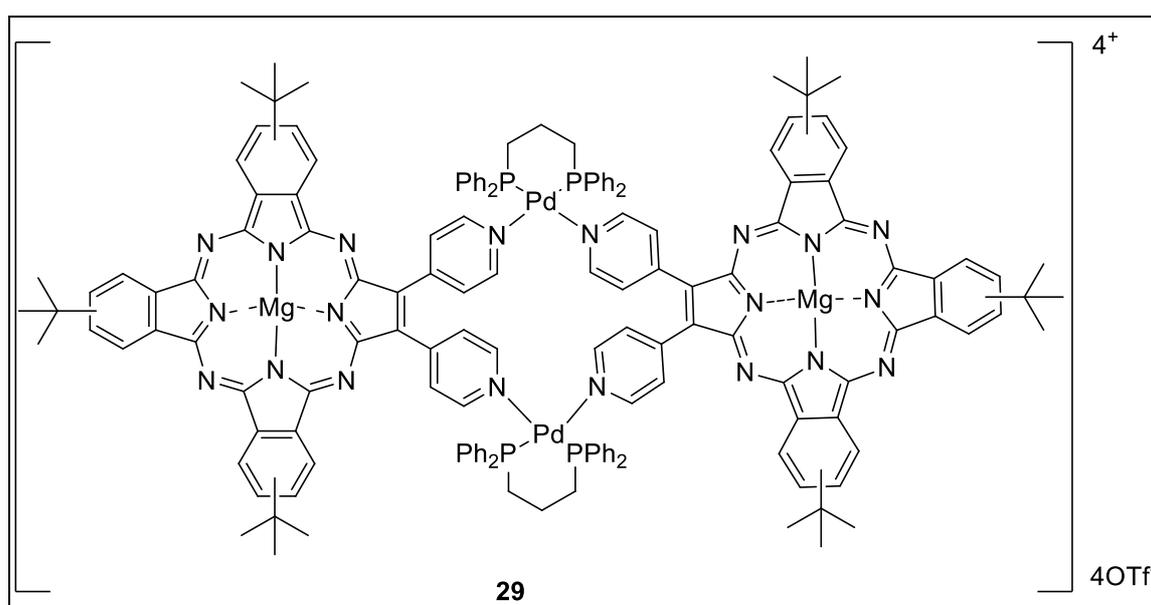


Figure 10: Kobayashi's dimer.⁷³

Molecular models suggested that the dimer should be almost planar.⁷³ In order to produce the target molecule, the monomer was prepared by cross-cyclotetramerisation reaction of 4-*t*-butylphthalonitrile and 2,3-di(4-pyridyl)-2,3-dicyanomaleonitrile. Then, the produced monomer was reacted with the bis-triflate salt of 1,3-bis(diphenylphosphino)propane palladium(II) to obtain the target dimer.

1.5.4 Dimeric sandwich compounds

Pcs can be used as macrocyclic tetradentate ligands for a wide variety of metals.⁷⁴ Complexation with large metal ions such as lanthanides or actinides gives sandwich-type complexes.⁷⁵ These types of complexes have important applications.⁷⁶ These applications include as gas sensors, electrochromic displays, photoconductors and field-effect transistors.⁷⁷

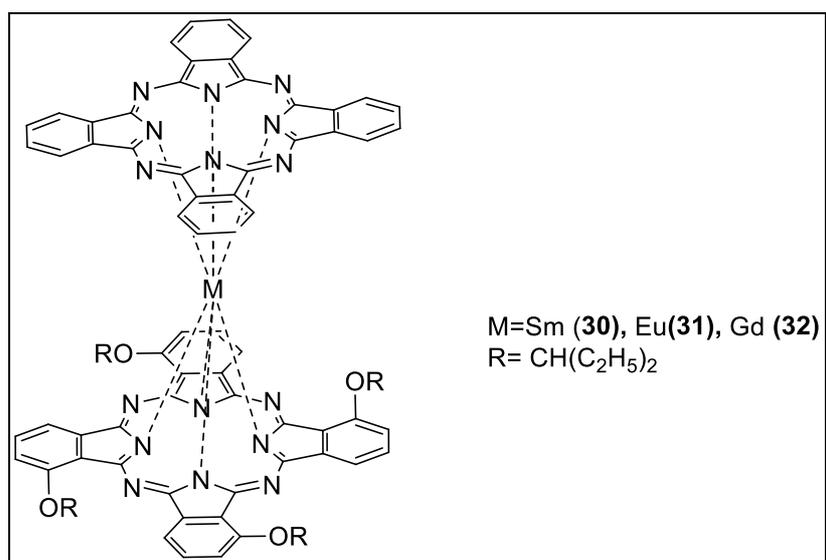


Figure 11: Unsymmetrical dimeric sandwich compound.⁷⁸

An example of this material was reported by Ng and co-workers. They described the preparation of mixed double-deckers $M(\text{Pc})[\text{Pc}(\text{OC}_5\text{H}_{11})_4]$ where M is Sm, Eu, Dd.⁷⁸ The synthesis of this type of dimers have two steps. The first stage involved the treatment of $M(\text{acac})_3 \cdot n\text{H}_2\text{O}$ with LiPc in 1,2,4-trichlorobenzene which produces the first half of the sandwich. This half then reacts further *in situ* with the metal free 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine to produce the mixed double-decker $M(\text{Pc})[\text{Pc}(\text{OC}_5\text{H}_{11})_4]$ which is shown in Figure 11.

1.6 Mechanism of Phthalocyanine Formation

Despite all suggestions made for the reaction mechanism, the mechanism is not fully understood since it is complex and involves many intermediates. There are generally different suggested mechanisms for the phthalocyanines formation depending on the starting materials and the reaction promoters.⁷⁹

The first scientist who was interested in the study of phthalocyanine formation was Sander.⁷⁵ He said the cyclisation depended on the intermediate formation shown in Figure 12.

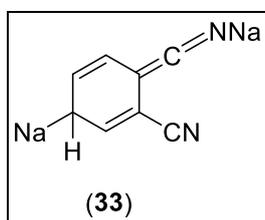
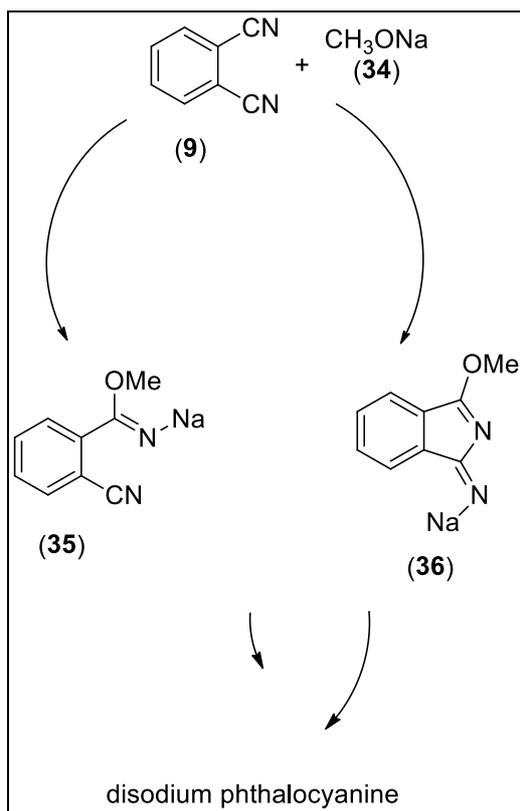


Figure 12: Sander's intermediate.

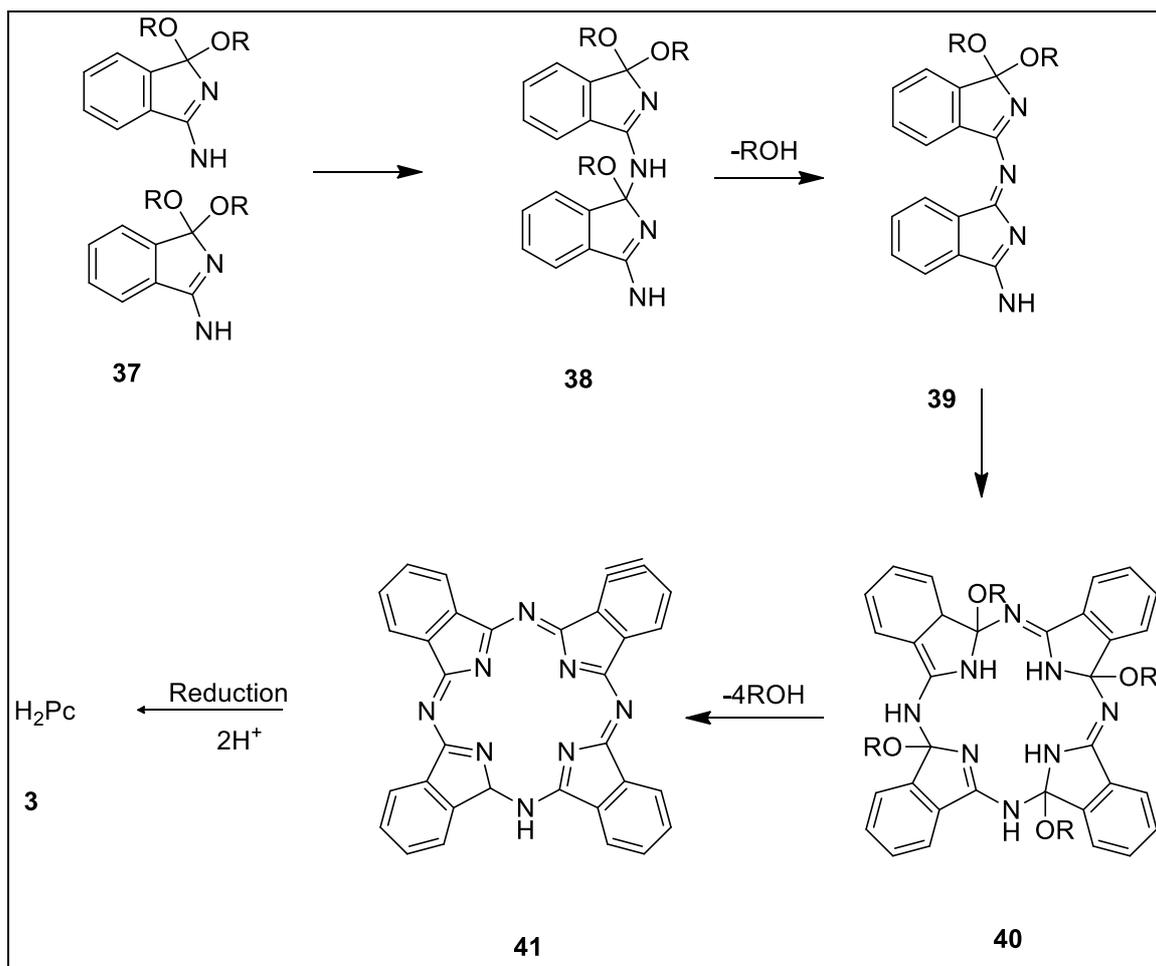
He proposed that the intermediate is formed from phthalonitrile using butanol and sodium metal and then cyclotetramerises to forming the corresponding Pc.⁸¹ However, Borodkin⁸² had some questions about Sander's intermediate and then he proposed that formation of Pc is dependent on formation of another intermediate as shown in Scheme 8



Scheme 8: Borodkin's intermediate.⁸²

It was proposed that generation of the intermediate by the reaction of the phthalonitrile and the methoxide leads to formation the methoxyiminoisoindoline.⁸²

A new cyclisation mechanism was proposed by Baumann.⁸³ The cyclisation takes place by way of the formation of a dialkoxide intermediate as shown in Scheme 9.



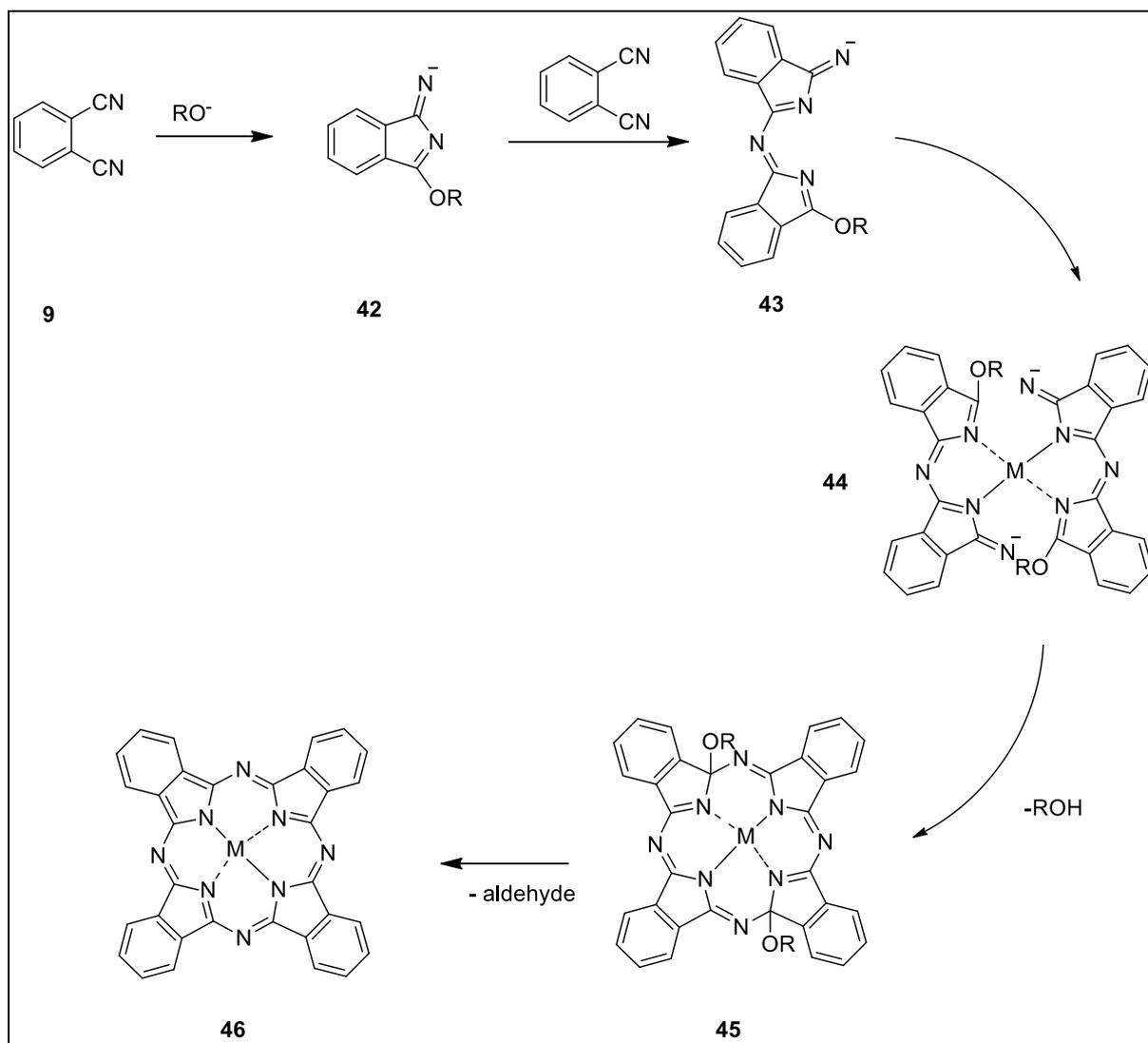
Scheme 9: Mechanism proposed by Baumann et al.⁸³

In 1977, Baumann *et al.*'s mechanism was supported by Pankertonova *et al.*,⁸⁴ and in 1990 again by Chambrier and Cook.⁸⁵ They confirmed the function of the dialkoxy intermediate.

Initial reaction forms the salt of the methoxyisindoline, followed by condensation of two units, and then in the last two stages the macrocycle closes.

In 1987, another mechanism was proposed by Oliver and Smith (Scheme 10).⁸⁶ Initial reaction is the deprotonation of the solvent (alcohol) by some basic promoters such as DBU or DBN resulting in strong nucleophilic alkoxide species, which has important role in the cyclisation and the final ring closer. The next step was attack of the phthalonitrile by the alkoxide followed by the production of intermediates which are suggested to condense or add

further phthalonitrile to form a dimer. Two dimers then surround metal-ion template to form the tetramer intermediate, which loses aldehyde and forms phthalocyanine molecule (PcM).



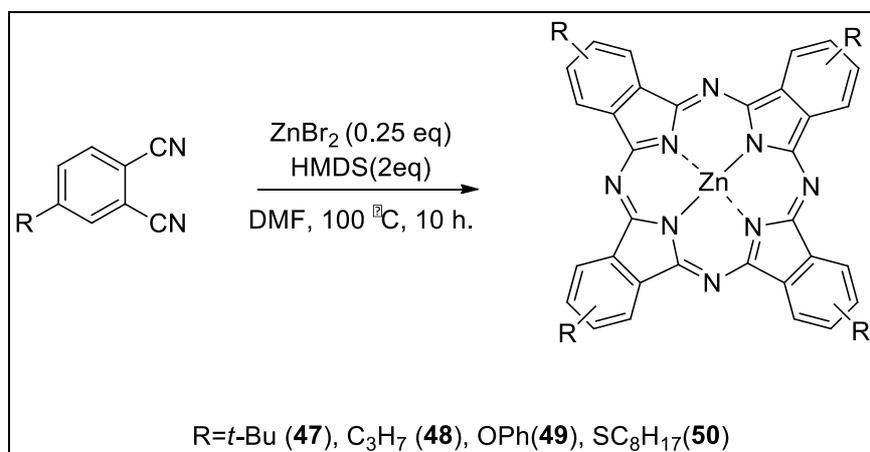
Scheme 10: Mechanism proposed by Oliver and Smith.⁸⁶

In 2002, a new cyclotetramerisation⁸⁷ was reported by Ng and co-workers⁸⁷ called a cerium-promoted formation of metal free phthalocyanine. The new methodology involves the treatment of phthalonitriles with 6 mol% of anhydrous $CeCl_3$ or $Ce(acac)_3$ in 1-pentanol at

160 °C for 24-72 h. Under these conditions, different phthalonitriles including nitro, alkoxy, thioalkoxy, and amino groups were converted into the corresponding metal free phthalocyanine in 20-64% yield. The observation of this methodology is that the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) leads to shorter reaction time and increases the yield of these reactions.

A convenient recent modification of standard preparation of metallated phthalocyanines from phthalonitriles has been accomplished by treatment of the latter with metal salts and hexamethyldisilane (HMDS) in DMF at 100 °C (Scheme 11).⁸⁸

The procedure provides a preparative method using mild conditions and can be applied to phthalocyanines having a variety of metals and substituents. Thus the procedure is compatible with a variety of metals salts such as ZnCl₂, Zn(OAc)₂, Zn(acac)₂, MgBr₂, CuBr₂ and InCl₃.



Scheme 11: Synthesis of Pc under mild conditions.⁸⁸

1.7 Applications of Phthalocyanines

Since their discovery and identification, phthalocyanines have seen a growth in the number of laboratories exploring their fundamental academic aspects and chemistry.

Phthalocyanines are important industrial commodities that have found many applications. They are found as commercial blue and green dyestuffs and pigments. The phthalocyanine macrocycles' properties can be easily modified in two ways. The first way is by incorporation a range of central metals ions, the other is by adding functional groups onto the periphery of the ring system,^{89,90,27,91} or both. The basic use of the phthalocyanines is as pigments because of their intensive colour and the notable stability to light, heat, acid and alkalies, and insolubility in water and organic solvents,⁷⁴ which makes them suitable candidates in printing ink, coatings and plastic. Phthalocyanine is interesting in many other applications, exploiting their electronic structure and redox properties, and their electro- and photocatalytic reactivity. Pcs have non-colorant applications. Potential uses of phthalocyanines include industrial catalysts,^{92,93} e. g for the oxidation of mercaptans and in petroleum⁹⁴ where it is polluted with sulfur compounds; for oxidation of cyclohexane where the oxidation process is done by using the iron perchlorophthalocyanine.⁹⁵ At high temperature, some phthalocyanine derivatives show liquid crystal behaviour.⁹⁶⁻⁹⁸ Thin films of phthalocyanine derivatives can be prepared by deposition from vapour phase, by spin coating, and by transfer of monolayer *via* Langmuir-Blodgett (LB) methods.^{89,19} The fabrication of the thin film phthalocyanine provides formulations of potential value in displays, chemical sensors, and photoconducting devices.⁷⁴ Another application is in optical data storage (computer recordable DVDs).⁹⁹ In agriculture, phthalocyanine is used as a controller of plant growth.¹⁰⁰ In car windscreens, since the Pc compounds can absorb near infrared radiation, they are used as heat shielding in the glass.⁸⁴ Also, phthalocyanines have engaged interest because of photovoltaic,¹⁰¹⁻¹⁰³ and

electrochromic,¹⁰⁴⁻¹⁰⁶ properties. Potential uses of phthalocyanines include nonlinear optical materials (NLO) due to their large nonlinearities, ultrafast response time and easy processability.^{89,107,108} Medical applications exist where some substituted derivatives of phthalocyanines are used as photodynamic reagents for cancer therapy and other medical applications (e. g. Zn and AlPcs).¹⁰⁹

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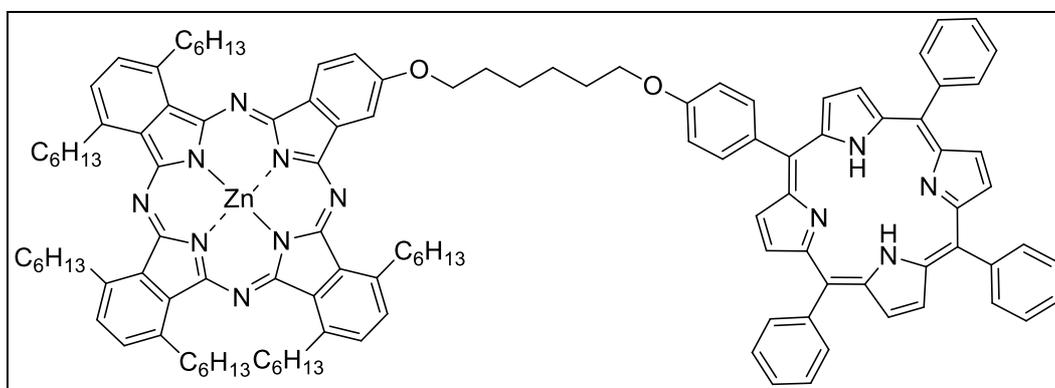
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CHAPTER 2

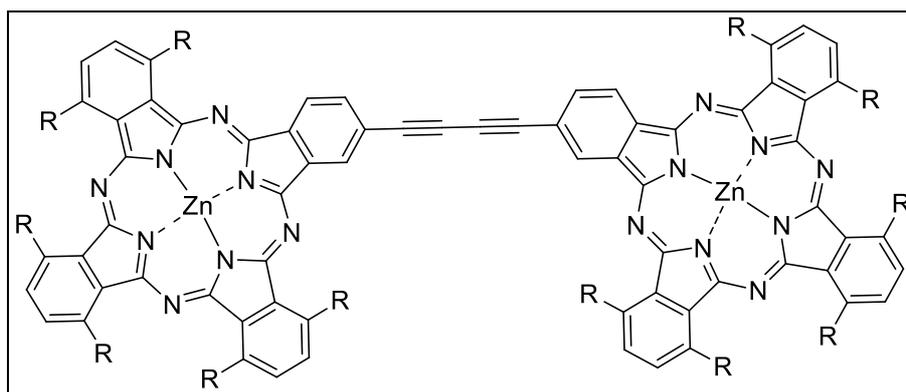
Results and Discussion

2.2 Aim of the project

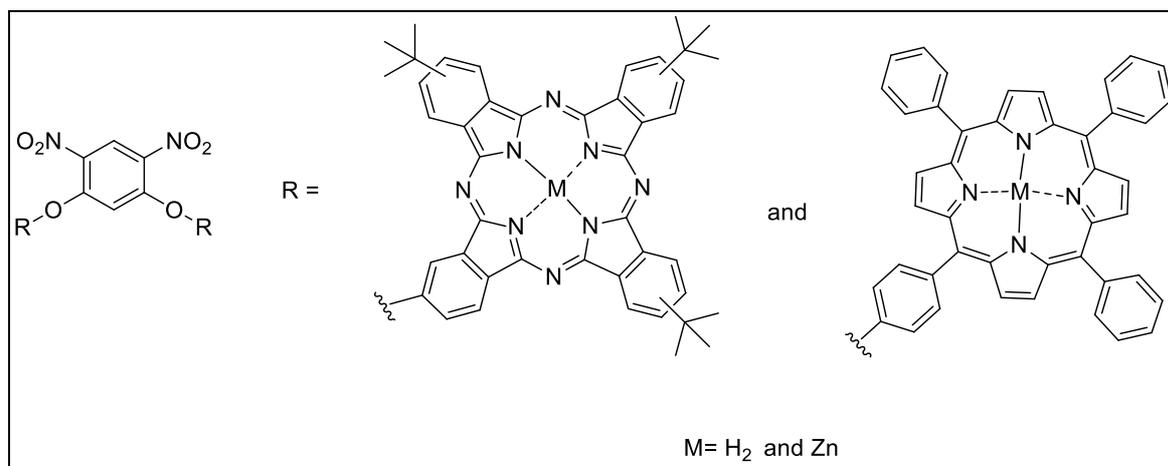
The objective of this work is a synthetic study on two types of dimer. The first type has two different macrocyclic species linked together, and the second one is where identical species (the same macrocyclic species) are linked together. These materials can be linked directly to each other or through a linker which could be either flexible or rigid. A rigid linker such as benzene and its derivatives would provide some control over the phthalocyanine and/or the porphyrins' relative position. A number of phthalocyanine and porphyrin dimers and oligomers have been generated using a variety of linkages. This project therefore had several main aims. The first target was to synthesise and characterise a series of phthalocyanine monomers and dimers with porphyrin. To achieve this, a range of reactions was explored with the aim of attaching a 1,6-hexanediol linker at the peripheral position of the phthalocyanine.



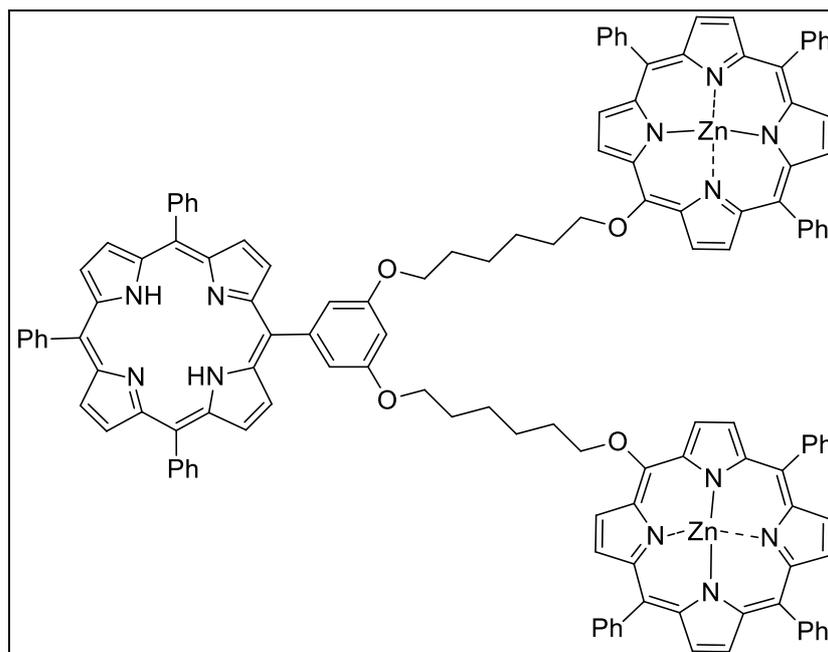
The second aim was to prepare a dimer of phthalocyanine material with enforced communication between the phthalocyanines. The structure considered was two metalated phthalocyanines linked by an alkynyl bridge, which is flat and fully conjugated. In order to investigate the influence of a rigid link on the liquid crystal behaviour of bridged Pcs, two ZnPc rings bound together through a butadiynyl linkage has been targeted. Their synthesis is envisaged as being achieved by oxidative Eglinton coupling of the corresponding monomer.



The third aim was to synthesise a dinitrobenzene-bridged bis macrocyclic system such as between a phthalocyanine and porphyrin. The strategy behind the synthesis of these dimers was to investigate chemistry which could be applicable to a variety of metallo- and free-based porphyrins and phthalocyanines.



The fourth aim was synthesis of a trimeric porphyrin with flexible linkages and different metal centres (to allow further selective complexation).



However, the synthesis of such models presents several challenges due to very long synthetic routes and tedious separation using currently available methods.

2.3 Porphyrins

Porphyrin materials are used as important components in our research work, so there follows a brief introduction about porphyrin synthesis, properties and some applications. Porphyrins are aromatic macrocycles containing a total of 22 conjugated π electrons, 18 of which are incorporated into the delocalised pathway in accord with Huckel's $[4n + 2]$ rule¹⁻³ for aromaticity ($n = 4$). As a result of the extended conjugation, porphyrins absorb light in the visible region and are highly coloured. The porphyrin core, figure 1, is made up of four pyrrole units linked by methine ($=CH-$) bridges with a central cavity sufficiently large to coordinate with metal ions having a maximum radius of 2 \AA .⁴ The metal can be removed from the porphyrin by acidification in most cases.⁵

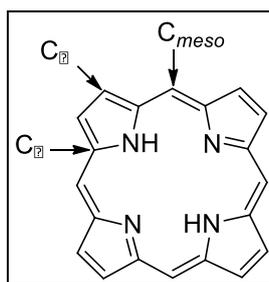


Figure 1: Structure of porphyrin and the types of carbons in the ring.

There are two main types of porphyrin substitution. These types are β -substituted porphyrins and meso-substituted porphyrins (figure 2):

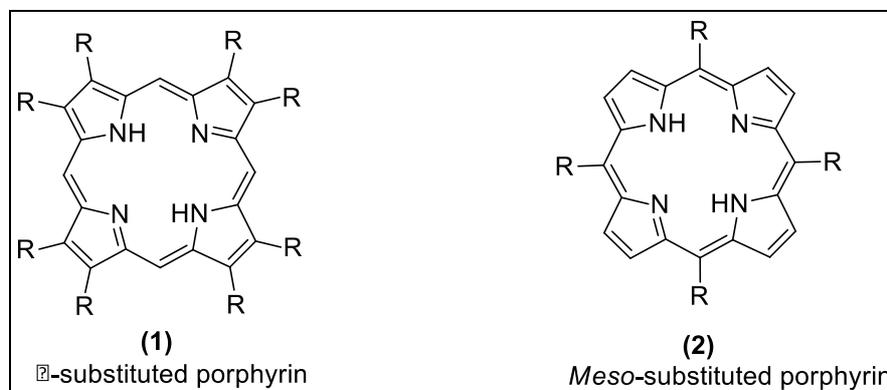


Figure 2: Structure of *meso*-substituted and β -substituted porphyrins

The first type is naturally found in many forms whereas the *meso* substituted porphyrins are the most interesting in synthetic chemistry.⁶ Unsubstituted porphyrin can exist in two different tautomeric structures (figure 3). The computational and spectroscopic calculations show that tautomer (2) which holds two hydrogens on two opposite pyrrole rings, is more stable than the tautomer (4) with two hydrogens at adjacent pyrrole rings.⁷

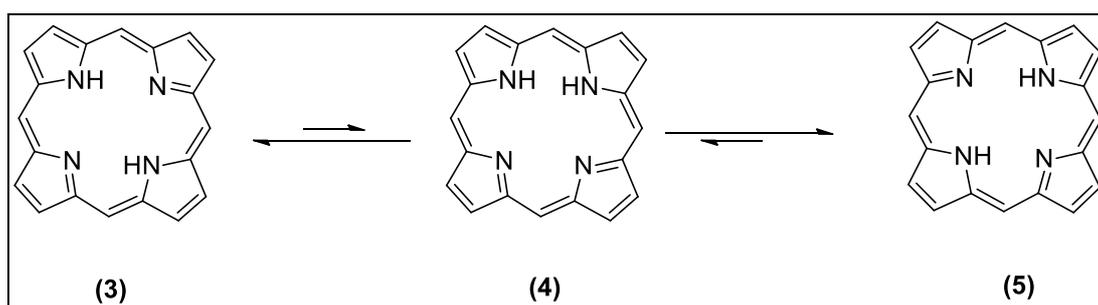


Figure 3: Tautomerisation of porphyrin.

The other four electrons are not formally participating in the delocalization and are located in the peripheral double bonds. These two cross-conjugated double bonds have isolated alkene properties as seen in figure 4.

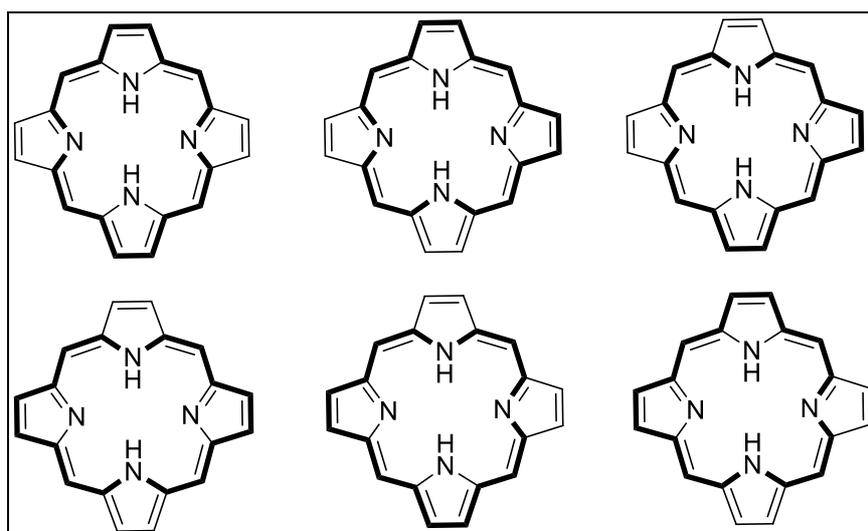


Figure 4: 18 π -Electrons delocalised on the porphyrin ring system.

2.31 Spectroscopic character of Porphyrins

Due to their highly conjugated π system, porphyrins show very characteristic absorption spectra. They show intense absorption around 380 to 420 nm, called the Soret band or B-band, and a few weaker absorption bands in the longer wavelength region (500 to 750 nm) of visible light, called Q bands or β - α bands.⁸

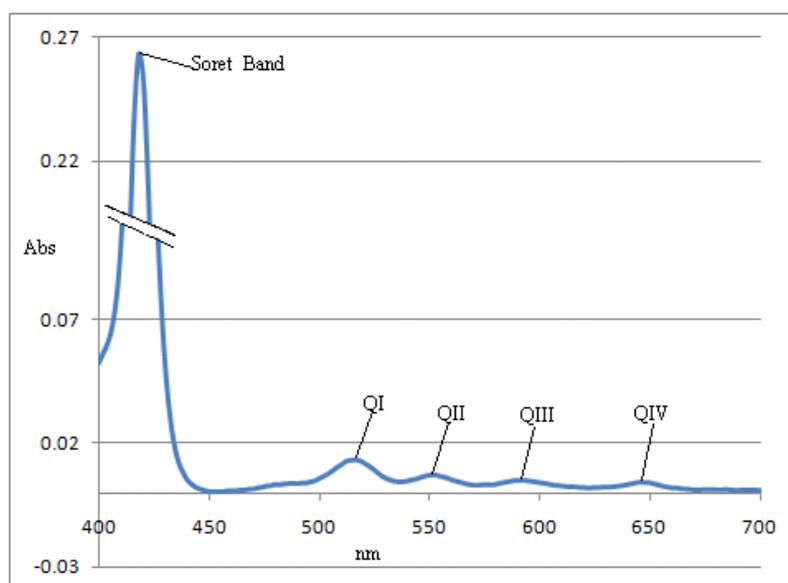


Figure 5: Typical H₂-Porphyrin UV-Vis Spectrum.⁹

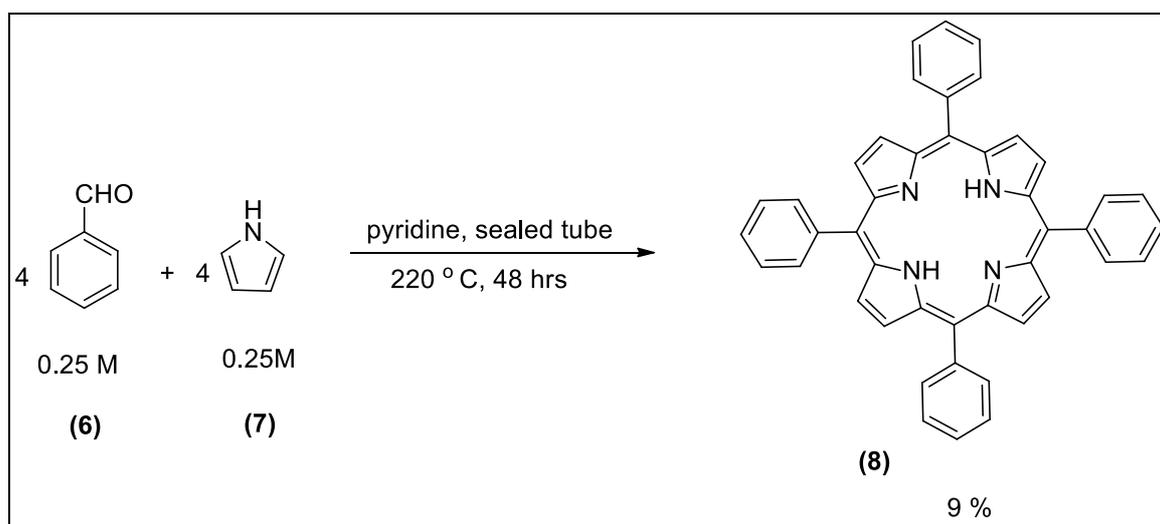
2.3.2 The synthesis of porphyrins

Many different substituents can be placed on the different positions on the porphyrin macrocycle. Control over these substituents allows us to tailor the macrocycle for specific applications. There are a number of methods for preparing porphyrins, from simple one-flask reaction of pyrrole and an aldehyde to extensive multistep synthesis, each method having some advantages and disadvantages. The first total synthesis of a porphyrin was reported by Fischer, known as the ‘Father of Porphyrin Chemistry’, who won a Nobel prize for this achievement.^{10,11} Since then, a great number of synthetic pathways have been developed to

prepare many porphyrin derivatives for different applications. Some porphyrin derivatives have been synthesised for biological, photophysical, structural, mechanistic and synthetic studies.¹² A variety of synthetic methods have been developed for the synthesis of non-natural porphyrins, especially for the meso substituted porphyrins using pyrrole and aromatic aldehydes. The synthesis of *meso*-substituted porphyrins can be achieved by different methods. However, we will focus on the three best known methods.

2.3.2.1 The Rothmund Synthesis

In 1936, the first synthesis of tetraphenylporphyrin was achieved by Rothmund.⁶ The reaction was done in a sealed tube at 220 °C. The benzaldehyde (6) was mixed with pyrrole (7) in a ratio of 4: 4 in the presence of pyridine and then the mixture heated to reflux for 48 h. The tetraphenylporphyrin was isolated as sparkling deep-purple needles from the by-products in 9 % yield as shown in scheme 1. In addition to the low and irreproducible yields, the most severe limitation of the Rothmund synthesis was due to the harsh reaction conditions, which led failure with all but a small selection of rather inert aldehydes.

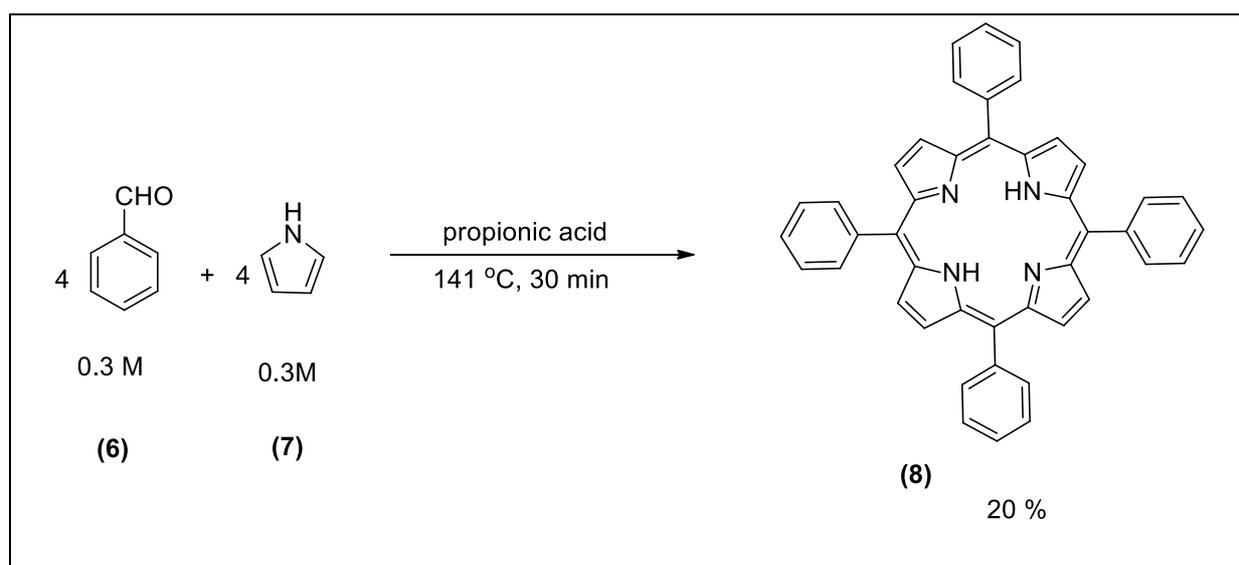


Scheme 1: The Rothmund synthesis of tetraphenylporphyrin.

In the Rothmund reaction the character of the substituent on the phenyl ring plays an important role determining the yield of tetraphenylporphyrins.¹³ Electron-acceptor substituents accelerate the reaction and increase the yields of tetraphenylporphyrins, whereas electron-donor substituents prevent the reaction and decrease the yields; this is apparently due to preferred polymerisation of pyrrole to give polypyrroles.

2.3.2.2 The Adler Synthesis

Adler successfully modified the Rothmund reaction and he was able to achieve tetraphenylporphyrin under milder conditions in better yield. He reacted benzaldehyde and pyrrole at low concentrations in refluxing propionic acid (141°C) for 30 minutes in the presence of air (scheme 2).¹⁴ Upon cooling porphyrin crystals were isolated by filtration, giving better yield (~ 20%). Importantly, by using propionic acid as a solvent Adler was able to avoid the limitations of dealing with sealed bombs. Additionally, the Adler reaction can be performed on a large scale and these milder reaction conditions were compatible with a wider selection of aldehydes.

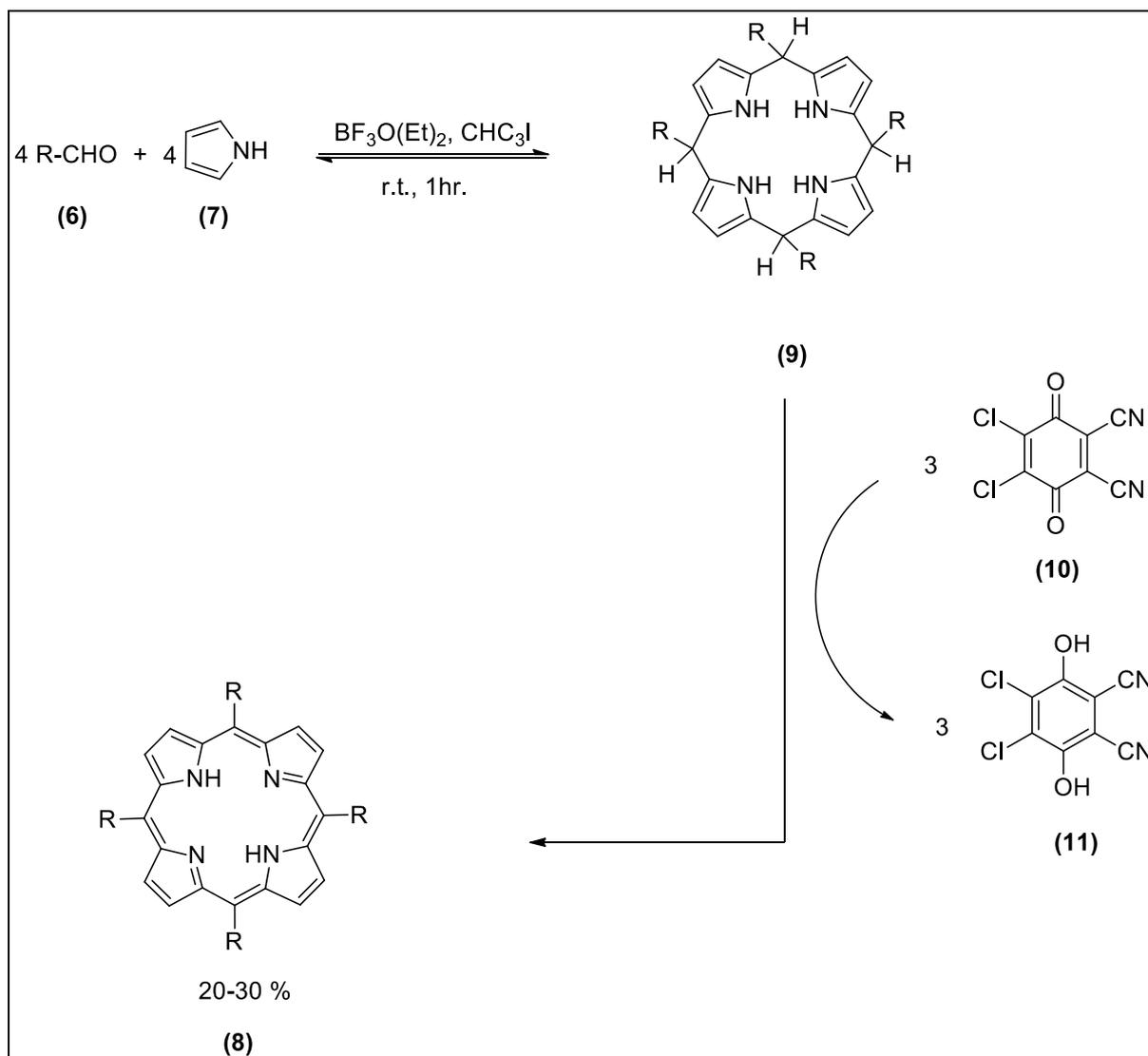


Scheme 2: Adler synthesis of tetraphenylporphyrin.

Basically, the Adler method works better than the Rothmund method. However, it still has some disadvantages. Some of these disadvantages were that the reaction totally failed with benzaldehydes bearing acid sensitive functional groups, and purification problems resulting from using propionic acid (there were some porphyrins that do not crystallise from solvent). The yields obtained are therefore sometimes low and are often not reproducible.¹⁵

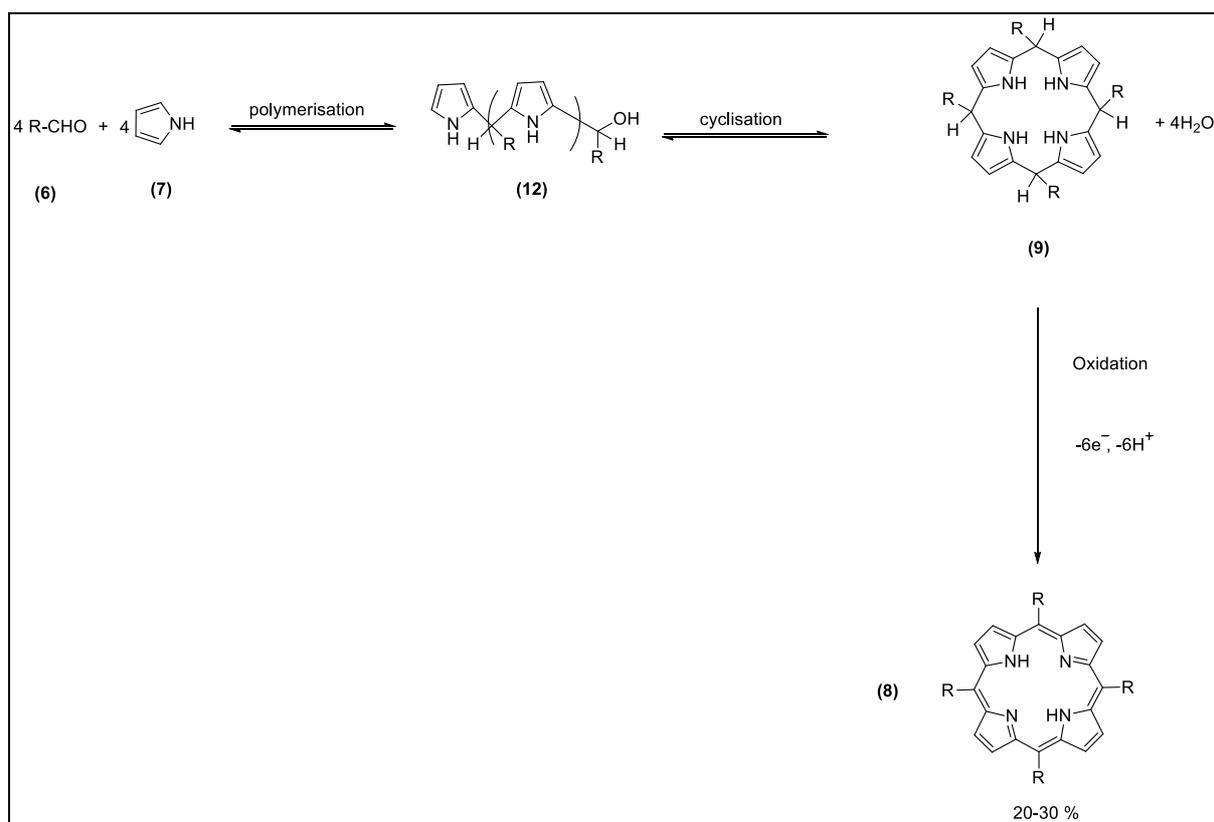
2.3.2.3 The Lindsey Synthesis

Lindsey developed a two-step, one-flask synthetic procedure for the synthesis of meso-substituted porphyrins, which gave an increase in the number of porphyrins that could be produced. It is an acid-catalysed pyrrole-aldehyde condensation using low concentrations (10^{-2} M) at room temperature in the presence of CHCl_3 or DCM for an hour. In this first step the reaction is monitored for the maximum formation of porphyrinogen, an intermediate formed by the cyclisation of a tetrapyrromethane, which is then rapidly oxidised to porphyrin in the second step by the addition of 3 equivalents of a high potential quinone oxidant (scheme 3).¹⁶ Isolation of the porphyrin usually requires two chromatographic procedures.



Scheme 3: Lindsey's two-step, one-flask synthesis of meso-substituted porphyrins.

The steps in the porphyrin-forming reaction presumably involve polymerisation of an aldehyde and pyrrole to give tetrapyrromethane with each addition of pyrrole in a series of electrophilic aromatic substitution reactions. The carbonyl carbon is converted from sp^2 to sp^3 and thus becomes the meso-carbon in the porphyrin. Cyclisation of the tetrapyrromethane affords the porphyrinogen. The addition of an oxidant then converts the porphyrinogen to porphyrin in a six proton, six-electron process, thus converting the 4 meso-carbons from sp^3 back to sp^2 (Scheme 4).¹⁷



Scheme 4: Lindsey synthesis in more detail.

In summary, there are three main methods for making meso-substituted porphyrins where all of the substituents are the same, the Rothemund method, the Adler method and the Lindsey method. Each reaction has pros and cons as mentioned earlier. Table 1 summarises the main differences between the three methods.

	Rothmund	Adler	Lindsey
Solvent	Pyridine	Propionic acid Acetic acid RCOOH+benzene	DCM Chloroform
Temperature (°C)	140-220	141	RT
Catalyst	--	Same as the solvents	TFA BF ₃ -etherate Clays, other acids
Concentration	0.4-3.6 M	0.3-0.1 M	0.1-0.001 M
Reaction time	24-48 h	30-60 mins	60 mins
Workup	Separate crystals	Filter crystals	Chromatography
Yield	~09 %	~20%	~40%

Table 1: Comparison of porphyrin synthesis methods.

2.4 Applications

Porphyrin derivatives play a key role in wide variety of applications, such as molecular electronic devices, catalysis, energy conversion, photodynamic cancer therapy, photosynthesis, di-oxygen transport and storage. Porphyrins can also be combined with other macrocycles to form hetero arrays. One such group of macrocycles are phthalocyanines. This combination can lead to

electron transfer and energy transfer depending on which part of this combination will be selectively excited.

2.5 Introduction to linked chromophores

The definition of dimerisation from a synthetic point of view is the coupling of two molecules through covalent bonding. This thesis is concerned with the interactions between dye molecules. The dimerisation involves the process in which two separate dye molecules interact as a result of physical forces between the two aromatic structures, whether or not they are also chemically bonded together. The characteristic difference is then between intermolecular and intramolecular dimerisation. Theoretically, the main difference between intermolecular dimerisation and aggregation is the number of interacting dye moieties forming the observed structure. Dimerisation may be encouraged or even enforced by synthetically connecting dye molecules together to form an intramolecular dimer. As mentioned in the introduction they can be divided into two types:

- 1) The face-to-face structures in which the two macrocycles are constrained to an approximately cofacial geometry.
- 2) The clamshell structures where two or more monomeric units are linked by a flexible chain.

There are many examples for both types of structure, some of which were discussed earlier in the introduction section.

2.6 Design and synthesis of phthalocyanine and porphyrin dimers and new structures

As mentioned earlier one of the aims of this project was to prepare some dimers of phthalocyanine and porphyrin materials. Different materials can be achieved depending on the type of the linker such as a flexible or rigid and the way they link to each other. These different dimers are illustrated in figure 6. The materials which have been synthesised will be discussed in this chapter. The dimers could be used as materials for different applications such as, energy harvesting, liquid crystals, host and guest chemistry, self-assembly and supramolecular chemistry.

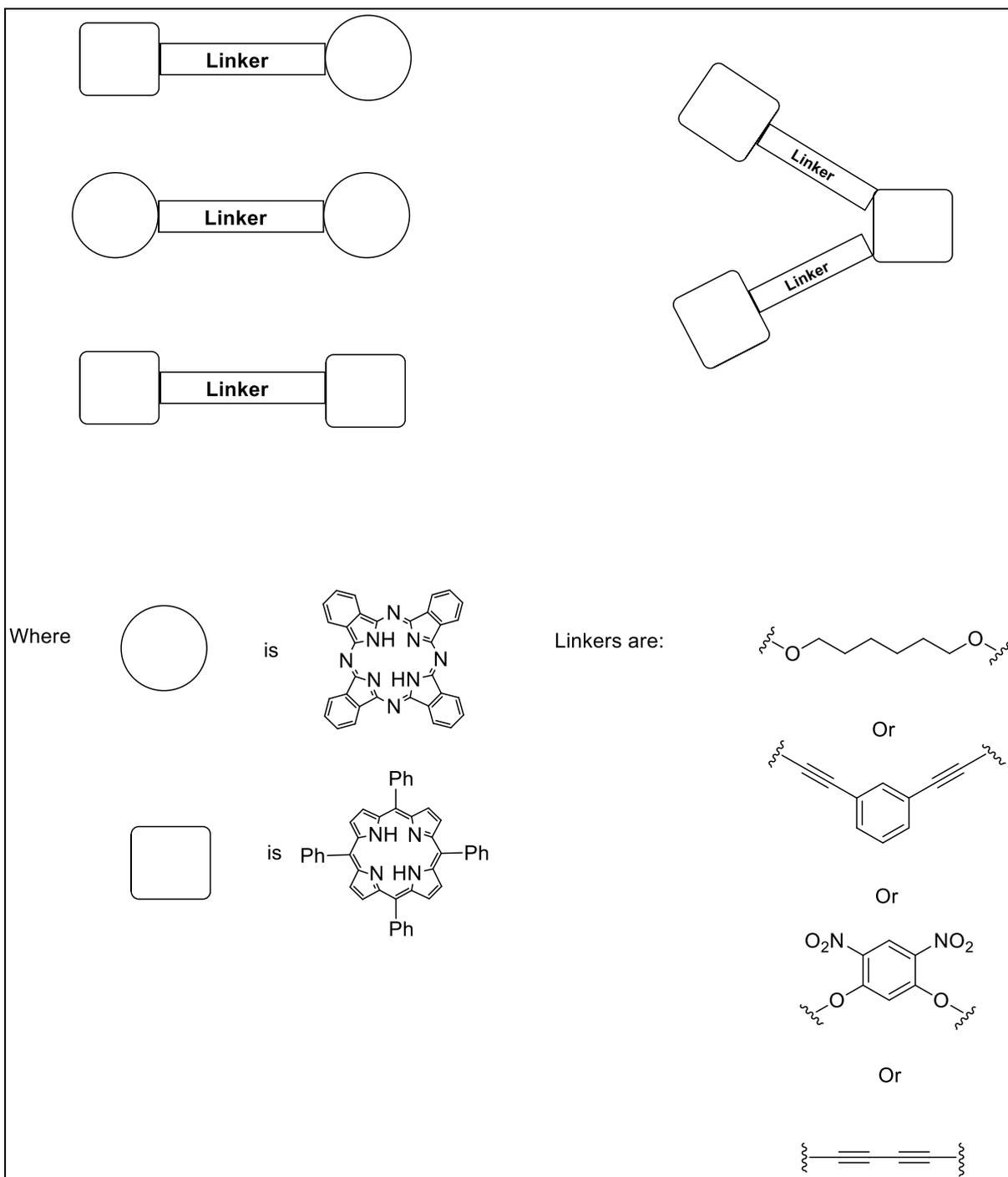
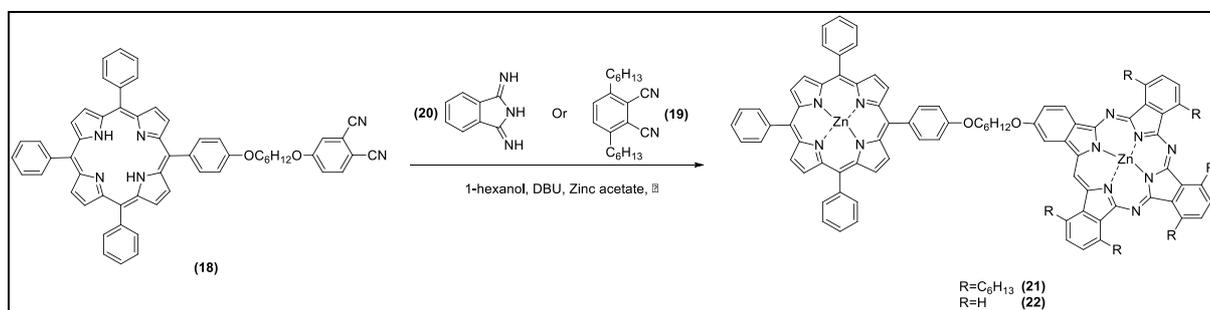


Figure 6: A cartoon representation of the dimers and trimer.

2.7 Retrosynthesis of alkyl substituted phthalocyanine-porphyrin dimer

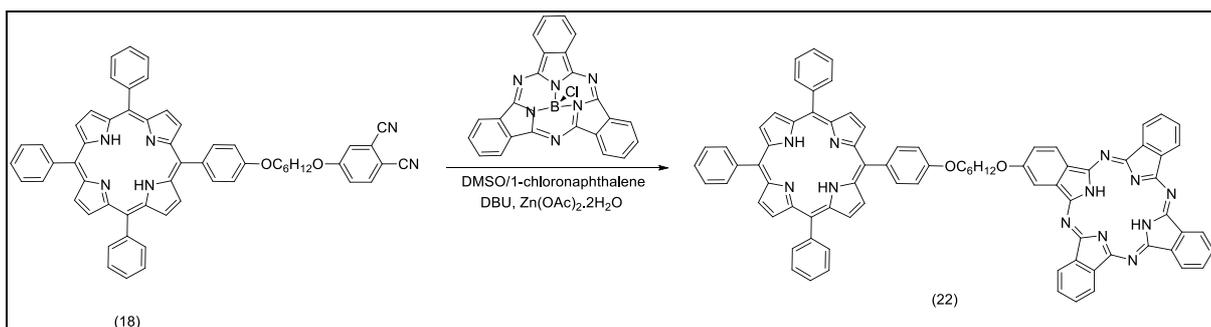
The first dimer that will be discussed here is illustrated in figure 6, where a phthalocyanine is linked to a porphyrin through a flexible linker such a hexyl ether chain. The synthesis of the target dimer involves the synthesis of an unsymmetrical 3:1 Pc (AAAB) bearing non-peripheral hexyl chains and a functional group on the fourth benzene ring. The target is to link this unsymmetrical Pc with a hydroxy porphyrin. The synthesis of such a phthalocyanine-porphyrin dimer can be accomplished in three ways:

- 1) The first method would use a porphyrin linked to a phthalonitrile, Pn-OC₆H₁₂-O-Phthalonitrile. Cyclisation of the phthalonitrile (located at the end of the hexyl chain) with another suitable phthalonitrile (such as **19**) will lead to the Pc-Pn dimer.



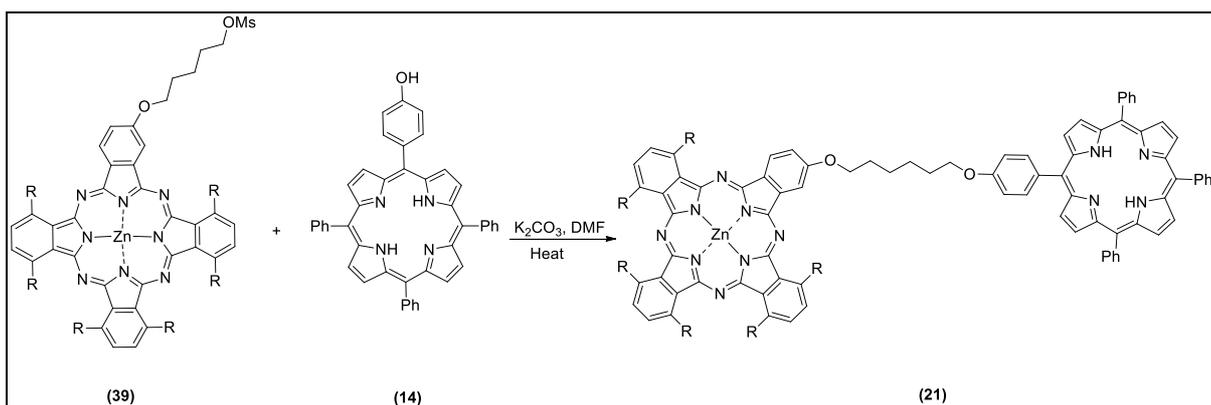
Scheme 5: Proposed synthesis of Pc-Pn dimer linked by a flexible chain.

- 2) Alternatively, using the same Pn-OC₆H₁₂-O-Phthalonitrile, cyclisation of the phthalonitrile at the end of the chain with a suitable subPc could lead to the Pc-Pn dimer **22**.



Scheme 6: Alternative synthesis of Pc-Pn dimer via subPc expansion.

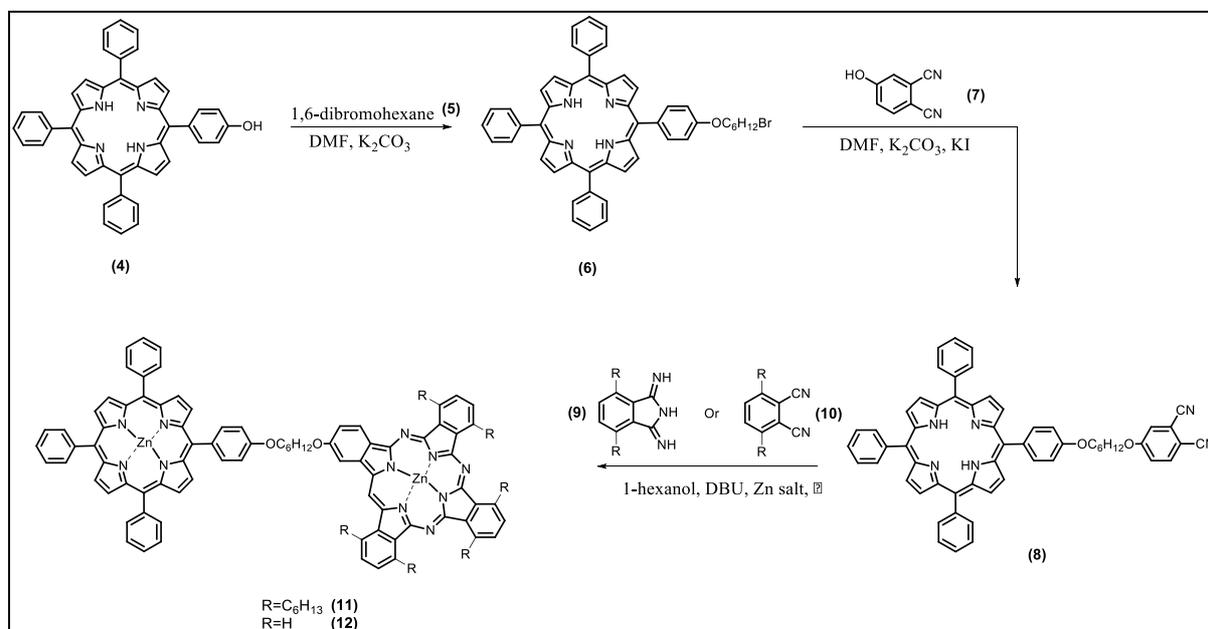
- 3) Using the terminal functionality (-OMs) on ZnPc with the hydroxy porphyrin under basic conditions would lead to the required dimer structure.



Scheme 7: Synthesis of Pc-Pn dimer via a simple substitution reaction.

The first approach was investigated as outlined in scheme 8. After reviewing the literature we decided to build the molecule starting from the porphyrin side. We selected hydroxy phenyl porphyrin (**14**) as the best candidate because hydroxy phenyl porphyrin is more easily prepared and purified compared to monohydroxy Pc and the yield is more promising than Pc. This method involves an alkylation of hydroxy porphyrin with excess of dibromoalkane, followed by reaction between the 4-hydroxyphthalonitrile and the remaining alkylbromide group

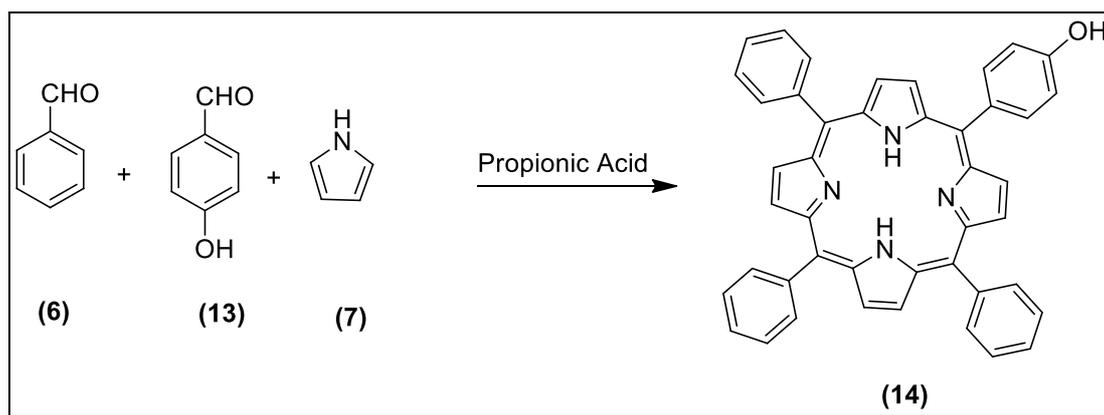
on the linking chain with simple S_N2 substitution reactions to produce the ether. The final step was the cyclisation with phthalonitrile in order to obtain the required porphyrin-phthalocyanine dimer.



Scheme 8: Synthesis of the Pc-Pn Dimer.

2.7.1 Preparation of the porphyrin component (14)¹⁶

In this step, an unsymmetrical mono substituted porphyrin was chosen. There are many ways to produce a *meso*-substituted porphyrin with an A₃B substitution pattern such as the Adler method^{14,18,19,20} and the Lindsey method.²¹⁻²⁴ Adler method was chosen to produce hydroxyphenylporphyrin. The main reason for using Adler's method was the purification procedure was much easier due to the porphyrin products crystallising out of solution on addition of ethanol. This method involved a reaction between pyrrole, benzaldehyde and a substituted benzaldehyde (4-hydroxybenzaldehyde in our case) in a 4:3:1 ratio as shown in scheme 9. The reaction will produce a large number of products which would need to be separated via column chromatography possibly resulting in low yields.

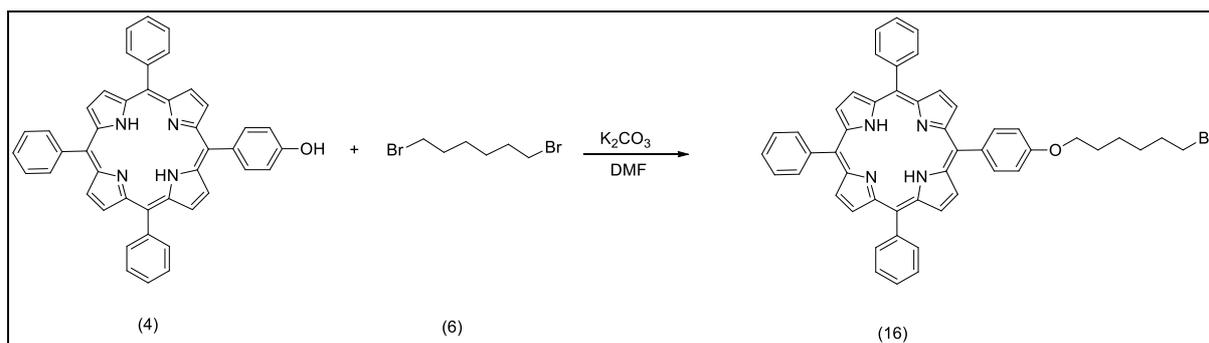


Scheme 9: Preparation of 5-(4-hydroxyphenyl)-10, 15, 20-triphenyl porphyrin (**14**).

The synthesis of the required porphyrin was obtained by following a literature procedure¹⁶ by refluxing a solution of benzaldehyde, 4-hydroxybenzaldehyde and pyrrole (in a 3:1:4 ratio) in propionic acid for 30 minutes open to the atmosphere. Following cooling and addition of ethanol, the crude purple solid was filtered off. The crude product was purified by column chromatography to produce hydroxyphenylporphyrin (**14**) in a yield of 6%, with its characterisation data consistent with that reported in the literature.

2.7.2 Preparation of (6-bromohexyloxy)phenylporphyrin (**16**)²⁶

Alkylation of hydroxy porphyrin (**14**) to bromoalkoxyporphyrin (**16**) was achieved with 1,6-dibromohexane in DMF in the presence of potassium carbonate. The reaction was monitored using TLC and, after two hours, the reaction mixture still had a substantial amount of unreacted starting material. The reaction was left for 18 h at room temperature. After workup, the product was purified by column chromatography to isolate the product (6-bromohexyloxy)phenylporphyrin (**16**) in a yield of 47 % as a purple solid, as shown in scheme 10.²⁶



Scheme 10: Synthesis of (6-bromohexyloxy)phenylporphyrin (**16**)

The unsymmetrical nature of bromoalkoxy porphyrin (**16**) is clearly apparent from inspection of its ^1H NMR spectrum, especially when you look to the aliphatic region of bromoalkoxy porphyrin. In the ^1H NMR spectrum of the product porphyrin, it can be seen that, at ca. 8.8 ppm we see signals corresponding to 8H for the porphyrin β -hydrogens. Because the phenyl groups around the porphyrin are not equivalent, broad signals are observed at ca. 8.2 and 7.8 ppm each integrating to 6H and 9H respectively that correspond to the hydrogens on the three unsubstituted phenyl rings. Signals for hydrogens on the substituted phenyl ring appear at 8.1 ppm and 7.2 ppm. The alkyl chain characteristic signals of the methylene groups appear at 4.25 ppm ($-\text{OCH}_2-$), 3.5 ppm ($-\text{CH}_2\text{Br}$), 2.0 ppm and 1.85 ppm. The distinctive signal for hydrogens in the centre of the porphyrins is observed at ca. - 2.7 ppm.

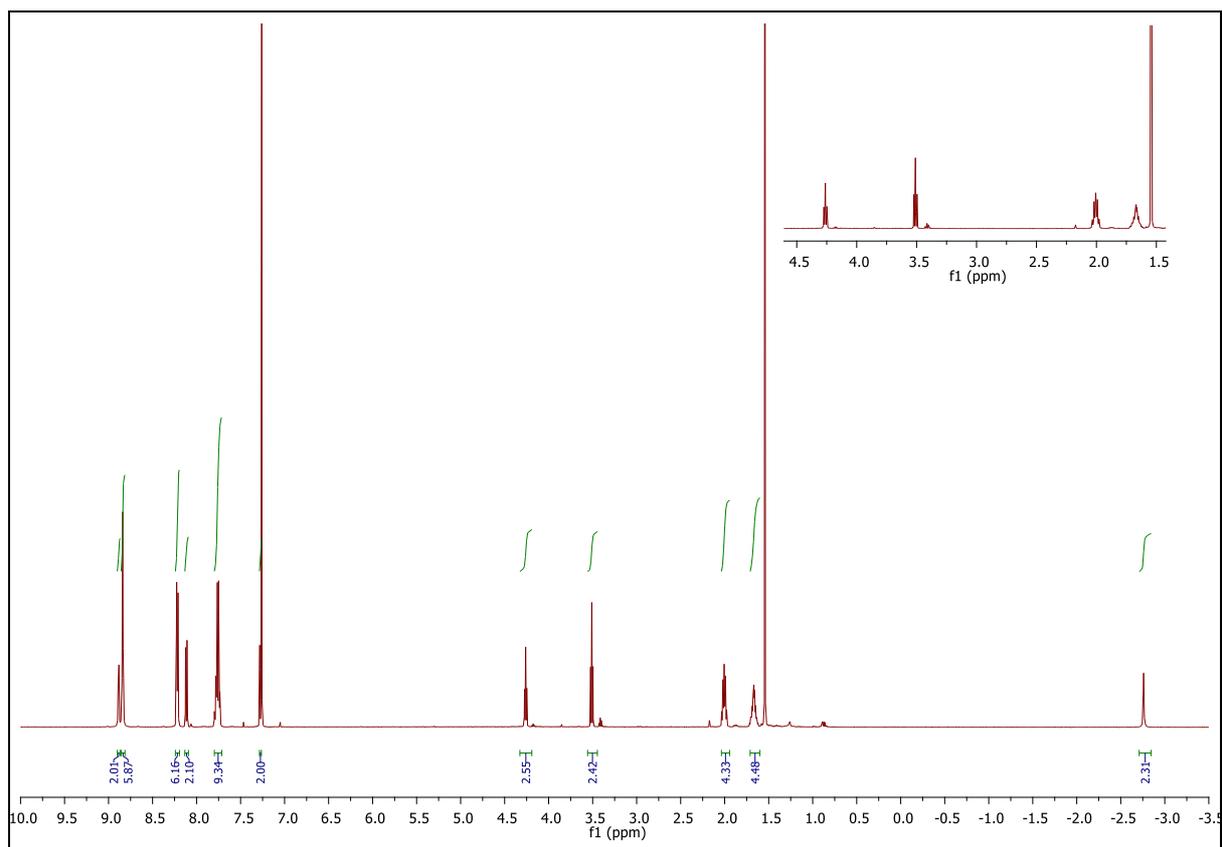
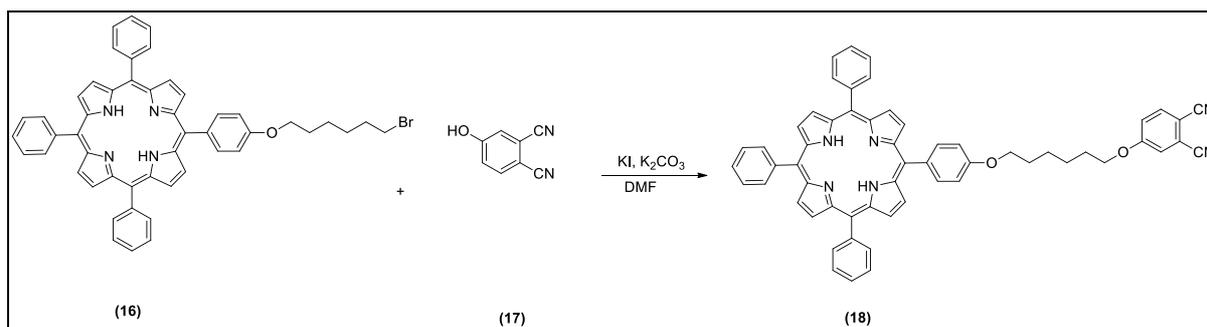


Figure 7: ¹H NMR spectrum of (6-bromohexyloxy)phenylporphyrin (**16**) in CDCl₃ at 25 °C.

2.7.3 Preparation of (6-(3,4-dicyanophenoxy)hexyloxy)phenylporphyrin (**18**)

With bromoalkoxyphyrin (**16**) in hand, the next step was to react it with 4-hydroxyphthalonitrile in a simple S_N2 substitution reaction to produce the ether. This step was achieved by reacting 4-hydroxyphthalonitrile with bromoalkoxyphyrin (**16**) in DMF in the presence of potassium carbonate and potassium iodide. The reaction was monitored using TLC and, after few hours, the reaction mixture still had a substantial amount of unreacted starting material. The reaction was left for 24 h at 80 °C. After workup, the product was purified by column chromatography to isolate the product in a yield of 47 % as a purple solid scheme 11.²⁶



Scheme 11: Synthesis of (6-(3,4-dicyanophenoxy)hexyloxy)phenylporphyrin.

The ^1H NMR spectrum of the product **(18)** is significantly different to the one observed for the starting material. Three new peaks appeared as d, d and dd at 7.61 ppm, 7.24 ppm and 7.08 ppm respectively. These new protons correspond to the phthalonitrile portion of the molecule. There are characteristic signals for the methylene groups of the alkyl chain appearing at 4.23 ppm ($-\text{OCH}_2-$), 4.02 ppm ($-\text{CH}_2\text{O}$), 1.94 ppm and 1.65 ppm.

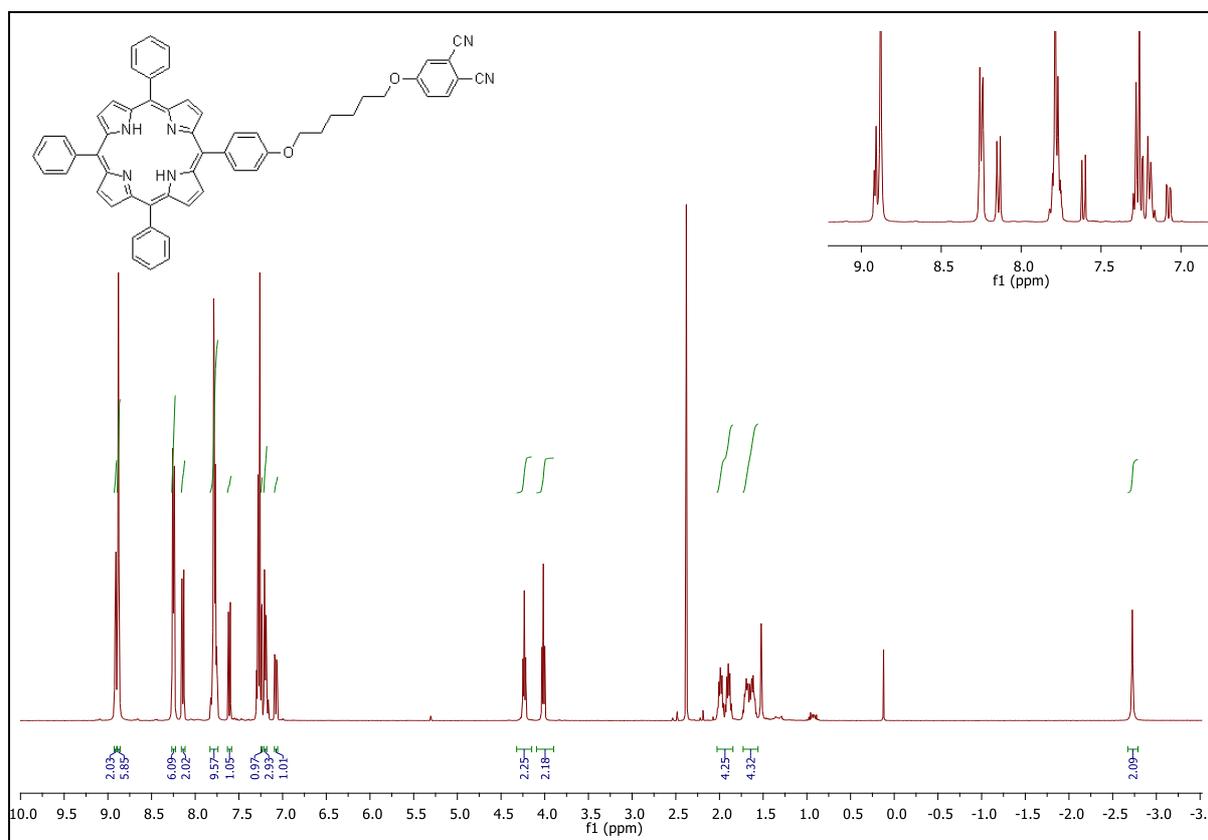
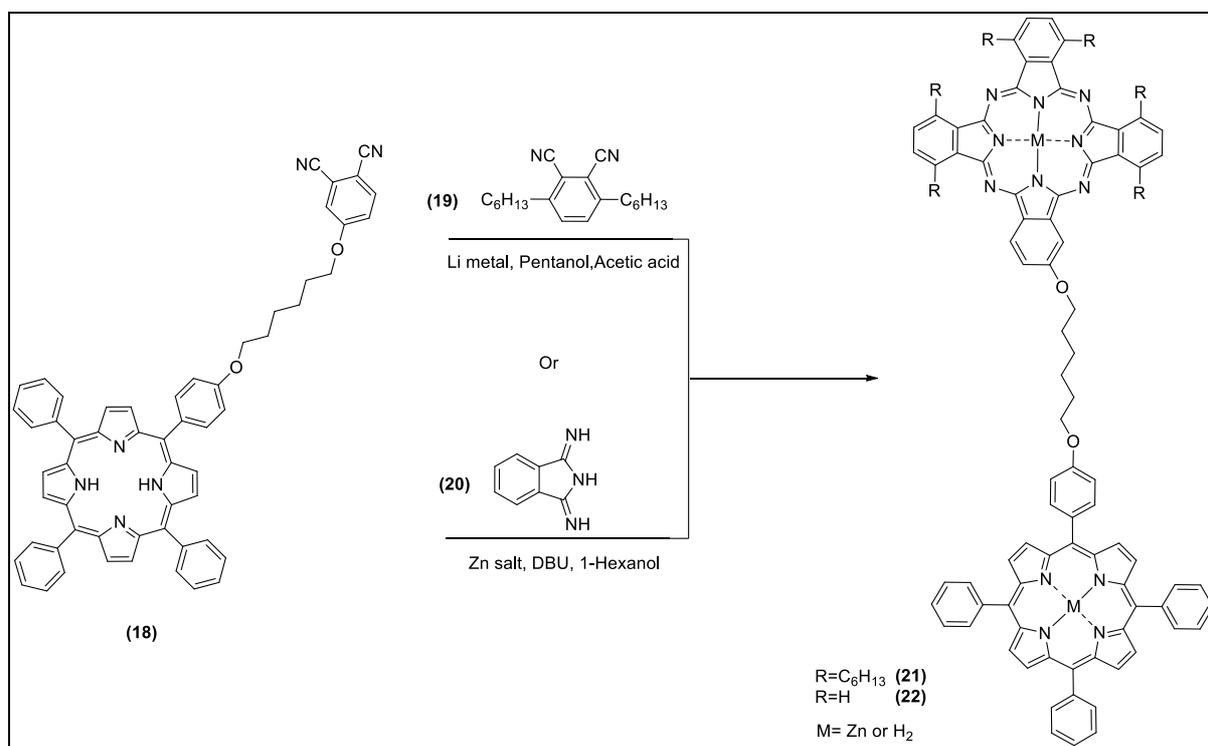


Figure 8: ^1H NMR spectrum of porphyrin **(18)** in CDCl_3 at 25°C .

2.7.4 Synthesis of Pc-Pn dimers **21** and **22**

Having successfully synthesised the phthalonitrile substituted porphyrin **18**, there remained the difficulty of cyclising it with phthalonitrile to form the required Pc-Pn dimer. The reaction would certainly lead to a mixture of compounds, and it had been envisaged from the very start that the isolation of the required product would be the most difficult part of the whole synthesis. At this stage we had two paths for the cyclisation. The first one, using Li metal in pentanol with excess of phthalonitrile, and then acetic acid to obtain metal-free Pc-Pn. The other path would use zinc acetate and DBU in *n*-hexanol to gain the metalated dimer, as shown in in scheme 12:

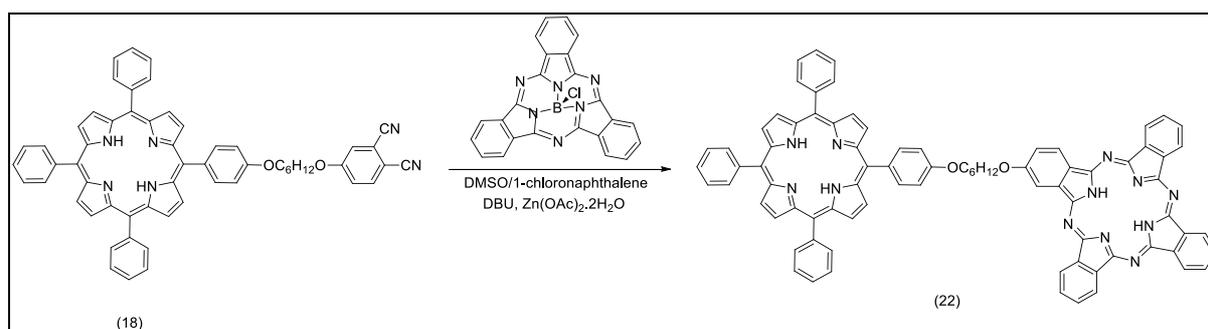


Scheme 12: Synthesis of Pc-Pn dimers (**21**) and (**22**).

Porphyrin (**18**) was mixed with 3,6-dihexylphthalonitrile in a ratio of 1:6 in pentanol. Lithium metal was added and the mixture heated to reflux for 6 h. The reaction was followed by TLC and MALDI-MS. After workup, the mixture was submitted to column chromatography on

silica gel. However, the required dimer compound could not be observed when checked by $^1\text{H-NMR}$ and MALDI mass spectroscopies. It was hoped that the use of a metal template would encourage formation of the required dimer. The reaction was therefore attempted several times using the Zn/DBU conditions but with the same disappointing result. Due to time considerations it was decided to move to the next approach.

The second method applied employed reaction of (**18**) with subphthalocyanine as mentioned in chapter 1.²⁶ This method has the advantage of producing only one product, however the procedure is difficult and the yields are often low. As we had the phthalonitrile-substituted porphyrin (**18**) in hand, we decided to investigate this strategy. The reaction scheme is shown below (scheme 13):



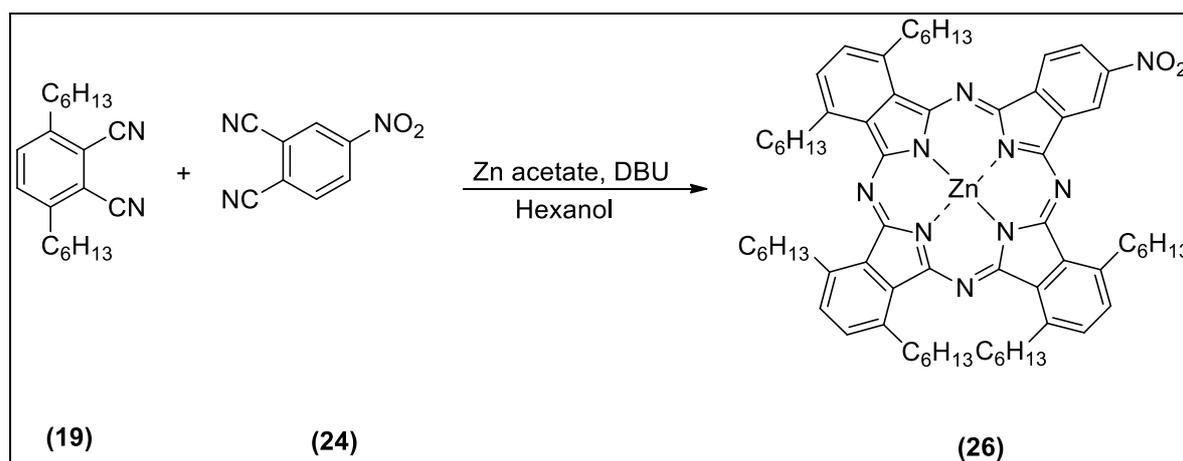
Scheme 13: Proposed synthesis of dimer (**22**) via subPc.

An excess of subPc was added to the reaction mixture of porphyrin **18**, DBU and zinc acetate in a combination of dry DMSO and 1-chloronaphthalene as solvents in ratio of 2:1. The reaction was stirred at 130 °C. After two hours the solution was quenched with methanol, and the reaction mixture was separated by column chromatography. Unfortunately the $^1\text{HNMR}$ and MALDI-MS spectra showed no evidence for product. At this point we decided to abandon the use of Pn-phthalonitrile (**18**) and turned our attention to synthesising unsymmetrical Pcs.

2.8 Strategies for the synthesis of unsymmetrical phthalocyanine (AAAB)

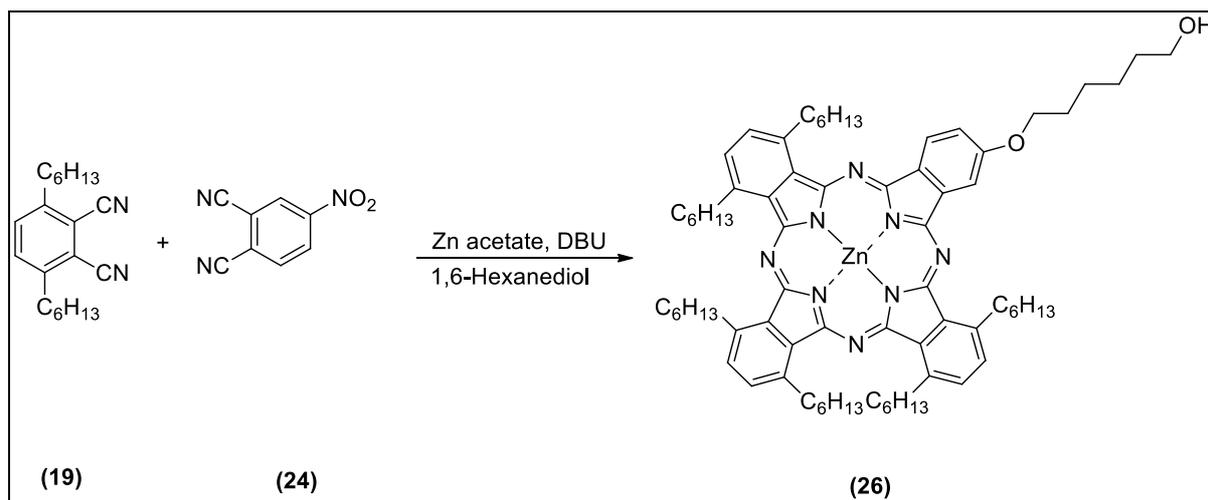
The proposed target molecule included hexyl chain substituents in the non-peripheral positions of three of the benzenoid rings in order to facilitate solubility in organic solvents. The remaining benzenoid ring will be substituted in the peripheral position with a hydroxy group. The presence of the hydroxy group is key for linking the Pc to a porphyrin or another interesting substituent. Three different methods were employed in order to gain such an unsymmetrically substituted ZnPc:

- I. The first method aimed to obtain an unsymmetrical nitro-phthalocyanine (3:1), by the reaction between 4-nitrophthalonitrile and the other phthalonitrile.



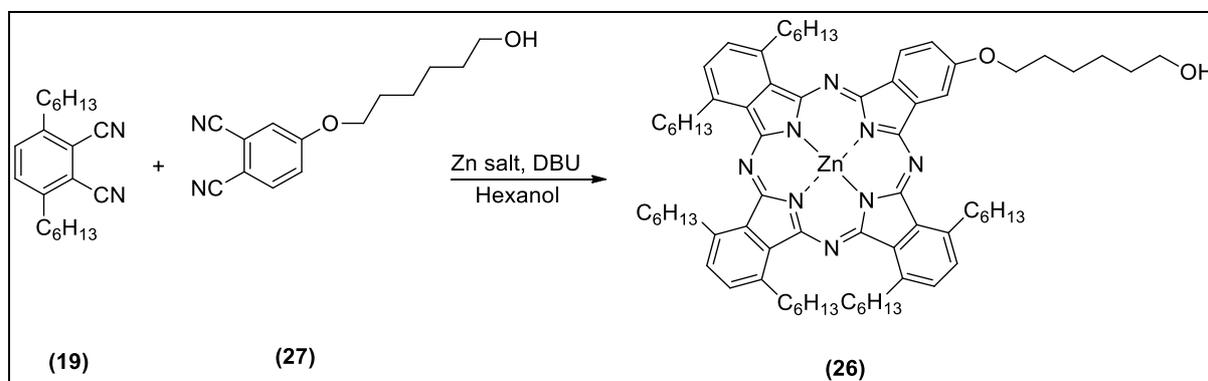
Scheme 14: Synthesis of unsymmetrical Pc (25).

- II. In the second strategy for making the Pc we employed 1,6-hexanediol as a reagent and solvent at the same time, instead of using alcoholic solvents.



Scheme 15: Synthesis of ZnPc (26)

III. The last way was making unsymmetrical phthalocyanine by the cyclisation between 4-(6-hydroxyhexyloxy)phthalonitrile (27) and 3,6-dihexylphthalonitrile (19) in 1:3 ratio as shown in Scheme 16:



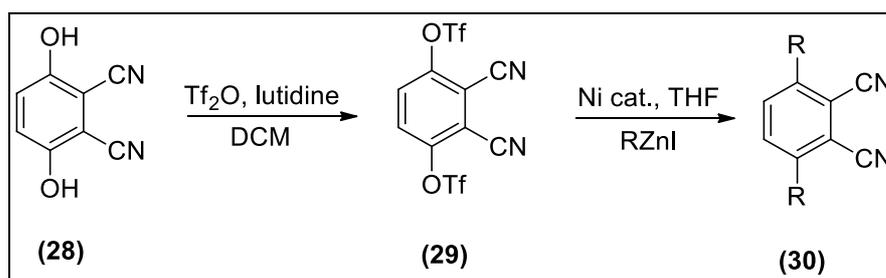
Scheme 16: Synthesis of ZnPc (26).

All the three methods were examined, and the first two methods were unsuccessful, and we will discuss the failure reasons for each reaction in this chapter. In order to obtain the proposed target molecule, there are two phthalonitriles that needed to be prepared.

2.8.1 Synthesis of phthalonitrile precursors

The preparation of 3,6-dialkylphthalonitrile can be accomplished by two routes as shown in scheme 17:

- I. The Negishi reaction to form carbon-carbon bonds from 3,6-bis(trifluoromethanesulfonyl)phthalonitrile via the triflate route.²⁷



Scheme 17: Synthesis 3,6-dialkylphthalonitrile (30).

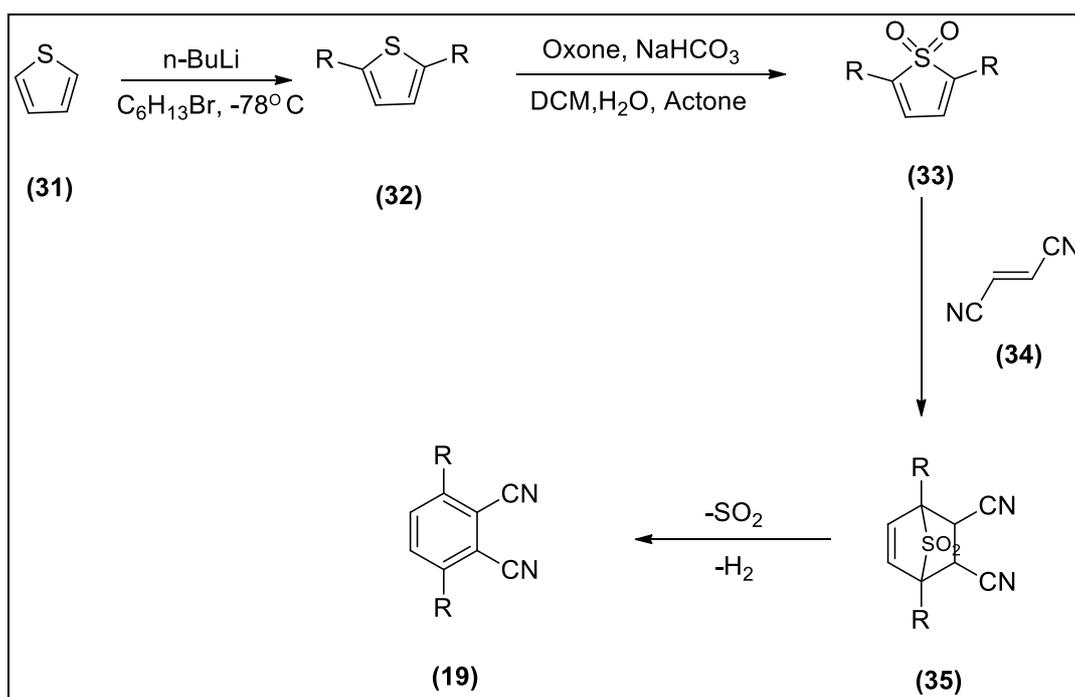
- II. The thiophene route to obtain 3,6-dihexylphthalonitrile.²⁸

In present work, the second method was used because it is economically better and time effective.

2.8.1.1 Preparation of 3,6-dihexylphthalonitrile (19)

The synthesis of 3,6-dihexylphthalonitrile (19) was carried out following a literature procedure,²⁰ by cooling a solution of thiophene in dry tetrahydrofuran to $-78\text{ }^\circ\text{C}$ and then adding two equivalents of $n\text{-BuLi}$. This step deprotonates thiophene in positions 2 and 5 after leaving it overnight. Then, the resulting thiophene dianion was cooled again to $-78\text{ }^\circ\text{C}$ and then alkylated by adding n -bromohexane to yield 2,5-dihexylthiophene. The unreacted bromohexane is removed during the work-up. The dialkylated thiophene is then dissolved in a mixture of three solvents (DCM , H_2O and acetone (1:1.5:1)) in the presence of NaHCO_3 . Then the mixture was stirred between $5\text{-}10\text{ }^\circ\text{C}$. Oxone is added portion-wise over two hours

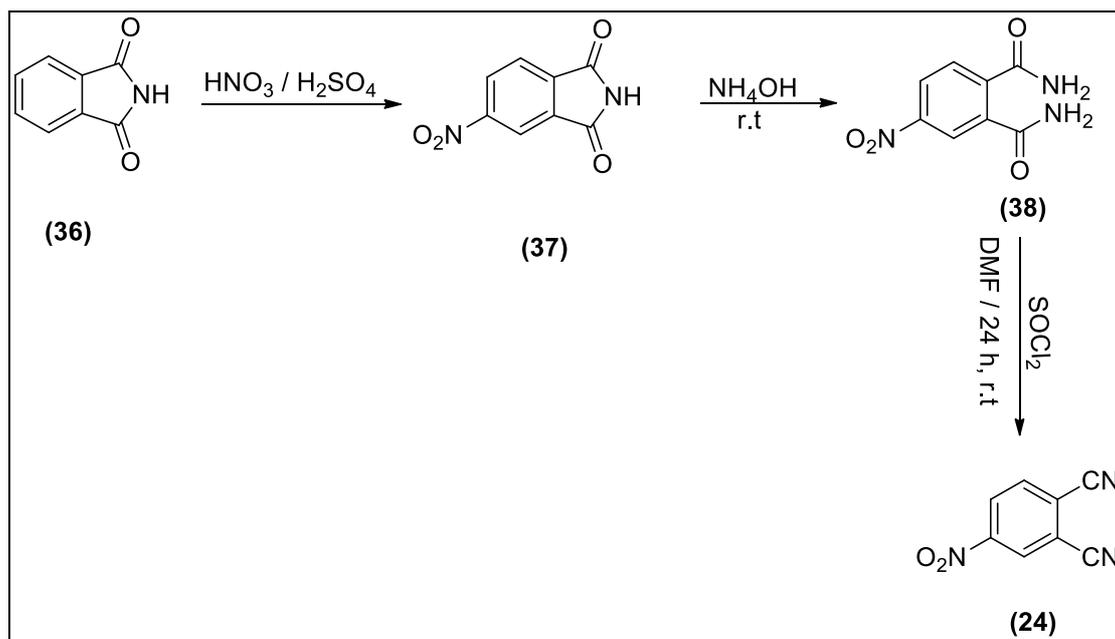
but carefully so that the temperature does not rise above 10 °C as side-reactions would occur which can affect the yield of the reaction. The resulting dialkylated thiophene dioxide **33** is then reacted with fumaronitrile by a Diels-Alder reaction. Subsequent extrusion of sulphur dioxide followed by aromatisation through dehydrogenation yields the expected phthalonitrile as shown in scheme 18:



Scheme 18: Preparation of a 3,6-dialkylphthalonitrile (**19**) via thiophene route.

2.8.1.2 Preparation of 4-nitrophthalonitrile (**24**)

The chosen phthalonitrile was 4-nitrophthalonitrile. It is commercially available, but expensive. However, it can be synthesised from the corresponding phthalamide as seen in scheme 19:



Scheme 19: Synthesis of 4-nitrophthalonitrile (24).

The synthesis of 4-nitrophthalonitrile involved three-steps.^{29,30} In the first step, the electrophilic aromatic nitration of the commercially available phthalimide gives 4-nitrophthalimide.³¹ Nitric acid was slowly added to sulphuric acid (6:1 v/v) in a round bottom flask cooled in an ice bath. The solution was stirred for approximately 20 minutes. Then, the ice bath was removed and the acidic solution was allowed to warm to room temperature. Phthalimide was stirred into the acid solution and heated at 35 °C until a clear, colourless, homogeneous solution was obtained. As the phthalimide dissolved, the reaction solution became yellow. The reaction solution was stirred for 4 hours. A powdery white solid was precipitated from ice water, collected via vacuum filtration, and washed with water. The precipitate was dried to produce a 60% yield. The second step, the ammonolysis of 4-nitrophthalimide with ammonium hydroxide produced 4-nitrophthalamide. 4-Nitrophthalimide and ammonium hydroxide were mixed and the resulting slurry was stirred at room temperature for approximately 5 hours. The slurry was vacuum filtered, and the solid was washed with cold water and dried to gain an 87% yield. The final step of the procedure

involved the dehydration of the 4-nitrophthalamide with thionyl chloride to produce 4-nitrophthalonitrile. In this reaction dry DMF was cooled in an ice bath and purged with nitrogen gas. Thionyl chloride was added slowly into the reaction flask and allowed to cool for approximately 20 minutes. 4-Nitrophthalamide was added to the solution which was then stirred at room temperature for 24 hours. 4-Nitrophthalonitrile was precipitated from ice water and then collected and dried. 4-Nitrophthalonitrile was produced in an 85 % yield.

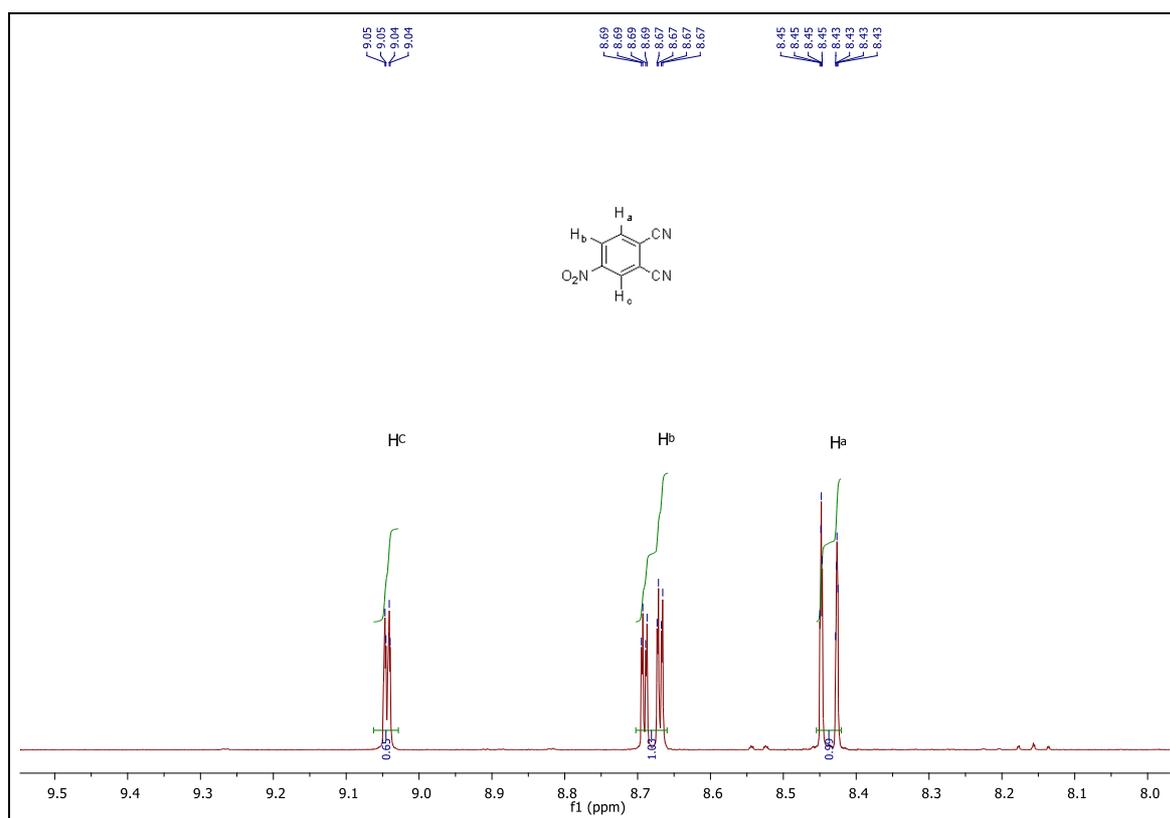
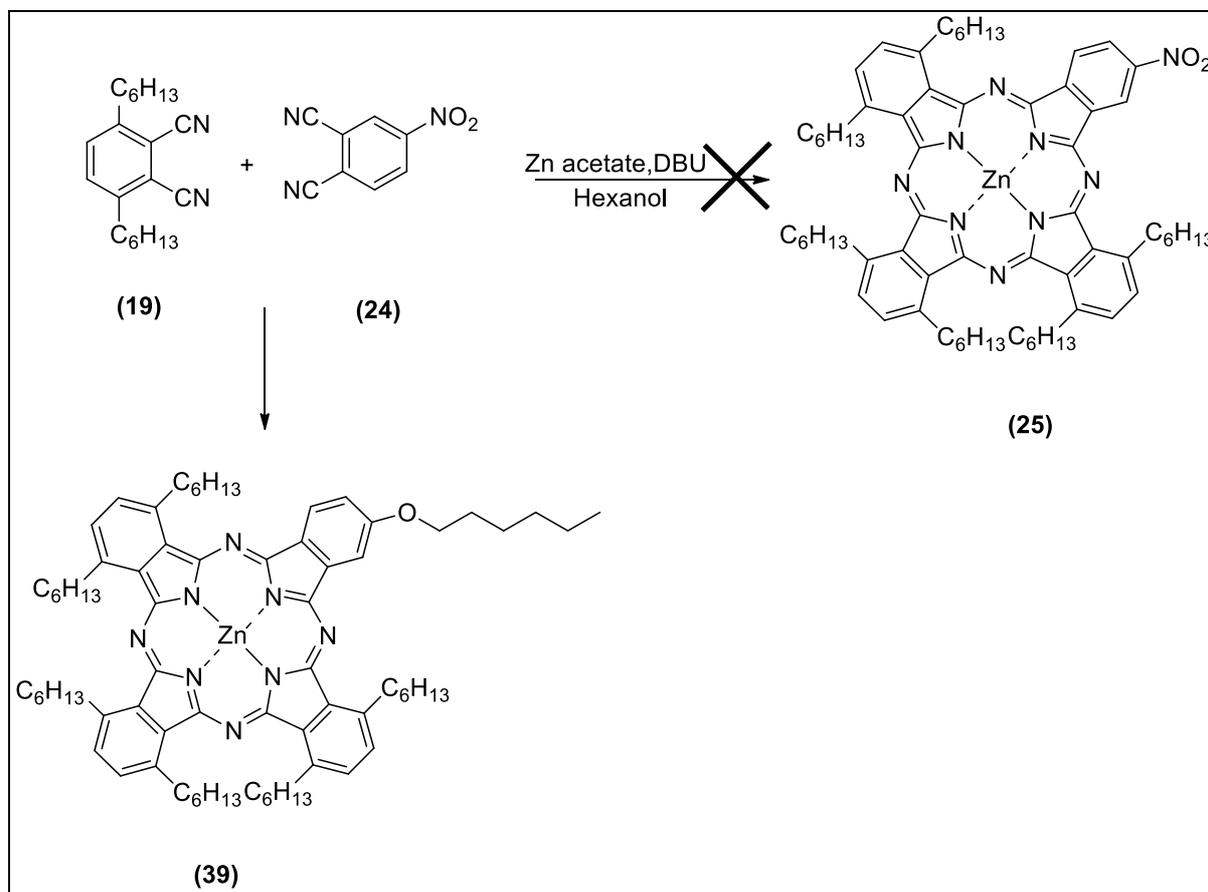


Figure 9: ^1H NMR spectrum of aromatic area of 4-nitrophthalonitrile in DMSO- d_6 at 25 °C.

2.9 Synthesis of unsymmetrically substituted Pc (26)

The synthesis of 1,4,8,1,15,18-hexakis(hexyl)-23-(6-hydroxyhexyloxy)phthalocyaninatozinc (II) monomer (**26**) is not straightforward on account of the asymmetry within the molecule. The synthesis of unsymmetrical Pcs requires a specialised approach. In the first method, the

strategy of the reaction was to save the nitro-group in the product in order to obtain unsymmetrical nitrophthalocyanine and then try to link via that group as shown in scheme 20:

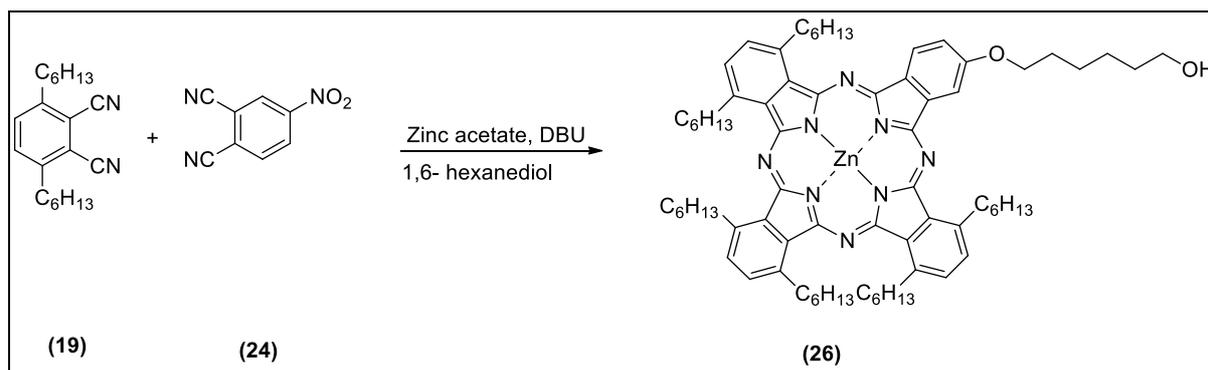


Scheme 20: Attempted of unsymmetrical zinc phthalocyanine (25).

The synthesis of the required unsymmetric (AAAB) phthalocyanine requires a mixed cyclisation of the 3,6-dihexylphthalonitrile (A) with the 4-nitrophthalonitrile (B). We chose a ratio of A to B of 3:1, giving a reasonable yield of the required product. The two phthalonitriles were stirred under reflux in *n*-hexanol in presence of excess of zinc acetate and DBU for 18h. The solution was allowed to cool and methanol was added. The mixture was filtered collecting a green precipitate which was washed with methanol to remove non-Pc impurities. The residue was then dissolved in a minimal volume of solvent mixture. The Pc products were collected by filtration and purified by column chromatography on silica gel. The samples were submitted for analysis by MALDI-MS and ¹HNMR spectroscopy for

identification. The results were not encouraging. Somewhat surprisingly, the reaction gave a different product, where the nitro group had not survived and behaved as a leaving group. The mechanism of the reaction involves a nucleophilic attack driven by *n*-hexanol in presence of the organic base DBU to produce the 23-hexyloxyphthalocyanine (**39**). The ¹H NMR spectrum of the product showed the appearance of two triplet peaks around 3.99 ppm and 3.57 ppm in 1:6 ratio which represent the OCH₂ and the CH₂ of the hexyl chains in non-peripheral position respectively.

In the second reaction, since the nitro group can be reacted under the reaction conditions, we can take advantage of this and try to obtain the target compound directly. In order to do that we used 1,6-hexanediol as solvent and reagent at the same time in the presence of DBU and zinc acetate for 18 h. The solution was allowed to cool and methanol was added. The mixture was filtered collecting a green precipitate which was washed with methanol to remove non-Pc impurities. The residue was then dissolved in a minimal volume of solvent mixture. The Pc products were collected by filtration and purified by column chromatography. The samples were submitted for analysis by MALDI-MS and ¹H NMR spectroscopy for identification. The formation of the required compound was confirmed by MALDI-MS (isotopic cluster 1199). However, the sample gave unresolved ¹H NMR spectra, even though different NMR solvents were used such as benzene, chloroform and pyridine. We tried to obtain clear NMR spectra by running samples at 70 °C, but the problem was not solved. The yield of the reaction was also poor, so it was not investigated further and we moved onto the last method for preparing the unsymmetrical Pc.

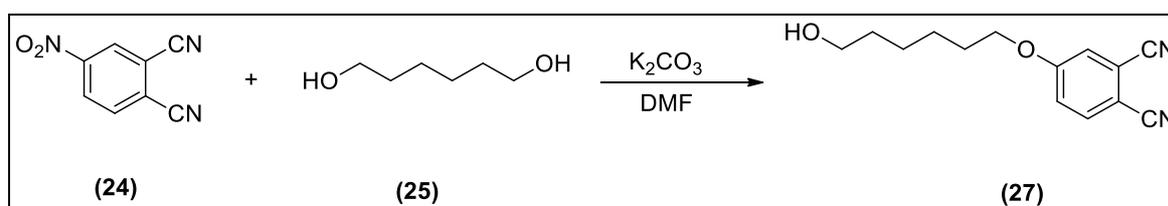


Scheme 21: The second approach to obtain unsymmetrical zinc phthalocyanine (26).

Since we could not obtain the required substituted phthalocyanine via the 4-nitrophthalonitrile directly, it was decided to move to an alternative approach. The main step in this approach was introducing a new 6-hydroxyhexyloxy functional onto one of the benzenoid rings of the target phthalocyanine. To achieve this step 4-(6-hydroxyhexyloxy) phthalonitrile was required as the intermediate. Therefore, the first step in this approach was preparing the 4-(6-hydroxyhexyloxy)phthalonitrile.

2.9.1 Preparation of 4-(6-hydroxyhexyloxy)phthalonitrile (27)

The required phthalonitrile was synthesised according to the procedure described in scheme 22:



Scheme 22: Preparation of 4-(6-hydroxyhexyloxy) phthalonitrile (27).

The synthesis of 4-(6-hydroxyhexyloxy)phthalonitrile was achieved by following a modified literature procedure³¹ using base-catalysed nucleophilic aromatic substitution reaction by heating a solution of 4-nitrophthalonitrile and 1,6-hexanediol in dry DMF under a nitrogen atmosphere in the presence of K_2CO_3 . Then, the mixture was heated to 80 °C overnight. After workup the crude product was purified by column chromatography. The pure product (**27**) was obtained in good yield (86%) as a pale yellow solid. The 1H NMR spectrum (figure 10) showed a broad singlet at 1.31 ppm corresponding to the hydroxy group. There are characteristic signals for the methylene groups of the alkyl chain appearing at 4.05 ppm (-OCH₂-), 3.67 ppm (-CH₂OH), 1.84 ppm, 1.61 ppm and 1.48 ppm.

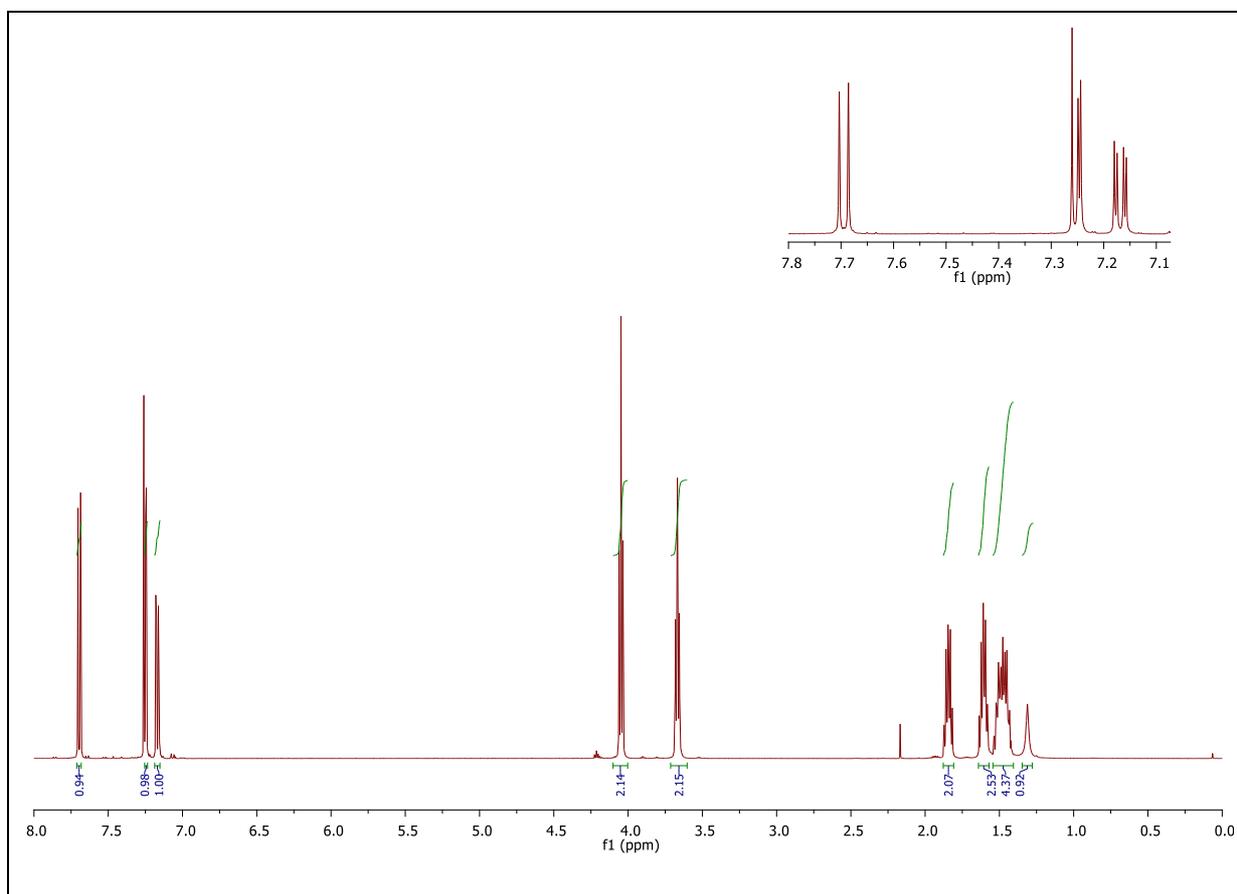
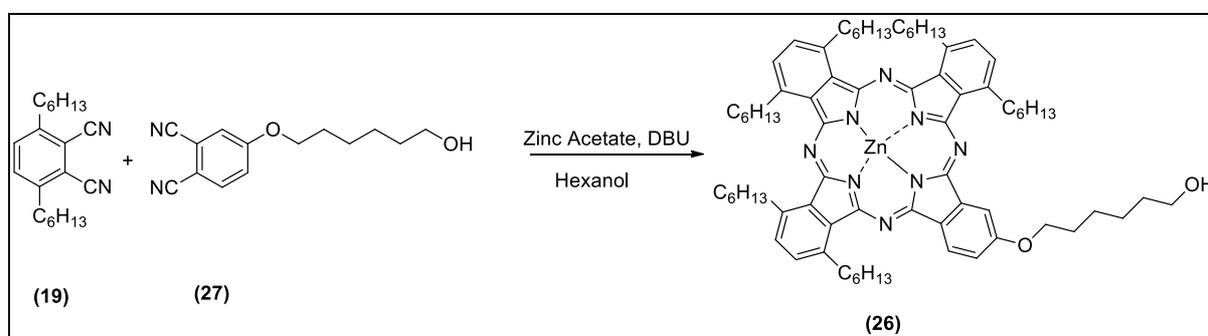


Figure 10: 1H NMR of 4-(6-hydroxyhexyloxy)phthalonitrile in $CDCl_3$ in 25 °C.

The synthesis of 1,4,8,11,15,18-hexakis (hexyl)-23-(6-hydroxyhexyloxy) phthalocyaninato zinc(II) (**26**) requires a mixed cyclisation of 3,6-dihexylphthalonitrile (**19**) with 4-(6-hydroxyhexyloxy)phthalonitrile (**27**) as shown in scheme 23. Statistics predict that the ideal ratio is 3:1, giving a reasonable yield of the required product. The two phthalonitriles were stirred under reflux in *n*-hexanol in the presence of excess of zinc acetate and DBU for 18h. The solution was allowed to cool and methanol was added. The mixture was filtered collecting a green precipitate which was washed with methanol to remove non-Pc impurities. The Pc products were purified by column chromatography on silica gel.



Scheme 23: Synthesis of ZnPc-OC₆H₁₂OH (**26**).

The reaction is expected to yield other symmetrical phthalocyanines (corresponding to each phthalonitrile) plus a number of unsymmetrical phthalocyanines such as two isomeric 2:2 phthalocyanines and another 3:1 phthalocyanine but containing three of the other unit as compared to the first 3:1 compound. Purification of the product afforded the required 3:1 phthalocyanine (**26**) in an 18 % yield. The phthalocyanine (**26**) showed the expected peak in the MALDI-MS at 1197 (figure 11) and gave a UV spectrum expected for unsymmetrical phthalocyanines.

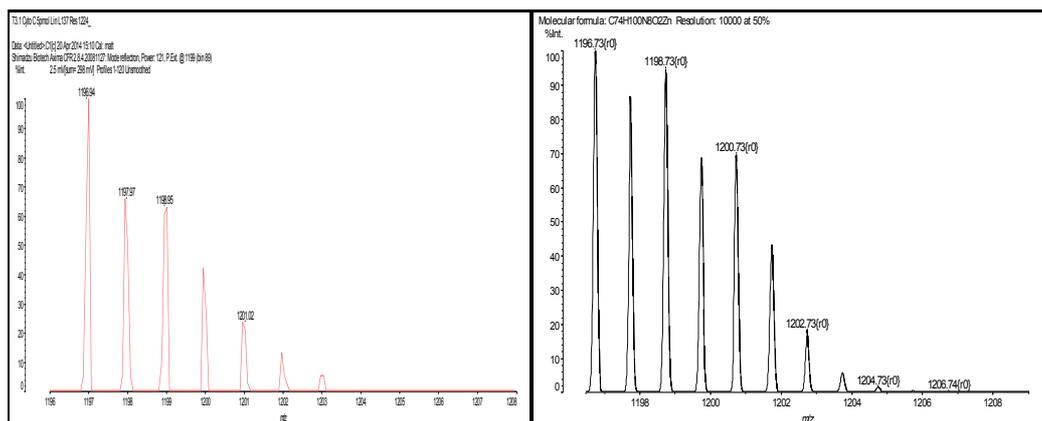


Figure 11: MALDI-mass spectrum of **26** (left) with its theoretical prediction.

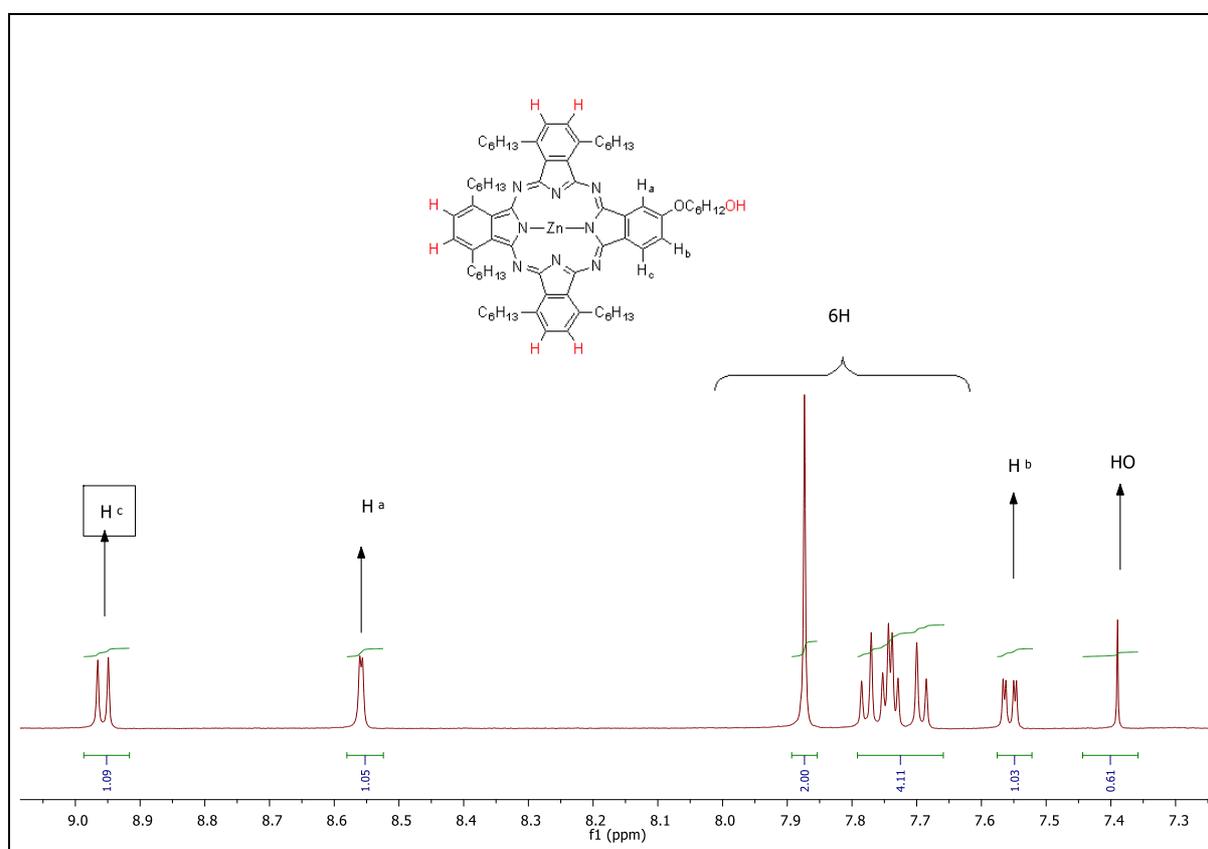


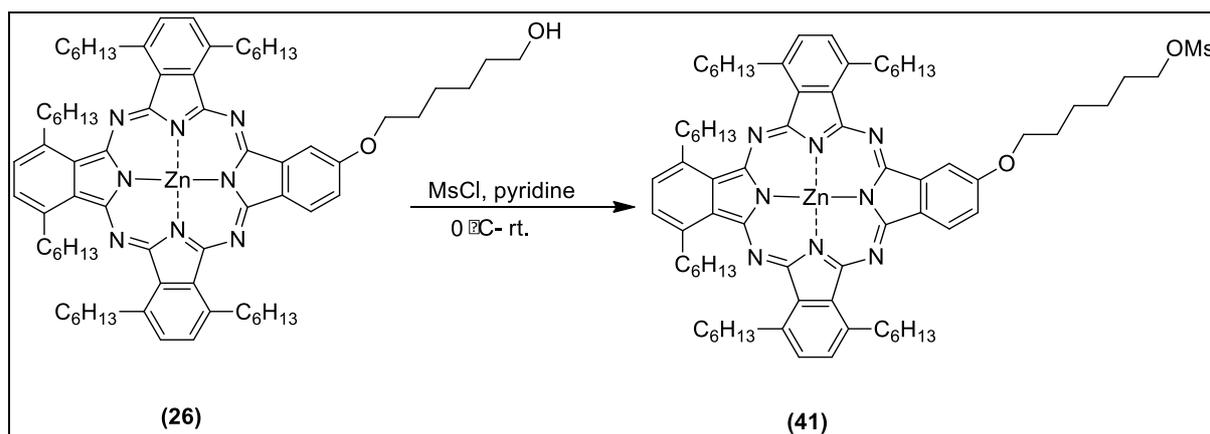
Figure 12: ^1H NMR spectrum of the aromatic area of 1,4,8,11,15,18-hexakis (hexyl)-23-(6-hydroxyhexyloxy) phthalocyaninatozinc(II) **26** in THF-d_8 at 25°C .

The ^1H NMR spectrum of 1,4,8,11,15,18-hexakis(hexyl)-23-(6-hydroxyhexyloxy) phthalocyaninatozinc (II) (**26**) in THF-d_8 showed the expected signals of the target as seen in

figure 12. Other solvents such chloroform, pyridine and acetone gave poor spectra, presumably due to strong aggregation.

2.9.2 1,4,8,11,15,18-hexakis(hexyl)-23-(6-methanesulfonate-hexyloxy) phthalocyaninatozinc(II) (41)

At this stage the terminal hydroxyl group on phthalocyanine (**26**) needed to be converted it to its mesylate counterpart. This was achieved by following a literature procedure³³ by using pyridine as solvent, followed by the addition of methanesulfonyl chloride at low temperature under standard reaction conditions to give the meslyted-phthalocyanine (**41**). The synthetic procedure is outlined in scheme 24:



Scheme 24: Synthesis of ZnPc-OMs (**41**).

The reaction was followed by TLC and when complete the mixture was poured onto ice, and extracted with dichloromethane. The crude product was purified by column chromatography and recrystallisation from MeOH and toluene to give the expected meslyted-phthalocyanine (**41**) in an acceptable yield of 72 %. Characterization of (**41**) was achieved using IR, UV-vis, MALDI-MS and ¹H NMR spectroscopies. The target compound (**41**) was found to be pure by ¹H NMR spectroscopy. Aromatic protons were observed between 7.68 and 9.17 ppm

integrating for 9 protons. A sharp signal of the mesylate leaving group were observed around 3.03 ppm, integrating for 3 protons as expected. The MALDI-Mass spectra of the complex showed a molecular ion peak at 1274.7 which is consistent with predicted structure.

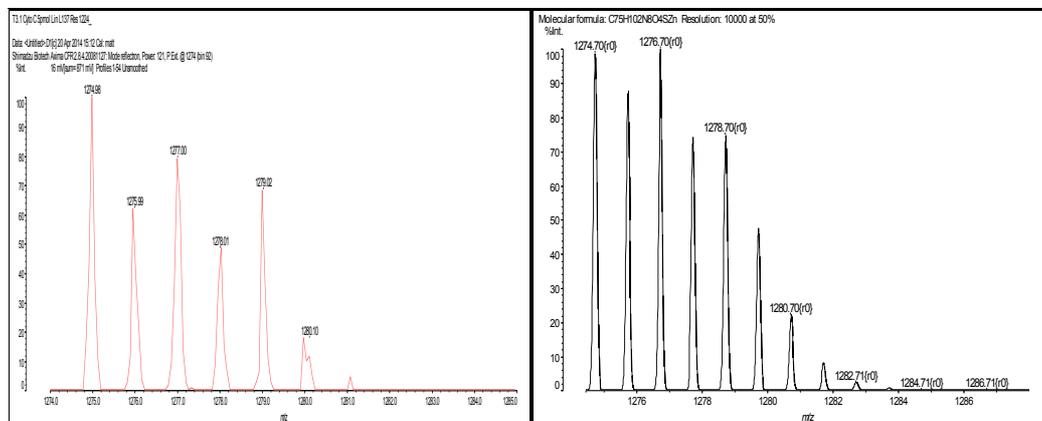


Figure 13: MALDI-MS spectrum of **39** (left) with its theoretical prediction.

The electronic absorption spectrum of ZnPc-OC₆H₁₂OMs showed the typical pattern. The Q-band absorption resulting from π - π^* transition of a MPC can be seen at 693 nm with a shoulder at 623 nm usually attributed to the vibronic band. Unsymmetrical phthalocyanines sometimes show split Q-bands but this is not observed.

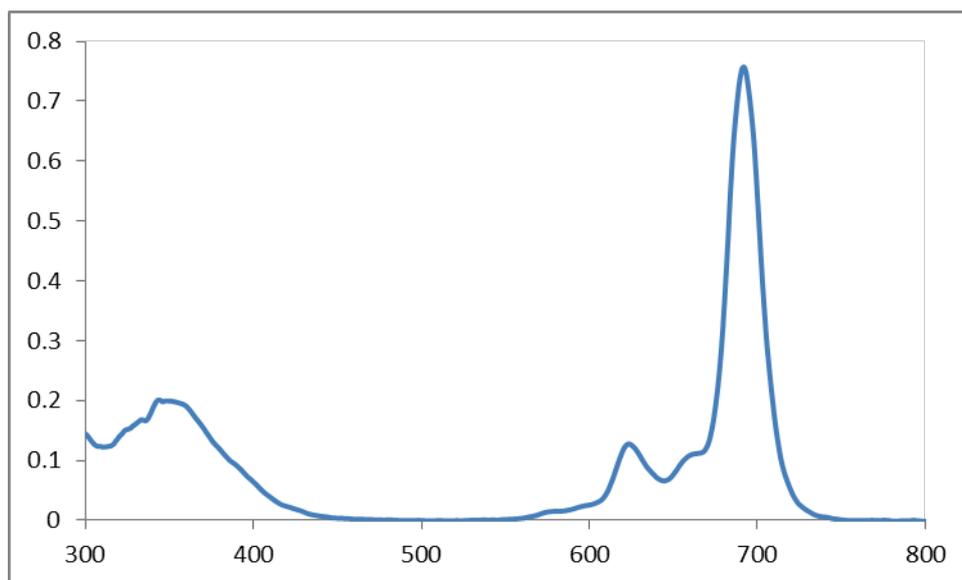
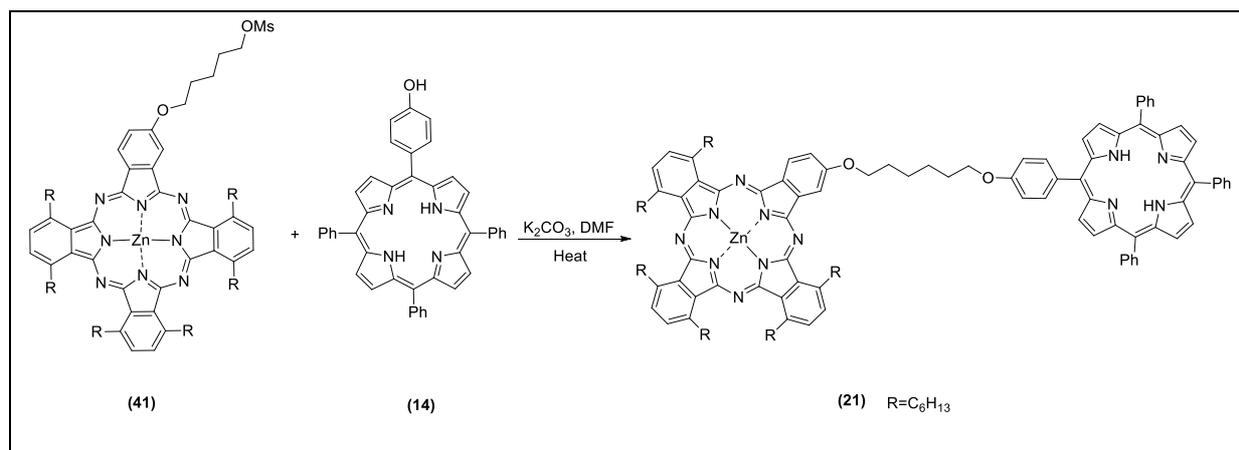


Figure 14: Shows the UV-vis spectra of ZnPc-OC₆H₁₂OMs (**39**) in THF.

Synthesis the PC-Pn dimer (21):



Scheme 25: Synthesis of the target dimer (21).

Theoretically, the synthesis of the target dimer could now simply be completed by connecting one phthalocyanine monomer with porphyrin monomer by means of a hexyl mesitylated bridge; the reaction seems to be straightforward as shown in scheme 25. The reaction was carried out in the normal basic nucleophilic substitution reaction conditions. Therefore mesitylated phthalocyanine (41) was heated in DMF and reacted with hydroxy porphyrin (14) employing K_2CO_3 . This method was found to be poor but the required product was obtained, albeit in poor yield. The MALDI MS also indicates presence of an unknown side product (figure 15).

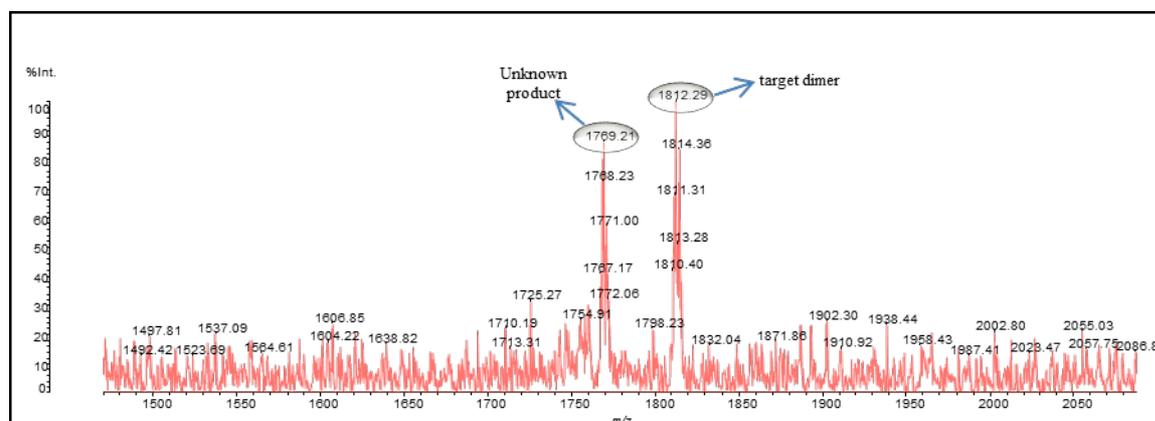


Figure 15: MALDI-MS spectrum of separated dimer product (21).

The reaction was attempted several times using different conditions with similar results (Table 2). The initial attempts used DMF, dry DMF and acetonitrile as solvents. However, no improvement in the product yield was obtained under these conditions. Eventually a switch was made to a stronger base and increase proportion of reaction materials. However, the Pc-Pn dimer was not successfully achieved in reasonable yield under all these modifications.

No	ZnPc-OC ₆ H ₁₃ OMs(eq)	TPP-OH	Base	Solvent	Yield (%)
1	1.0 eq	1.2 eq	K ₂ CO ₃	Dry DMF	Less than 30*
2	1.3 eq	1.0 eq	K ₂ CO ₃	Dry DMF	Less than 30*
3	2.0 eq	1.0 eq	K ₂ CO ₃	Dry DMF	Less than 30*
4	2.0 eq	1.0 eq	K ₂ CO ₃	DMF	Less than 30*
5	2.0 eq	1.0 eq	NaH	CH ₃ CN	Decomposed
6	2.0 eq	1.0 eq	DBU	DMF	Decomposed

* The same unknown compound shown in figure 15 was observed.

Table 2: Selected conditions which have been used to gain Pc-Pn dimer (**21**).

We then decided to use cesium carbonate. There were two reasons for this suggestion; its solubility is higher in organic solvents compared to other carbonates like potassium and sodium carbonates. The second reason was that caesium carbonate strength is higher comparing to potassium carbonate. The reaction was performed using CsCO₃ in DMF. After workup the crude product was chromatographed on silica gel. The ¹H NMR spectrum of the dimer in THF-d₈ (the substance was insoluble in CDCl₃) shows the disappearance of the mesylate protons at 3.03 ppm in the ZnPc component. The presence of a new signal at 4.75 ppm is seen in the product spectrum and this chemical shift suggested that it had formed a

new ether link. The remaining methylene groups of the alkyl chains appear as broad peaks between 0.0-2.19. The characteristic signal for the phthalocyanine and porphyrin protons appear as expected as shown in figure 16:

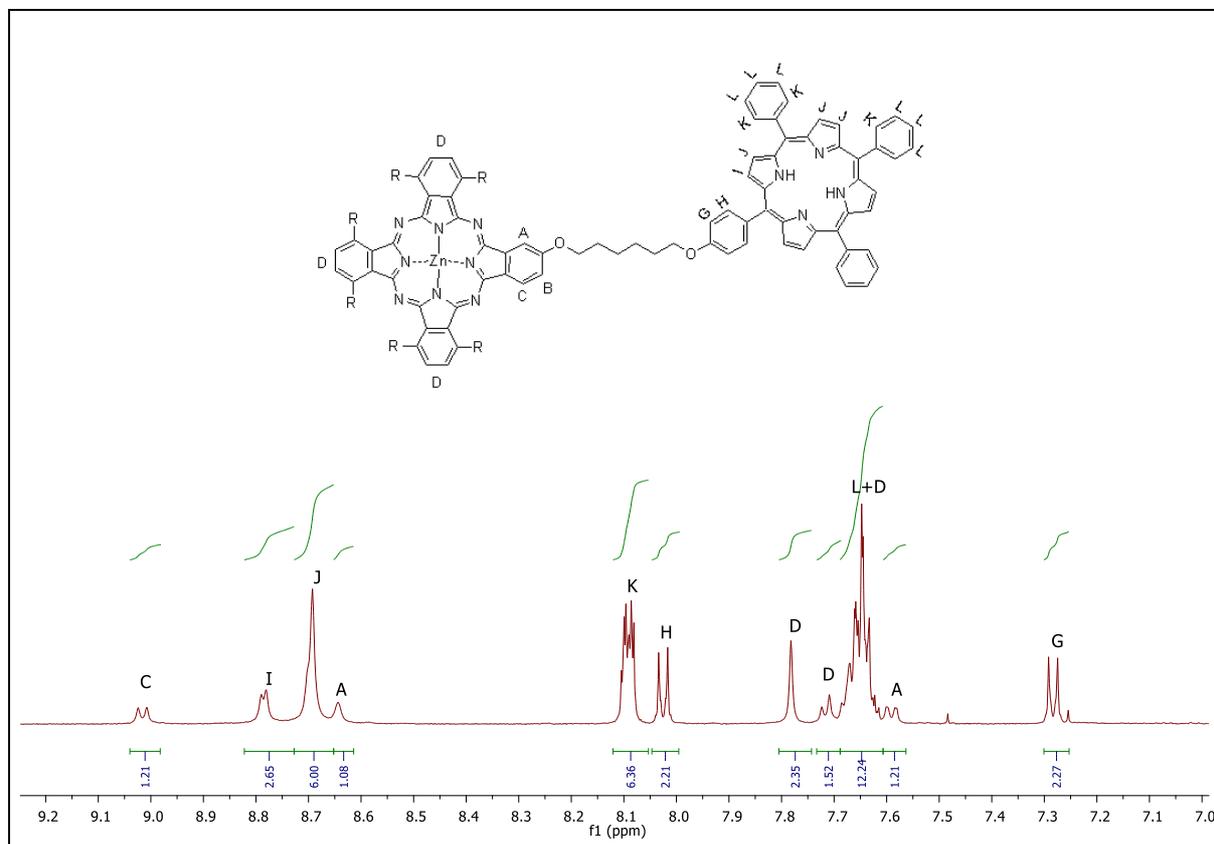


Figure 16: ¹H NMR spectrum of the aromatic area of ZnPc-OC₆H₁₂O-Pn (**21**) in THF-d₈ at 25 °C.

The MALDI-MS spectrum of the dimer is shown in figure 17 and shows a peak at 1812 corresponding to the expected molecular ion.

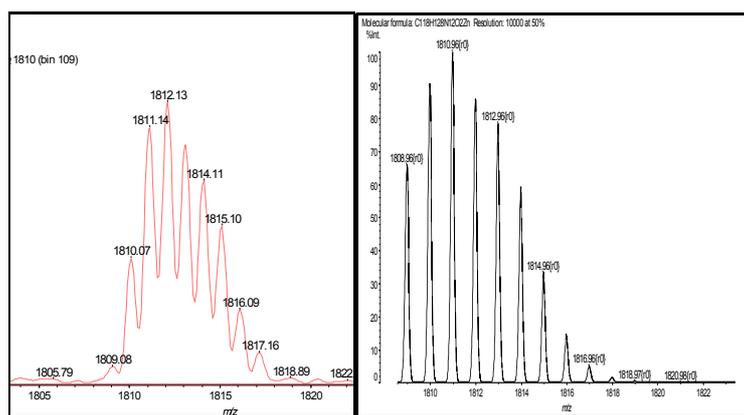


Figure 17: MALDI-MS spectrum of **21** (left) with its theoretical prediction.

The UV-vis spectrum of Pc-Pn dimer (**21**) is shown in figure 18 alongside the spectrum of phthalocyanine starting material (**41**). The spectrum obtained in THF shows a slightly broadened Q-band. The main different between the two spectra is the appearance of porphyrin peaks at 418 nm, 519 nm, 553 nm and 597 nm respectively. Essentially, the observed spectrum is a direct combination of the porphyrin and phthalocyanine spectra, indicating that there is little or no electronic perturbation in the dimer in its ground state (e.g. by face-to-face intramolecular dimerization).

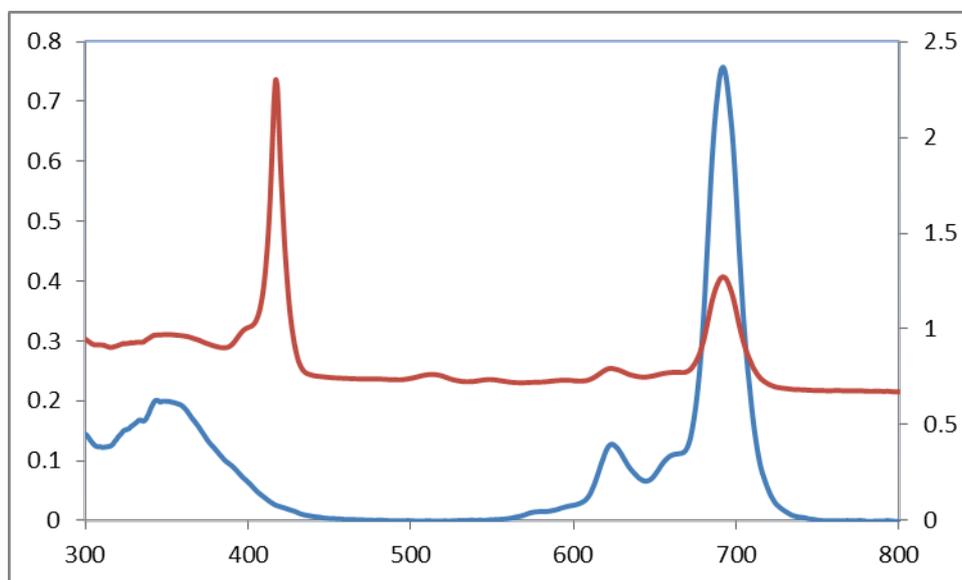


Figure 18: comparative UV-vis spectra of dimer (**21**) (red line) and ZnPc-OMs (blue line) in THF.

As mentioned earlier some of the objectives of this work are a synthetic study on two types of dimer. With the first one (phthalocyanine-porphyrin dimer with flexible linker) successfully synthesised we then decided to turn our attention to synthesis of the second type of dimers where identical species as Pc and Pn are linked. These species could link together using rigid linkage such butadiynyl bridge or 1,5-difluoro-2,4-dinitrobenzene as illustrated previously in figure 1. All these dimers as well as a porphyrin trimer will be discussed next.

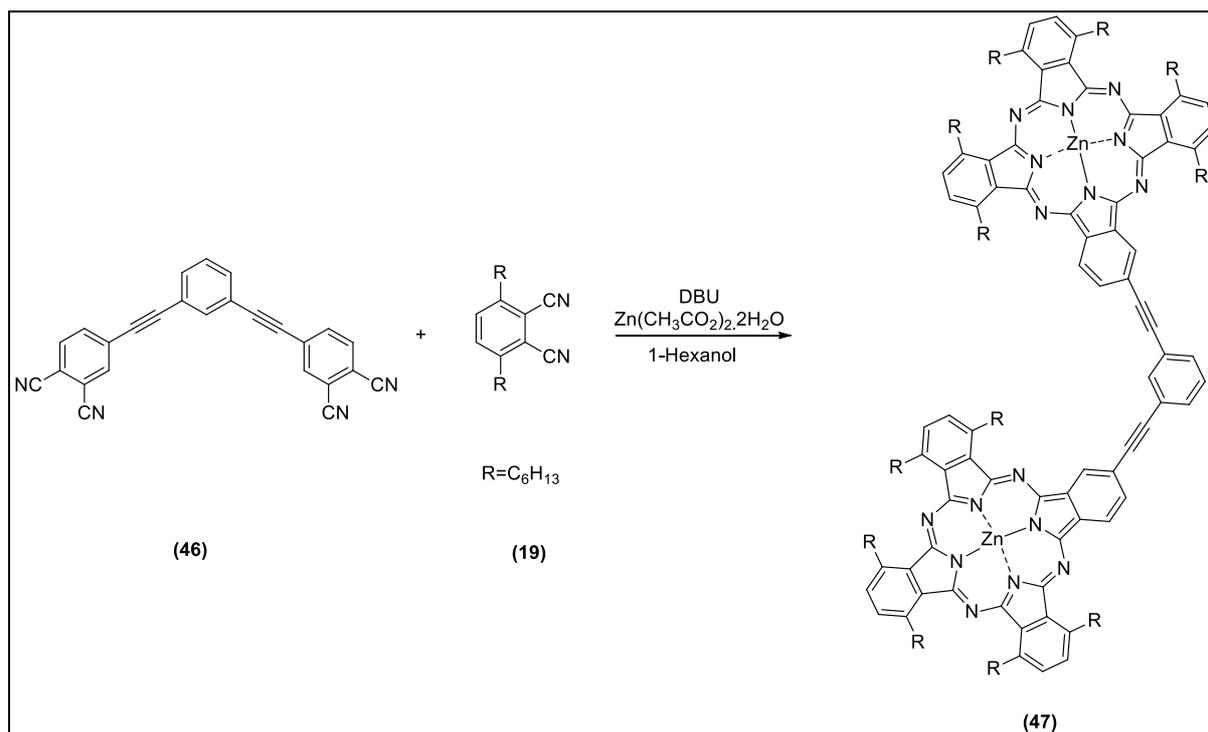
2.10 Design and synthesis of butadiynyl-bridged bisphthalocyaninatozinc system

One of the interests in our group is the important properties of liquid crystal materials and part of the basic design of molecules in this part of this project was the study the LC behaviour of Pc dimers. Studies have been undertaken with phthalocyanine oligomers³⁷ in an attempt to investigate the liquid crystal behaviour. However, no such studies have been undertaken with non-peripherally substituted hexyl zinc phthalocyanine dimer. In this section, there were two dimers attempted to be synthesised. The main differences between the two dimers were the linker and the route of the reaction. In our strategy two specially functionalised phthalocyanine subunits were to be synthesised separately, and then linked together.

2.10.1 The first Pc-Pc dimer (47)

The first target dimer (47) may be synthesised in one step, using a mixed cyclisation of a diphtalonitrile with an excess of monomeric phthalonitrile. The synthetic approach is described below. It appeared likely that several different products, including polymeric species, might result making purification of the resultant mixture extremely problematic.

However it was hoped that separation of the required molecule would be feasible. These difficulties are compensated by the fewer steps involved in this route to Pc dimers. The mixed cyclisation is also likely to be more flexible, the same chemistry offering a route into dimers with spacer groups theoretically ranging from two atoms upwards, although it was anticipated that the yield of the required product would become very low.



Scheme 26: Proposed synthesis of dimeric Pc (47).

In order to obtain the target, two phthalonitriles needed to be prepared as shown below:

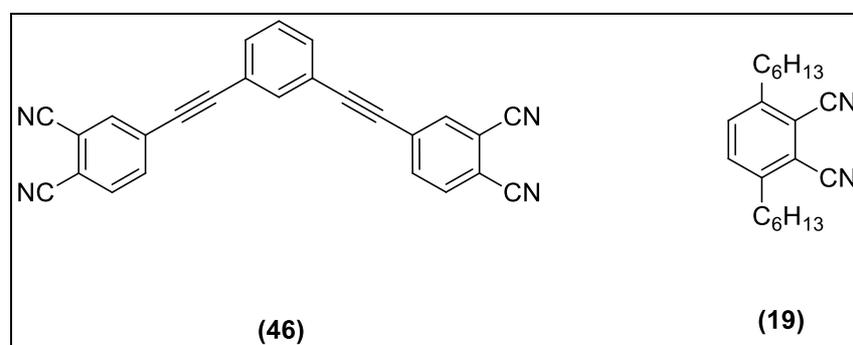


Figure 19: The used phthalonitriles.

The synthesis of 3,6-dihexylphthalonitrile was discussed previously. The main synthetic challenge was therefore the synthesis of the phthalonitrile dimer (**46**).

Attempts were made to synthesise phthalonitrile dimer by one route of the two initially considered (paths 1 and 2, figure 19). The choice of the second approach was made as the immediate precursors to the required dimeric Pcs were readily available.

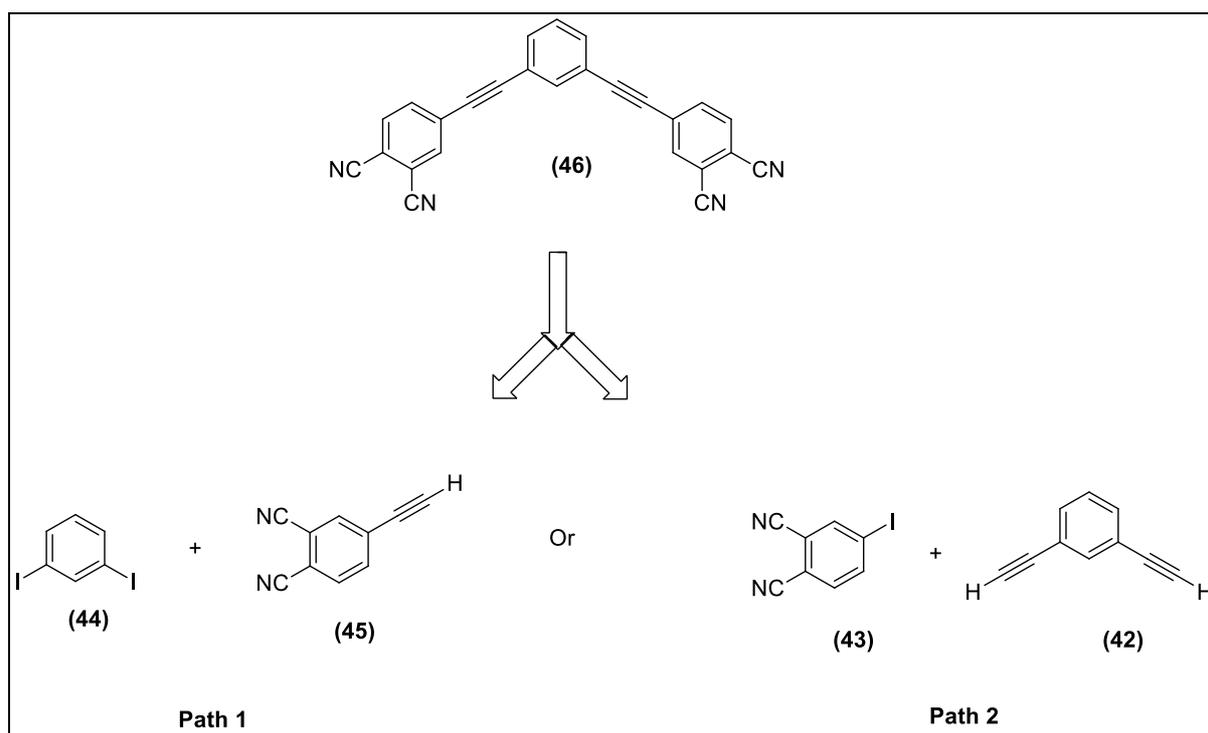
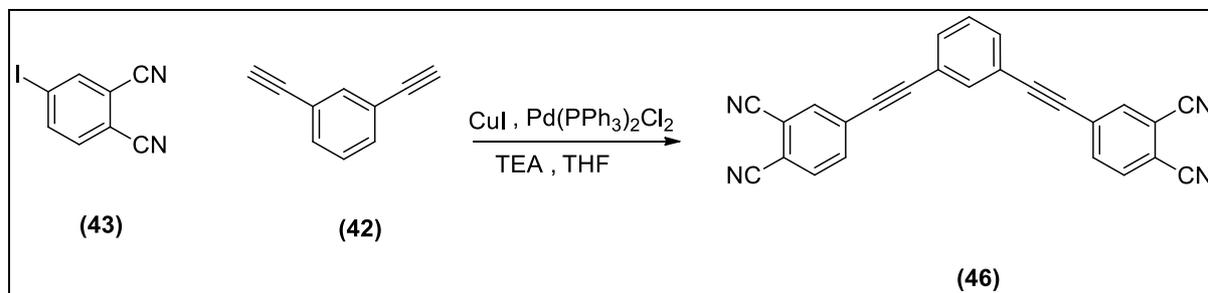


Figure 20: Retro-synthesis of the dimeric phthalonitrile (**46**).

2.10.1.1 The synthesis of 4,4'-(1,3-phenylenebis(ethyne-2,1-diy))diphthalonitrile (46)



Scheme 27: Preparation of diphthalonitrile (46)

The chemistry of the synthesis of dimeric phthalonitriles is well studied and it seemed logical simply to extend this approach to the dimeric system. Consequently 4-iodophthalonitrile (43) was mixed with 1,3-diethynylbenzene (42) in a ratio of 2.2:1 in dry TEA and THF. CuI and Pd(PPh₃)₂Cl₂ were added in catalytic quantity and then the mixture heated to reflux for 16 h. After workup, column chromatography yielded the product which was characterised by NMR spectroscopy which showed the expected signals.

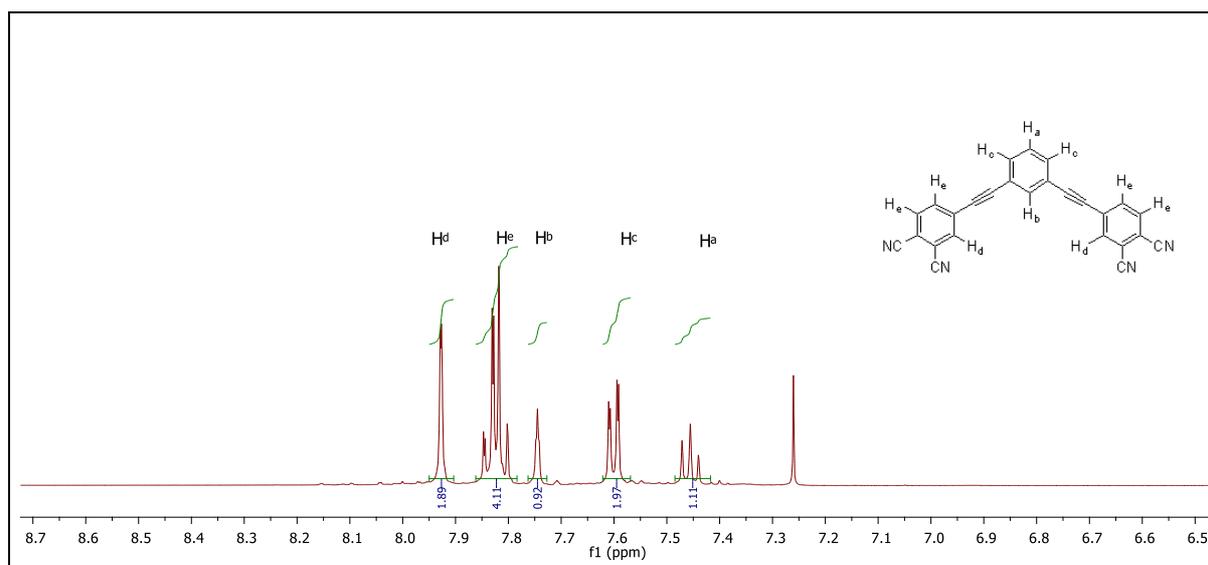


Figure 21: ¹H NMR spectrum of aromatic area of diphthalonitrile 46 in CDCl₃ at 25 °C.

Synthesis of the target Pc-Pc dimer (**47**) was attempted by the mixed cyclisation of a 8:1 ratio of 3,6-dihexylphthalonitrile and diphtalonitrile (**46**). The mixture was stirred under reflux in *n*-hexanol in the presence of excess of zinc acetate and DBU for 18 h. It was found that in this cyclisation most of the material decomposes before any significant amount of phthalocyanine is created. A green solid was recovered which was washed with methanol. However the green material was found to be insoluble in all common organic solvents, making purification impossible.

We then tried a different approach to prepare a dimer of phthalocyanine material with enforced communication between the phthalocyanines. It was decided to attempt to synthesise Pc dimers consisting of subunits, each with six alkyl chains to confer solubility in organic solvents, connected by a butadiynyl bridge. An ethynyl group was chosen as the seventh substituent on each of the Pc subunits to facilitate the synthetic route. The first structure considered was the bis [(23-ethynyl-1,4,8,11,15,18-hexakis(hexyl)-phthalocyaninato)zinc(II)] butadiyne (**51**), which is fully conjugated (figure 22).

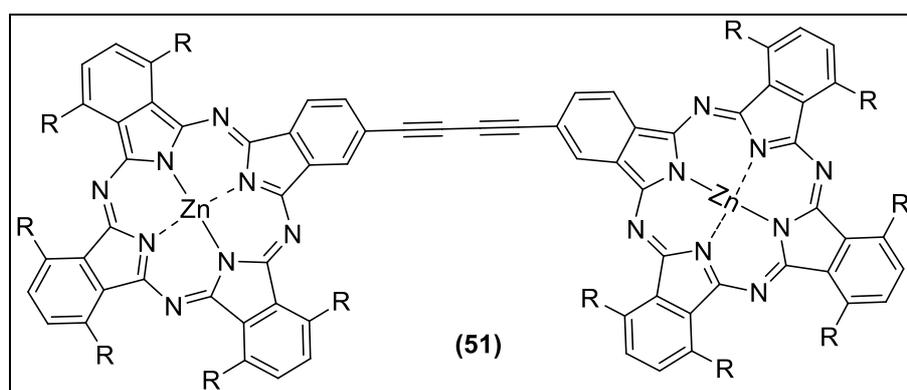
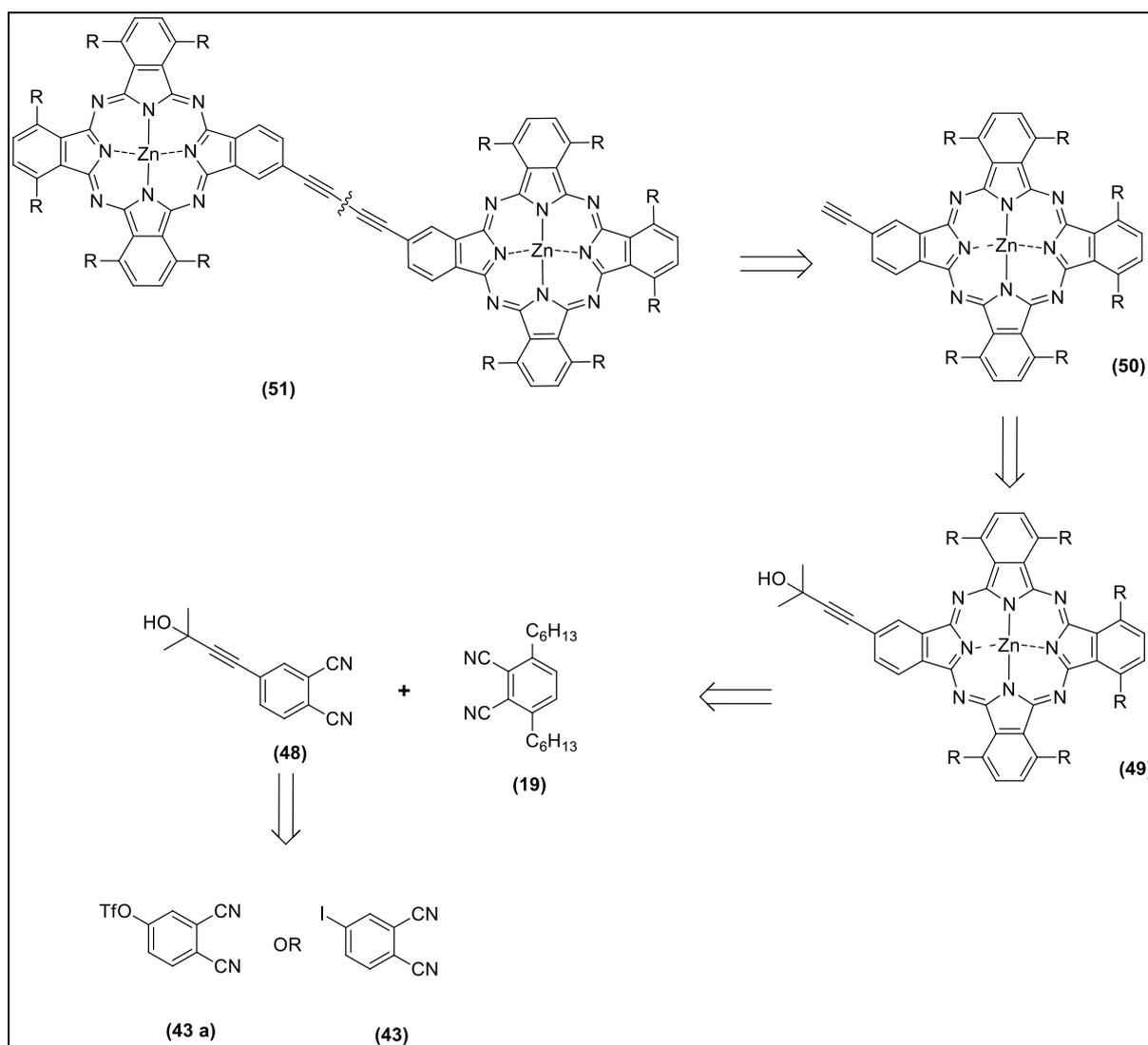


Figure 22: Structure of target Pc dimer (**51**).

In order to achieve the target compound, we proposed to follow the route in scheme 28, and thus the dimerisation could be accomplished *via* an oxidative coupling reaction between two acetylenes. Compound (**50**) was proposed to be made by the deprotection of the protected

ethynyl Pc (**49**), which could be achieved from the 4-iodophthalonitrile (**43**) or unsymmetrical 23-iodophthalocyanine *via* Sonogashira coupling.

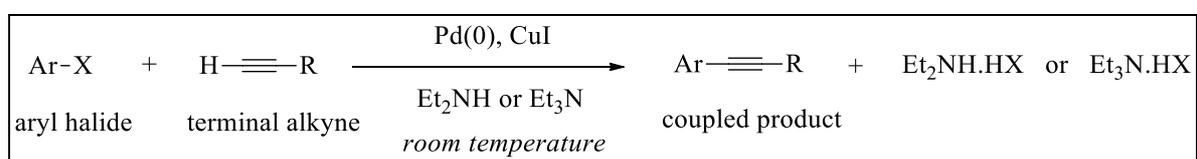
The retro-synthetic route (scheme 28) also shows that the desired of 1,4,8,11,15,18-hexakis(hexyl)-23-(3-hydroxy-3-methyl-1-butynyl)-phthalocyaninatozinc(II) (**49**) required the condensation of 3 molecules of 3,6-dihexylphthalonitrile (**19**) with 1 molecule of 4-(3-hydroxy-3-methylbut-1-yn-1-yl)phthalonitrile (**48**).



Scheme 28: Retro-synthesis of butadiynyl-bridged bisphthalocyaninatozinc system.

2.10.2.1 Sonogashira Cross-Coupling

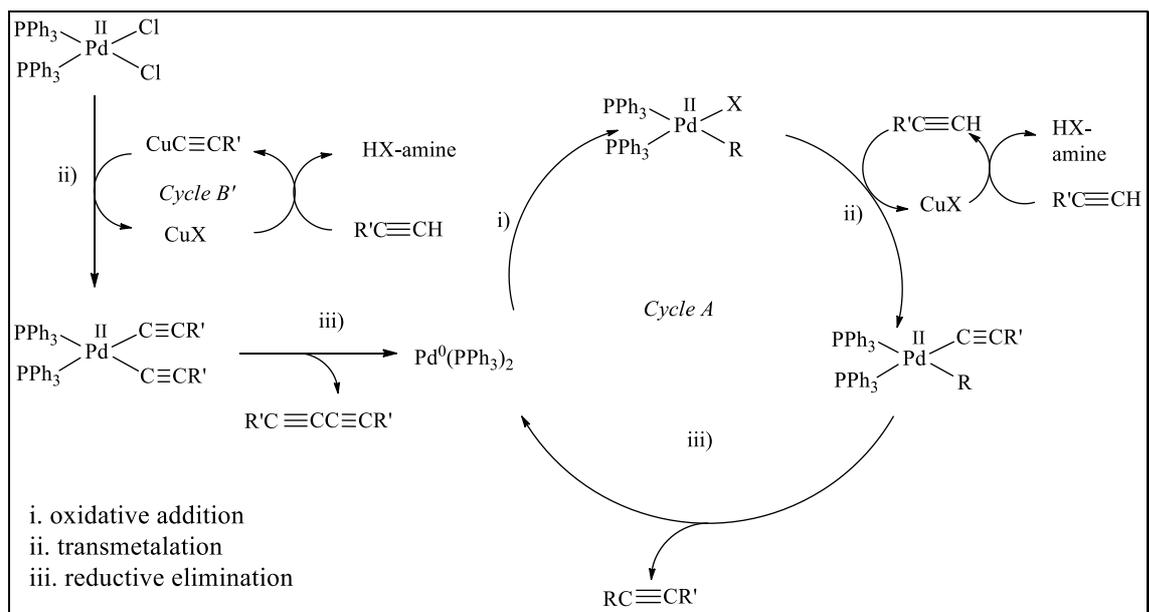
The introduction of an acetylene group in phthalonitrile or phthalocyanine compounds can be achieved through Sonogashira cross-coupling (Scheme 29).³³ The reaction involves a Pd/Cu-catalysed cross-coupling of organohalides with terminal alkynes. This catalytic process requires the use of a palladium (0) complex and is performed in the presence of base, generally using copper iodide as a co-catalyst.



Scheme 29: General Sonogashira reaction

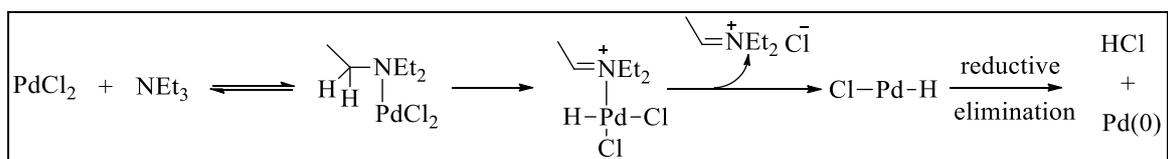
One of the most important advantages of the reaction is that it can be used with thermally sensitive substrates. The absence of oxygen in these reactions is essential in order to prevent the formation of homocoupling compounds from the terminal alkyne.

The mechanism of the reaction is similar to that of the Stille and Suzuki couplings. Oxidative addition of the organic halide gives a palladium (II) intermediate that undergoes transmetalation with the alkynyl copper (generated from the terminal alkyne, base and copper iodide). Reductive elimination with coupling of the two organic ligands gives the product and regenerates the palladium (0) catalyst. (Scheme 30)



Scheme 30: Mechanism of Sonogashira cross-coupling reaction.

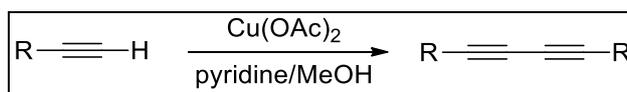
Generally the use of a stable and soluble Pd(II) derivative is more favourable such as *bis* (triphenylphosphine)palladium(II) chloride instead of Pd(0). This is rapidly reduced *in situ* to give a coordinatively unsaturated, catalytically active, palladium(0) species. However, Et₃N may reduce Pd(II) to Pd(0) as well (scheme 31), where Et₃N is oxidised to iminium ion at the same time:



Scheme 31: Process of reduce Pd(II) to Pd(0) by Et₃N.

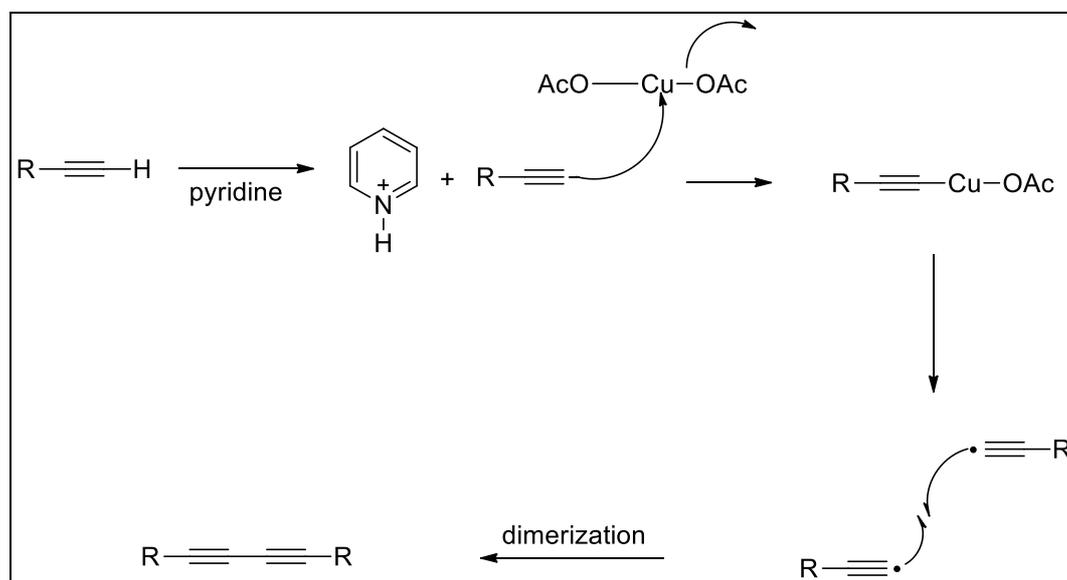
2.10.2.2 Eglinton Reaction

The oxidative coupling of acetylenic copper compounds provides a useful method of forming carbon-carbon bonds under mild conditions³⁴ as shown in scheme 32. In this reaction the terminal alkynes are coupled in presence of Cu(II) salt and base such pyridine. Eglinton reaction can produce symmetrical diynes in high yields



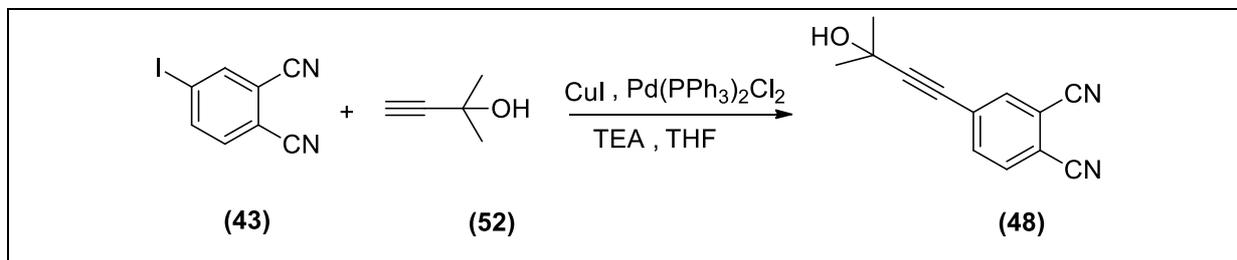
Scheme 32: General Eglinton Reaction.

The mechanism in this coupling proposed that the pyridine reacts with alkynes to form alkyne anion. The anion reacts with cupric salts in order to form the corresponding free radical. In the last stage two free radicals undergo dimerisation to form a coupled product as shown in scheme 33:



Scheme 33: Mechanism General Eglinton coupling reaction.

2.10.2.3 The synthesis of 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile (48)



Scheme 34: Preparation of 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile (48).

The synthesis of 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile (48) followed a literature procedure³⁵ using Sonogashira cross-coupling by refluxing a solution of 4-iodophthalonitrile (43) and 2-methylbut-3-yn-2-ol in the presence of *bis* [triphenylphosphine]palladium dichloride and copper(I) iodide in freshly distilled triethylamine and THF. Then, the mixture was brought to reflux overnight. An aqueous work up was followed by purification over silica gel eluting with 3:2 hexane / ethyl acetate. The product (48) was obtained in reasonably good yield (61%). The pure product (48) was isolated in as an oil, which upon cooling became a colourless solid. The ¹H-NMR spectrum (figure 23) showed a singlet at ca. 1.50 ppm assigned to the two methyl groups and a singlet at 5.66 ppm for hydroxyl group. In Sonogashira coupling, trimethylsilyl (TMS) protecting groups are often employed, but use of 2-hydroxyprop-2-yl protection is becoming more popular because the reagent is cheap (so can be used in excess) and less volatile than TMS-acetylene.

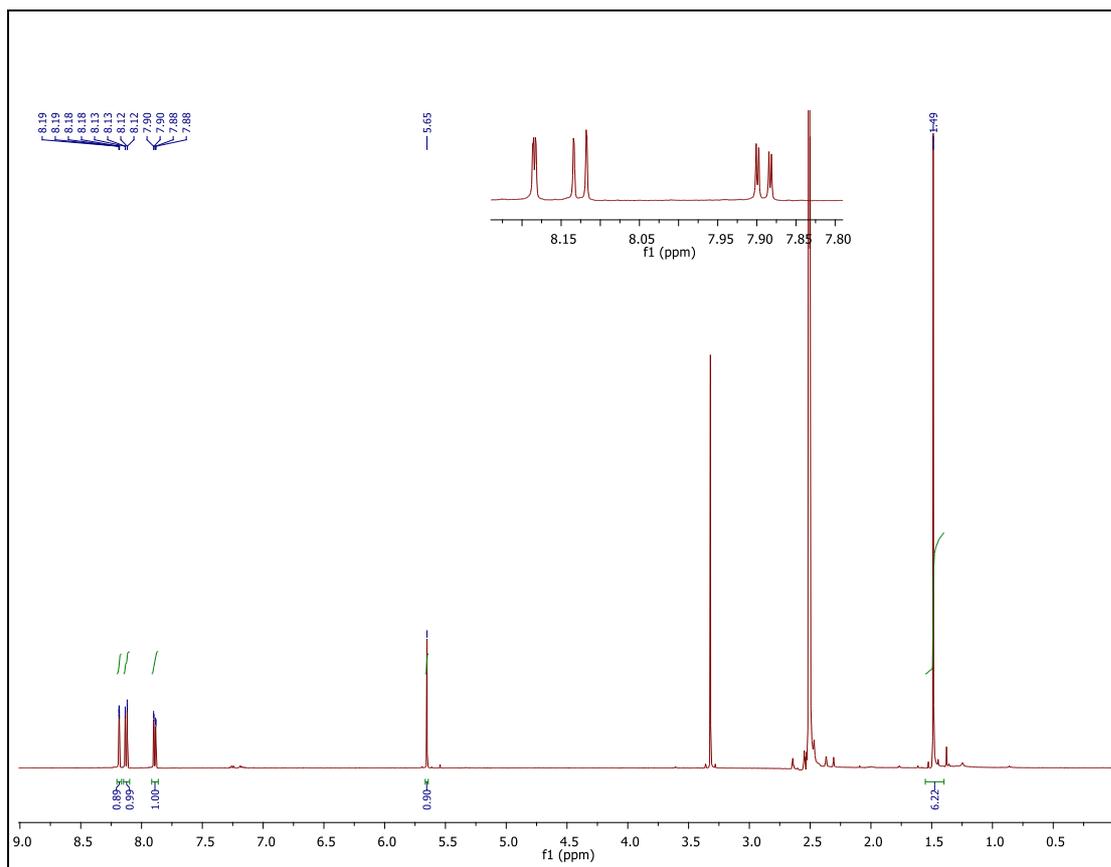
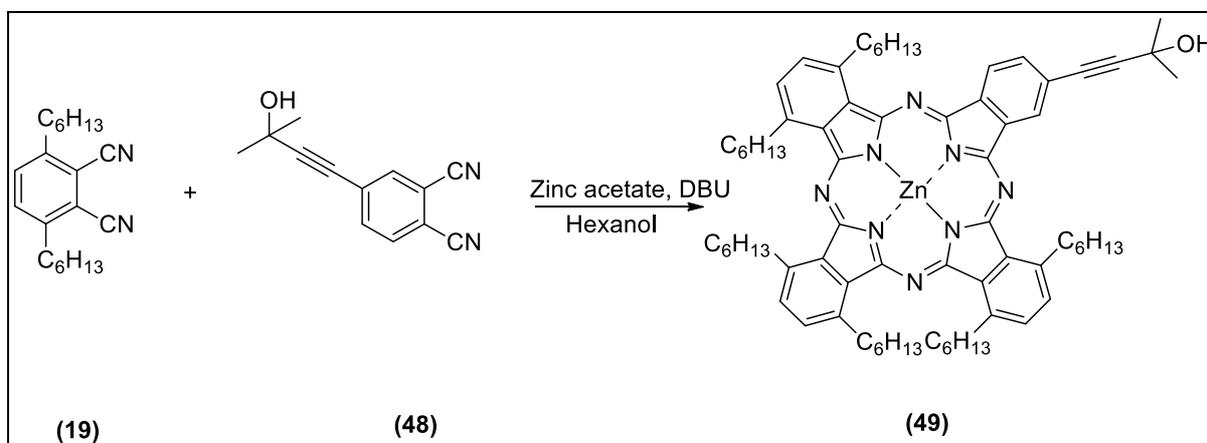


Figure 23: ^1H NMR of 4-(3-hydroxy-3-methyl-1-butynyl) phthalonitrile in DMSO-d_6 in 25°C .

2.10.2.4 Preparation of 1,4,8,11,15,18-hexakis(hexyl)-23-(3-hydroxy-3-methyl-1-butynyl)-Phthalocyaninatozinc(II) (49)



Scheme 35: Synthesis of Pc (**49**).

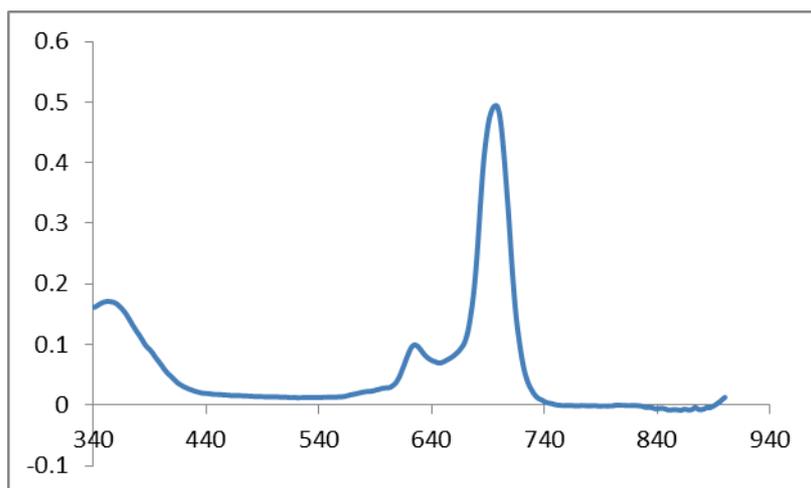


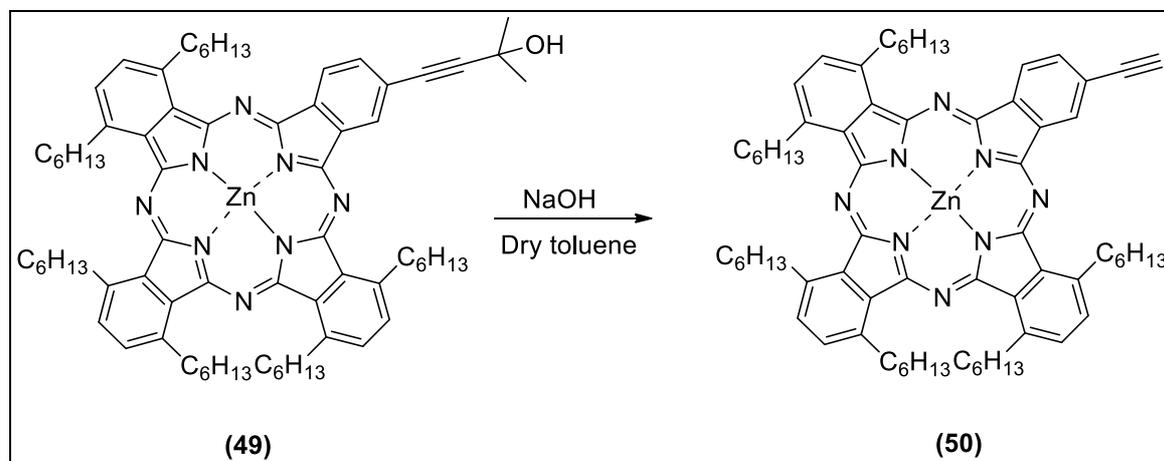
Figure 25: UV-vis spectrum of (49) in THF.

Phthalocyanine (49) is crystalline, but despite many attempts we could not grow crystals suitable for X-ray crystallography.



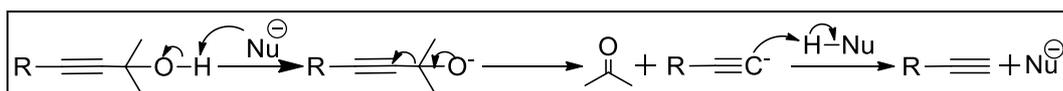
Figure 26: Small crystals of phthalocyanine (49).

2.10.2.4 Preparation of 1,4,8,11,15,18-hexakis(hexyl)-23-ethynyl-phthalocyaninatozinc(II) (50)



Scheme 36: The deprotection of Pc (50).

Deprotection of Pc (49) was achieved by refluxing in dry toluene in the presence of sodium hydroxide for 4 hours under argon to afford the unsymmetrical Pc bearing one terminal alkyne. The mechanism of the deprotection step is shown in Scheme 37:



Scheme 37: Mechanism of the deprotection of (49).

The formation of the required compound was confirmed by MALDI-MS (isotopic cluster 1106) as shown in figure 27.

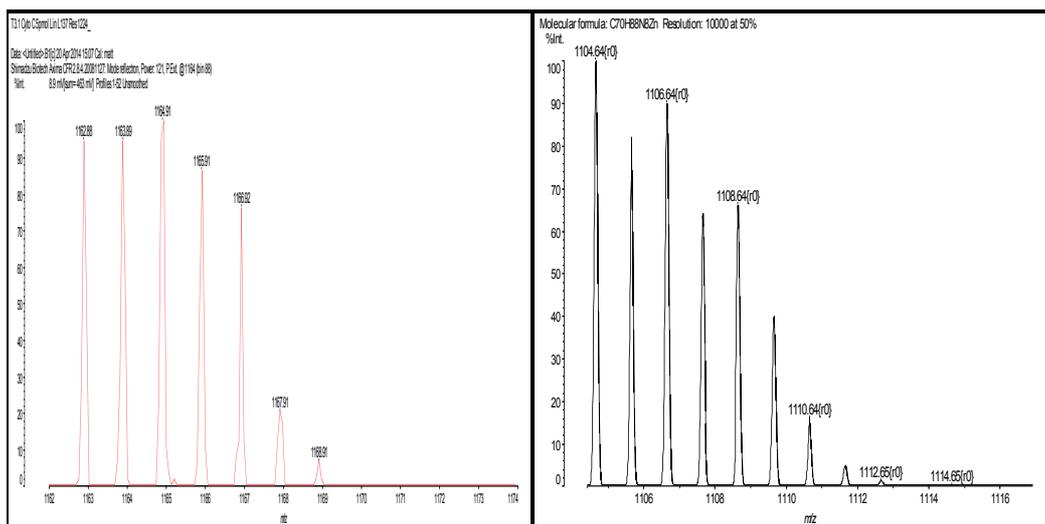


Figure 28: MALDI-mass spectrum of **50** (left) with its theoretical prediction.

The ^1H NMR spectrum (THF- d_8) showed the expected appearance of the signal of ethynyl proton at 3.94 ppm as shown in figure 28. Again, THF- d_8 had to be used as NMR solvent to give very clear signals for the Pc.

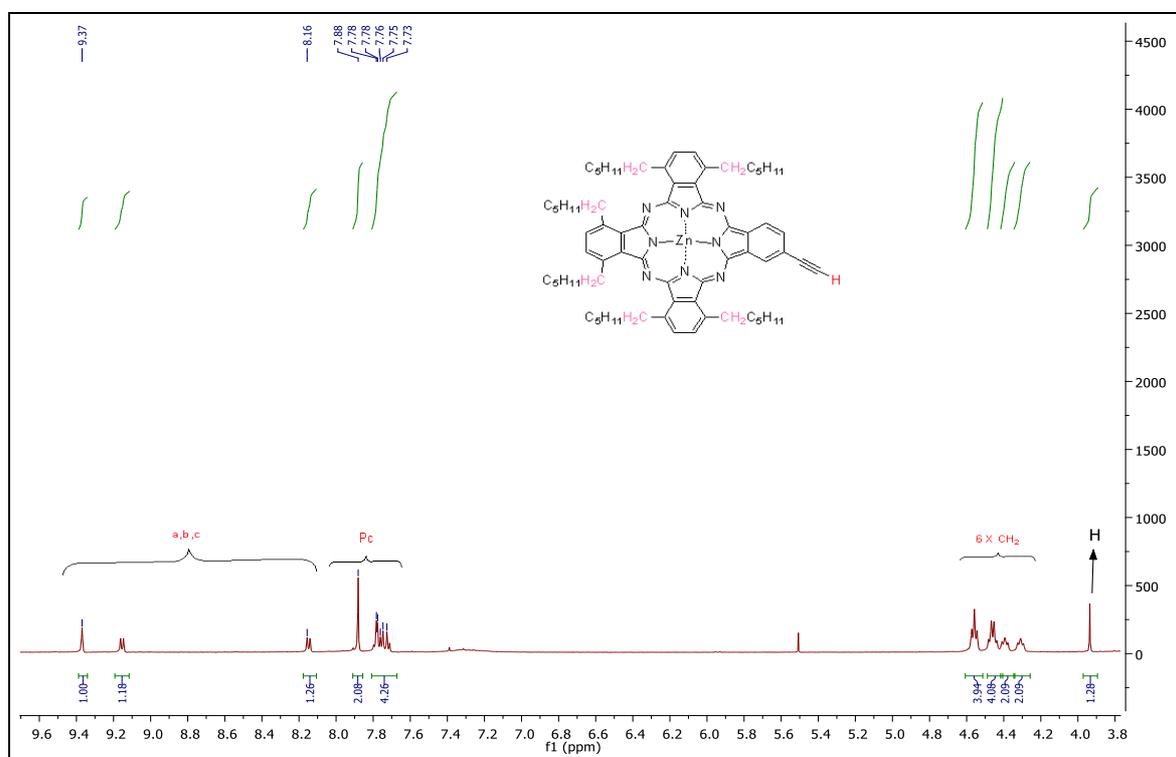
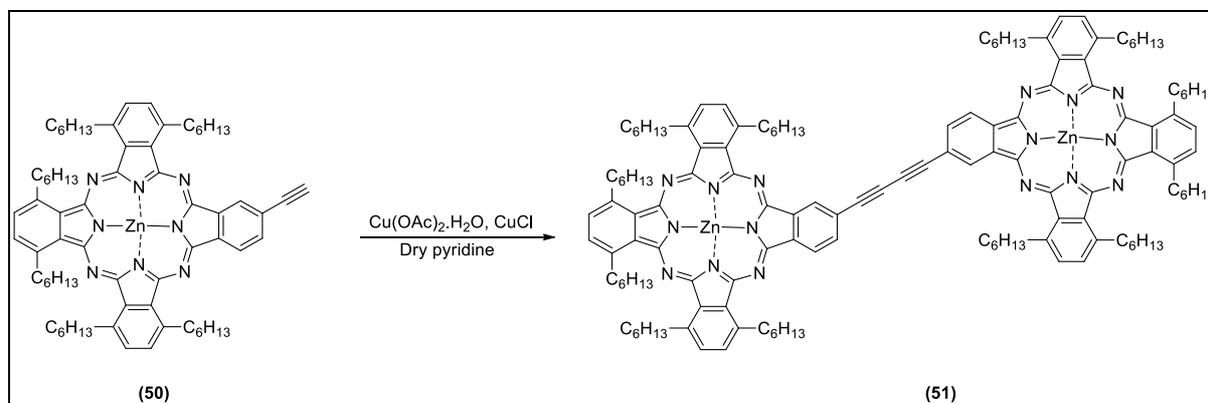


Figure 28: ^1H NMR spectrum of 1,4,8,11,15,18-hexakis(hexyl)-23-ethynyl-phthalocyaninatozinc(II) **50** in THF- d_8 at 25 °C.

The unsymmetrical nature of (**50**) is immediately apparent from inspection of its ^1H NMR spectrum. At ca. 9.37, 9.15, and 8.15 ppm we see signals corresponding to 3H for the unsymmetrical phenyl ring hydrogens. The six aromatic hydrogens of the remaining phenyl rings appear at ca. 7.85 as singlet and 4 hydrogens appear as multiplet signals between 7.82 to 7.68 ppm. After purification by chromatography and crystallisation from toluene and ethanol the product was isolated in 70 % yield. The next step then involved oxidative coupling to give the dimer.

2.10.2 Preparation of Bis[(23-ethynyl-1,4,8,11,15,18-hexakis(hexyl)phthalocyaninato)zinc(II)]butadiyne (**51**)



Scheme 38: The dimerisation of Pc (**51**).

The connection of two molecules of Pc (**50**) to form the required dimer is a theoretically straightforward reaction as illustrated in scheme 38. The reaction is an oxidative coupling reaction using copper salts in presence of pyridine. The reaction was monitored by TLC and stopped after 24 h. The reaction was worked up including a wash with EDTA to make sure

we removed any copper salts. Then, the crude product was purified by two types of chromatography. The first one was the normal column chromatography and the second one was the size exclusion chromatography to isolate the dimer.

The ^1H NMR spectrum had to be performed in THF-d_8 again and showed that the compound was pure. It still gave broad signals for the aromatic protons as can be seen in figure 29. The broad signals were most likely caused by aggregation of the molecules.

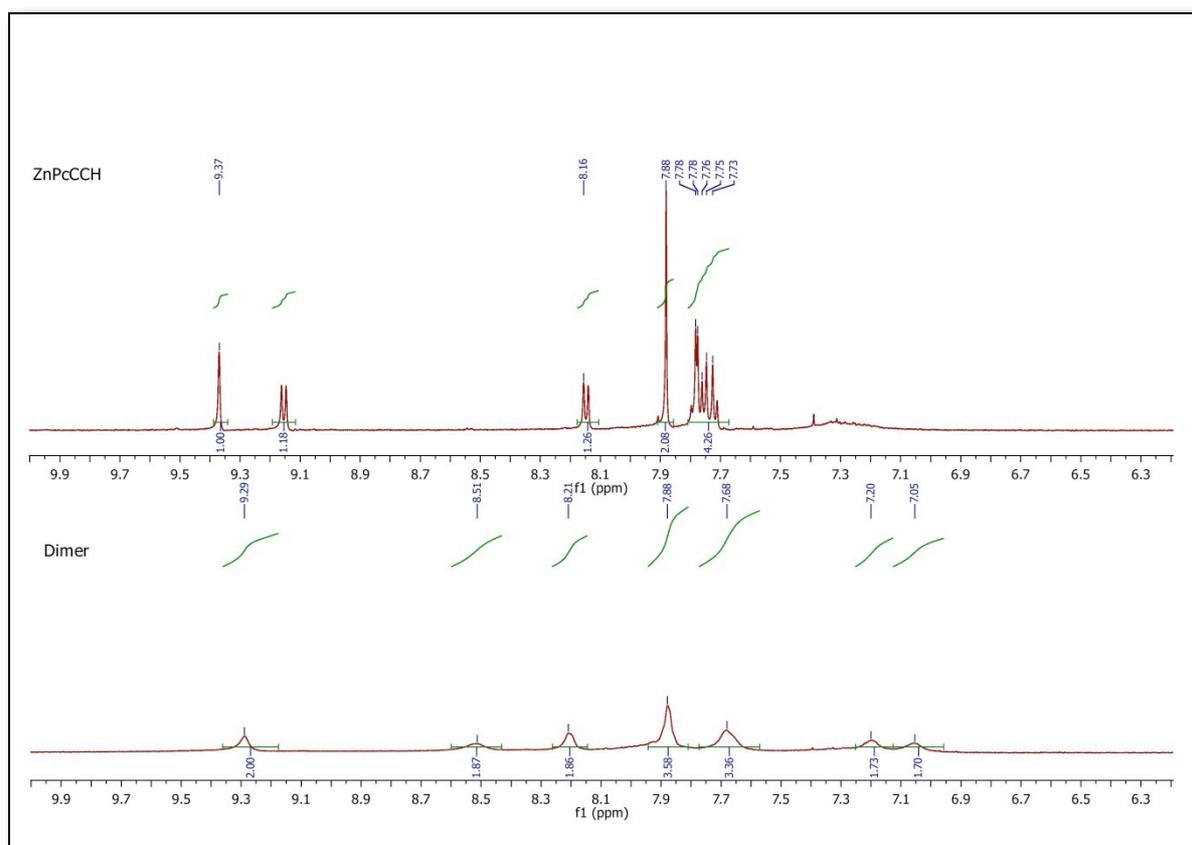


Figure 29: Comparison of the ^1H MNR spectra of **50** and **51** in THF-d_8 .

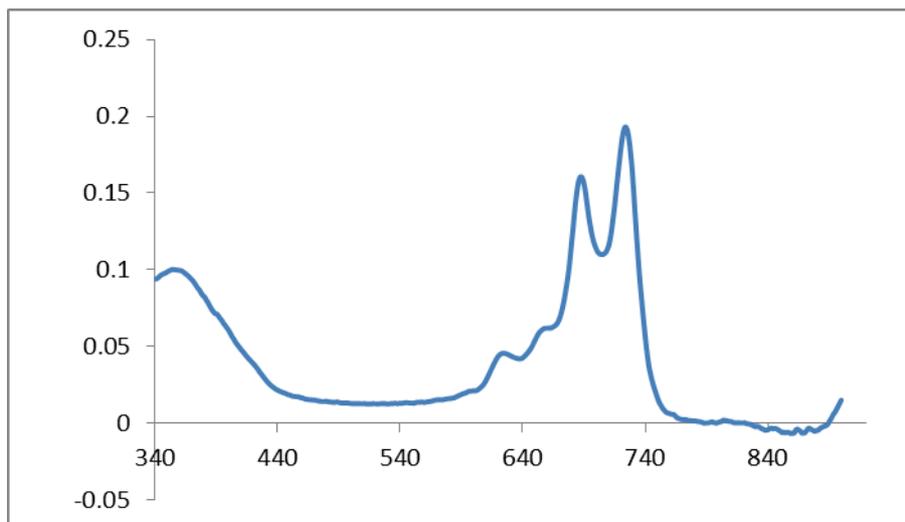


Figure 30: UV-vis spectra of **(51)** in THF.

The UV-vis spectrum of the Pc-Pc dimer is very different from ZnPc-CCH (**50**). There is a clear red-shift and split of the Q-band which appears at 722 and 690 nm. This is a consequence of electronic coupling between the Pc subunits and demonstrates that there is conjugation (communication) between the two Pc units. We anticipated interesting liquid crystal behaviour for this dimer, and perhaps formation of a nematic phase. However, when analysed we found that the compound melts directly into an isotropic liquid and is therefore not a liquid crystal.

2.11 Alternative linking strategies

The research was further developed to examine different rigid linkers with other macrocyclic cores, such as unsymmetrical phthalocyanines and porphyrins. We chose to examine 1,5-difluoro-2,4-dinitrobenzene as a core/precursor since it has labile functional groups (the fluorides) enabling links to be made with suitable Pc and Pn derivatives. In the porphyrin case the reaction again involves a 5-(4-hydroxy phenyl)-10,15,20-triphenyl porphyrin and this will be

discussed later. Firstly, the synthesis of Pc-Pc dimers, as illustrated in figure 31, will be described.

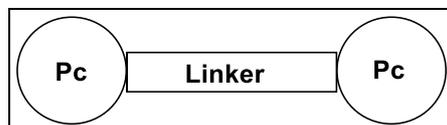
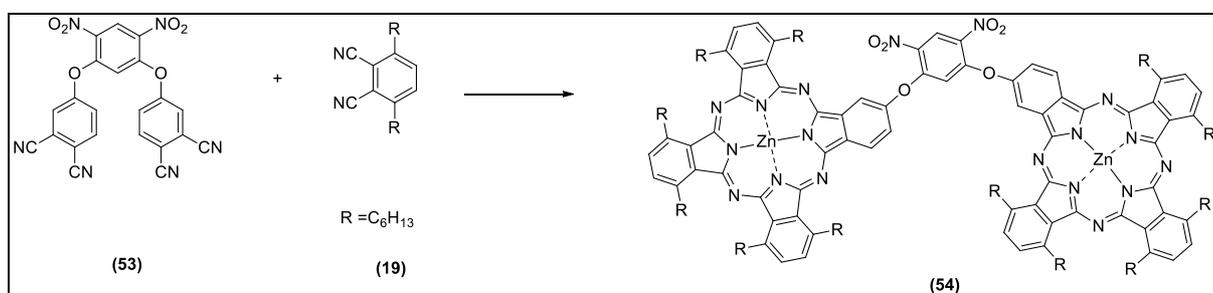


Figure 31: A cartoon representation of the dimer.

2.11.1 Design and synthesis of dinitrobenzene-bridged bisphthalocyaninatozinc system

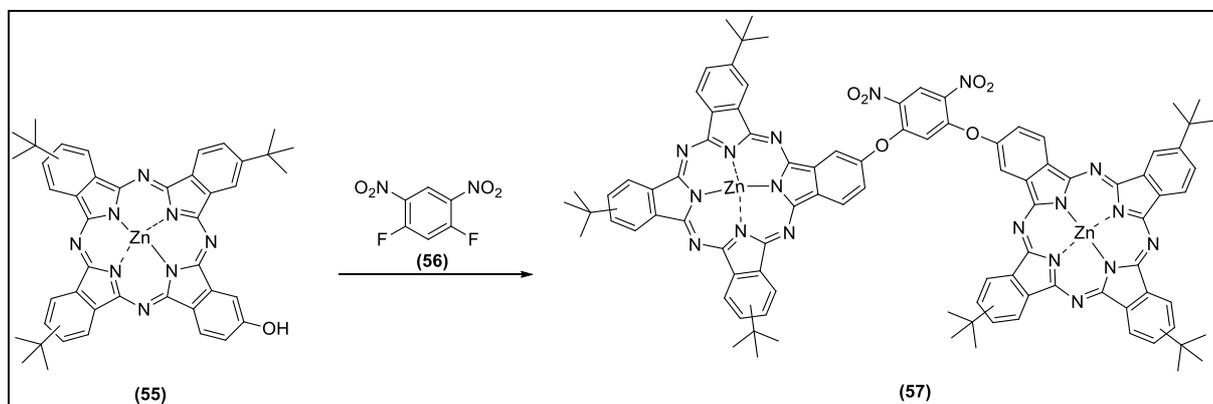
This dimer comprises two phthalocyanines linked to each other through a rigid linker such as 2,4-dinitrobenzene. There were two approaches in order to obtain the required dimer as follows:

- I. The dimeric phthalocyanine may be synthesised in one step, using a mixed cyclisation of a dimeric phthalonitrile with an excess of monomeric phthalonitrile, similar to the strategies previously described.



Scheme 39: Proposed synthesis of dimer (54).

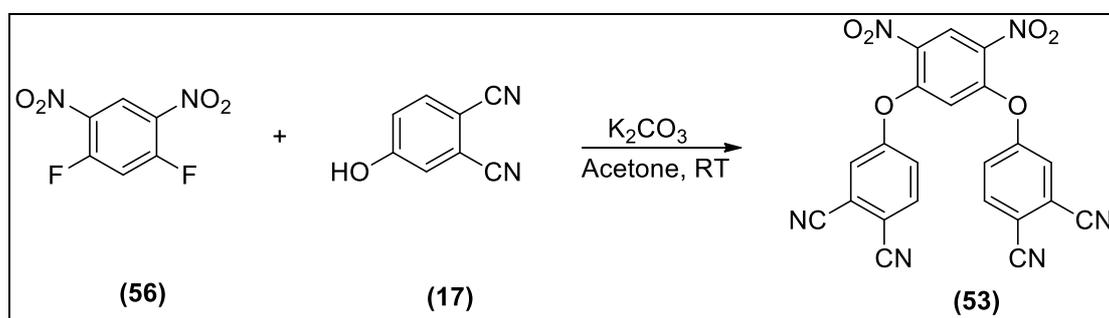
II. Two specially functionalised phthalocyanine subunits may be synthesised separately, and then linked to the commercially available 1,5-difluoro-2,4-dinitrobenzene under basic conditions in order to obtain the Pc-Pc dimer.



Scheme 40: Synthesis of dimer (57).

In order to obtain the required dimer two phthalonitriles needed to be prepared 3,6 dihexylphthalonitrile (19) and diphthalonitrile (53). The first phthalonitrile was discussed earlier. The main synthetic challenge was therefore the synthesis of the phthalonitrile dimers.

2.11.1 Synthesis of novel diphthalonitrile (53)



Scheme 41: Synthesis of diphthalonitrile 53.

The chemistry of the synthesis phthalonitriles by substitution is well studied and it seemed logical simply to extend this approach to the dimeric system. The synthetic route shown in Scheme 41 was designed. Consequently, 4-hydroxyphthalonitrile (**17**) was mixed with 1, 5-difluoro-2,4-dinitrobenzene (**56**) in a ratio of 3:1 in acetone. Three equivalents of freshly ground potassium carbonate were added to the reaction mixture. The solution was stirred for 24 h at room temperature under air. TLC was used to follow the reaction. After workup, purification over silica gel gave the target compound as the second fraction. Diphthalonitrile (**53**) was obtained as yellow crystals in 66.3 % yield. The $^1\text{H-NMR}$ spectrum (figure 33) shows singlets at ca. 9.05 and 7.75 ppm assigned to the two protons of the linker.

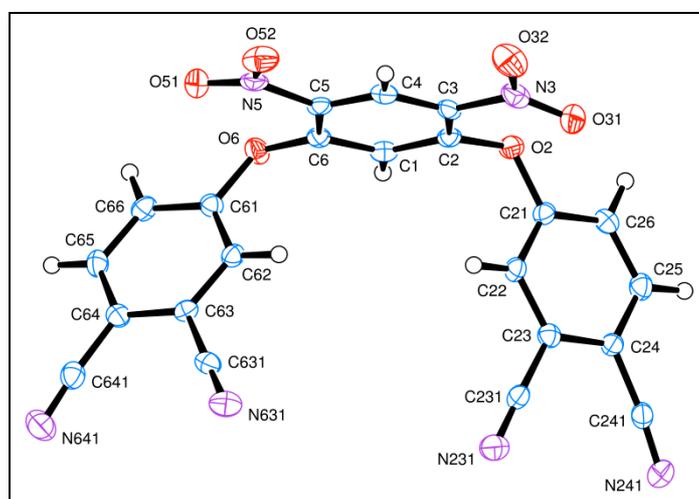


Figure 32: X-ray structure of (**53**).

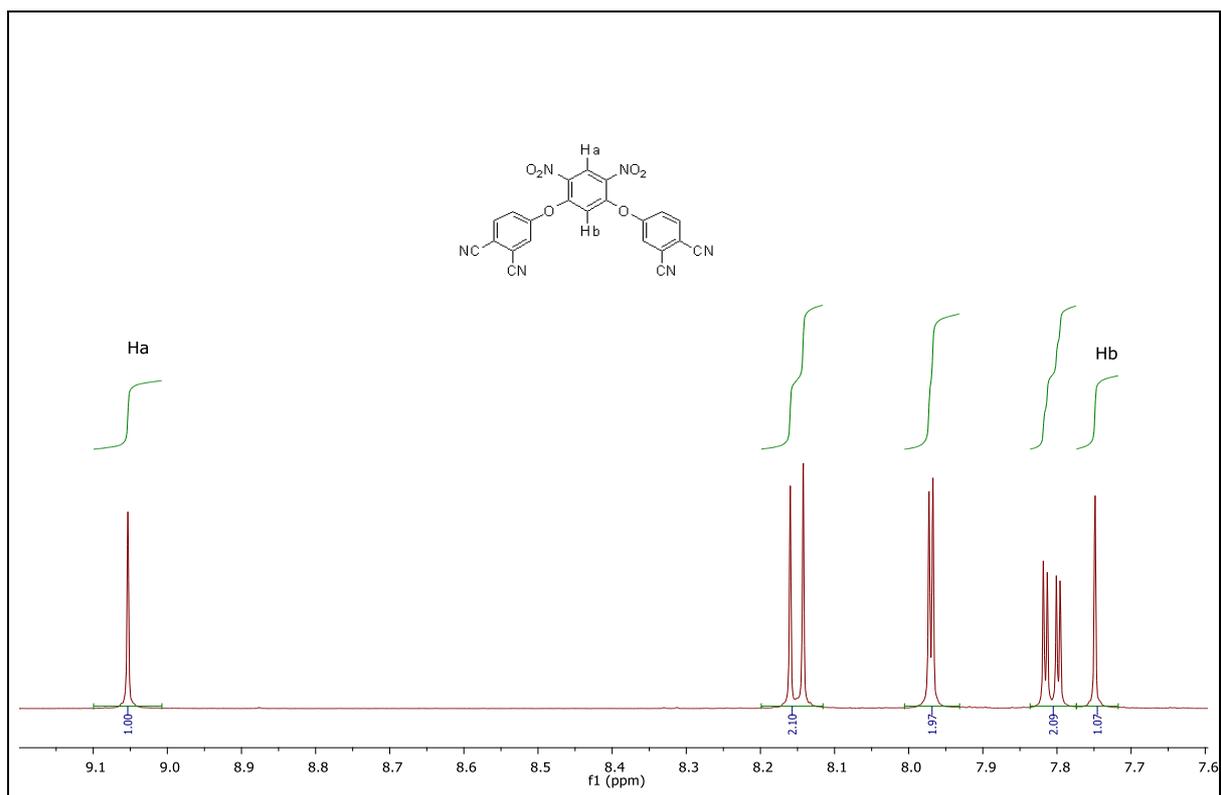


Figure 33: ¹H NMR of diphthalonitrile (**53**) in acetone-d₆ in 25 °C.

The combination of two different phthalonitriles permits the preparation of phthalocyanines with high functionality. As described, the synthesis shown in scheme 39 allows us to obtain the dimeric Pc linked with dinitrobenzene. To obtain the phthalocyanine dimer (**54**) a statistical condensation with a 1:8 stoichiometry was carried out, by reacting 1 equivalent of diphthalonitrile (**53**) and 6 equivalents of 3,6 dihexylphthalonitrile (**19**) with zinc acetate in *n*-hexanol at 155 °C for 18 h, in the presence of catalytic amounts of DBU as shown earlier in scheme 39. The reaction mixture was allowed to cool to room temperature and methanol was added. The mixture was filtered collecting a green precipitate which was washed with methanol to remove non-Pc impurities.

The residue was then dissolved in a minimal volume of solvent mixture. The Pc products were collected by filtration and purified by column chromatography on silica gel.

The second method was ^1H NMR spectroscopy which as well confirmed that the dimer had not been formed and the product was the metalated hydroxyl phthalocyanine.

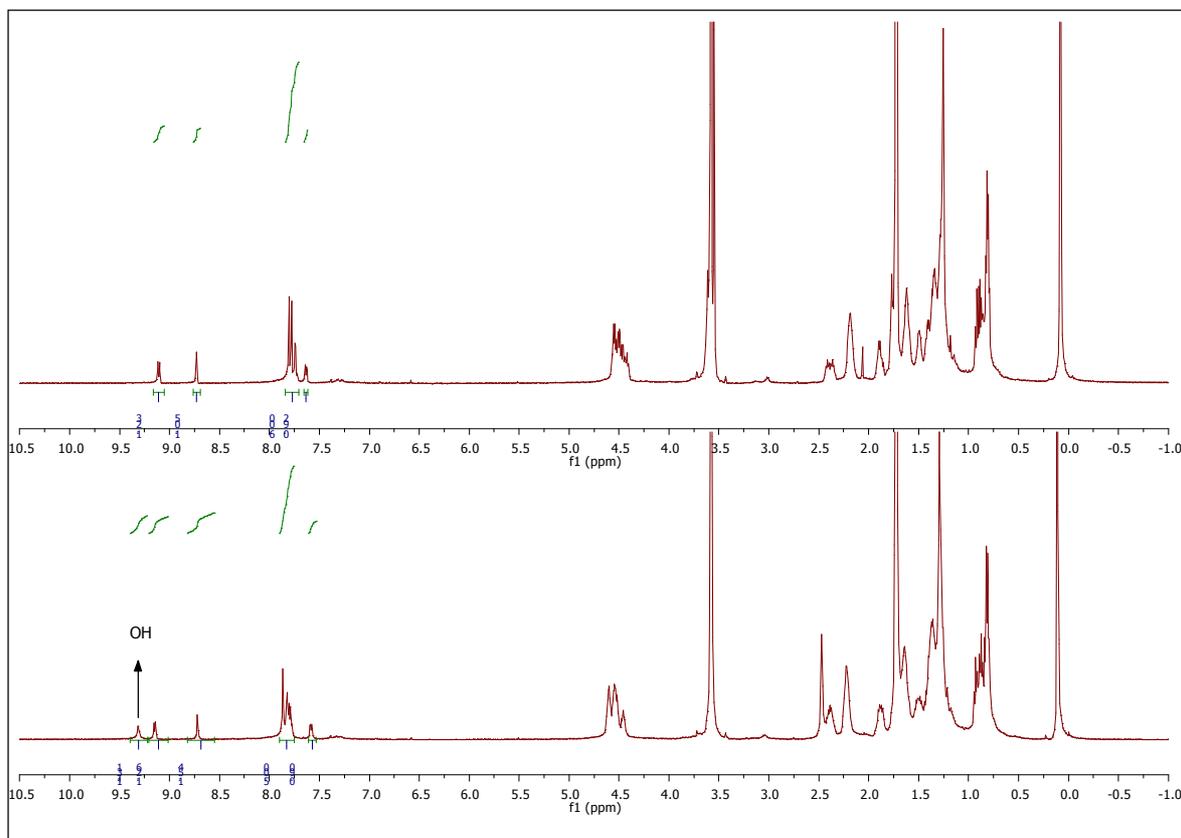


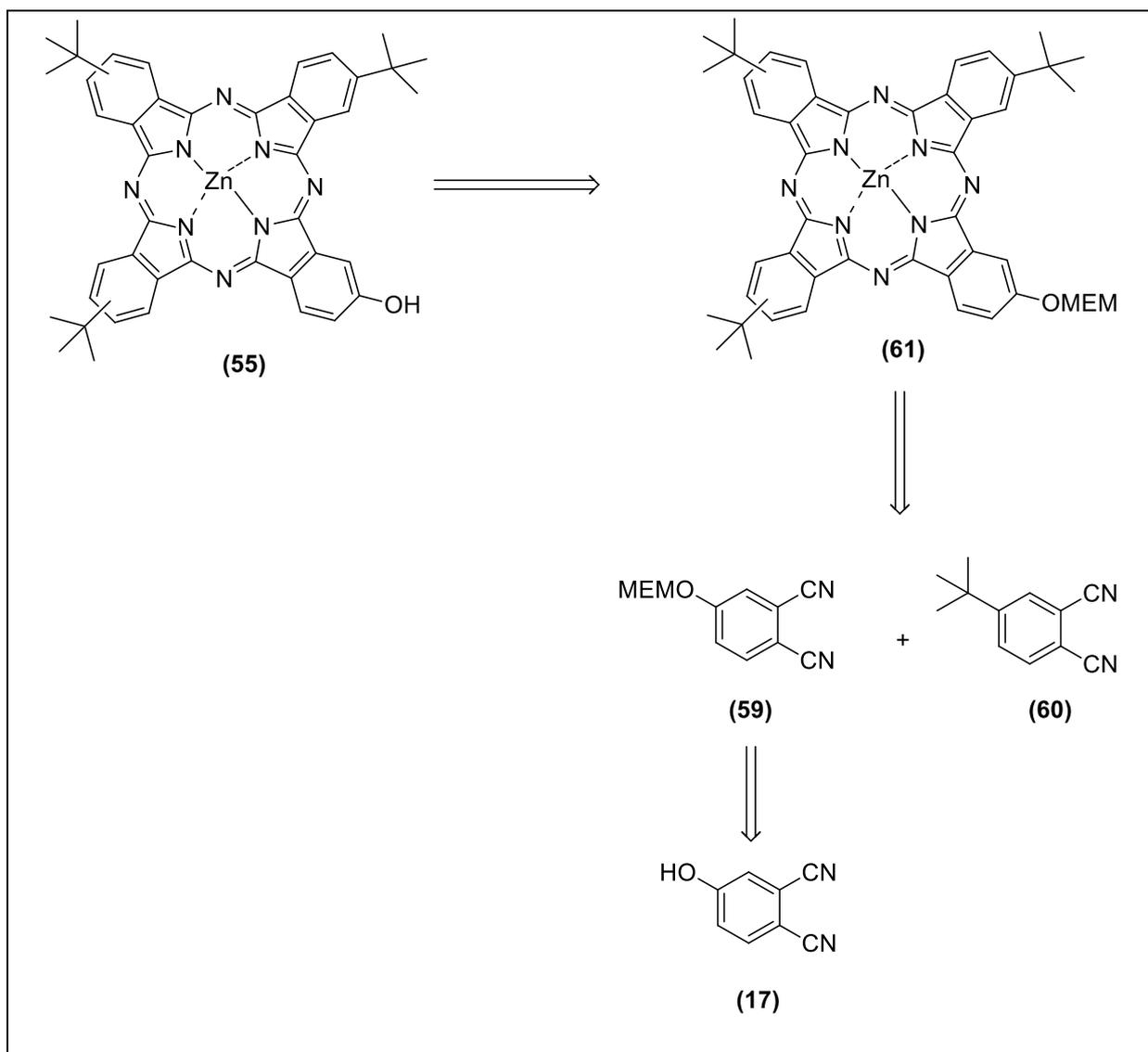
Figure 36: Comparison of the ^1H MNR spectrum of **58** in THF-d_8 (lower trace) and **58** in $\text{THF-d}_8+\text{D}_2\text{O}$ (upper trace).

The unsymmetrical nature of 1,4,8,11,15,18-hexakis(hexyl)-23-hydroxyphthalocyaninato zinc(II) is immediately apparent from inspection of its ^1H NMR spectrum. The ^1H NMR spectrum distinguished the unsymmetrical nature of 1,4,8,11,15,18-hexakis(hexyl)-23-hydroxy-phthalocyaninatozinc(II). At ca. 9.15, 8.72, and 7.57 ppm we see signals corresponding to 3H for the unsymmetrical phenyl ring hydrogens. The six aromatic hydrogens of the remaining phenyl rings appear around ca. 7.82 as multiplet signals. The hydroxyl signal appears at 9.31 ppm as a singlet, and to confirm that this signal is corresponds to the hydroxyl group two drops of D_2O were added to the NMR tube to examine

the disappearance of that signal, and it was confirmed. Therefore, phthalonitrile dimeric route was not successful to gain the aimed dimer.

2.11.2 Alternative route toward phthalocyanines dimer (57)

Due to the unsuccessful dimerisation attempts using diphthalonitrile (**53**), the synthetic strategy was modified to attempt to synthesis the identical Pc dimer via a different approach. The main important part in the new approach was synthesis hydroxy phthalocyanine. The hydroxy phthalocyanine has been synthesised as seen in scheme 40. The metalated hydroxyl Pc (**55**) was prepared by condensation of 3 equivalents of 4-(*tert*-butyl) phthalonitrile (**60**) with 1 equivalent of 4-(2-methoxyethoxymethoxy) phthalonitrile (**59**). Following this condensation, the MEM protected metalated hydroxyl Pc is obtained, and the final step in this stage involves the deprotection of the MEM group under acid conditions.



Scheme 43: Retrosynthesis of Pc (55).

In order to obtain 4-MEMphthalonitrile we had to prepare 4-hydroxyphthalonitrile (17). The hydroxyphthalonitrile was prepared following a literature procedure³⁶ by heating to 120 °C a solution of 4-nitrophthalonitrile in dry dimethyl sulfoxide in the presence of sodium nitrite and potassium carbonate for 24 h. Then, the mixture was cooled to room temperature and poured onto iced-water. After leaving it in a fridge for another 24 h we obtained the 4-hydroxyphthalonitrile as a cream powder in 72 % yield. The ¹H NMR spectrum confirms the

presence of the hydroxyl group with a distinguished deshielded signal at 11.48 ppm attributed to the hydroxy proton.

The preparation of 4-(2-methoxyethoxymethoxy) phthalonitrile was done by deprotonation of 4-hydroxyphthalonitrile by n-BuLi in dry THF in 0 °C under argon atmosphere. Then, the anion was reacted with the MEM chloride. A dark red solution was obtained, and then added to 30% aqueous ammonia. After extraction twice with THF and DCM, the purification was achieved by column chromatography over silica gel eluting with DCM to obtain the protected phthalonitrile as colourless crystals in 31% yield. The characteristic proton NMR chemical shifts indicated that there are new proton signals such as methoxy group at 3.35 ppm and the rest of the MEM protection group protons can be seen clearly in figure 35.

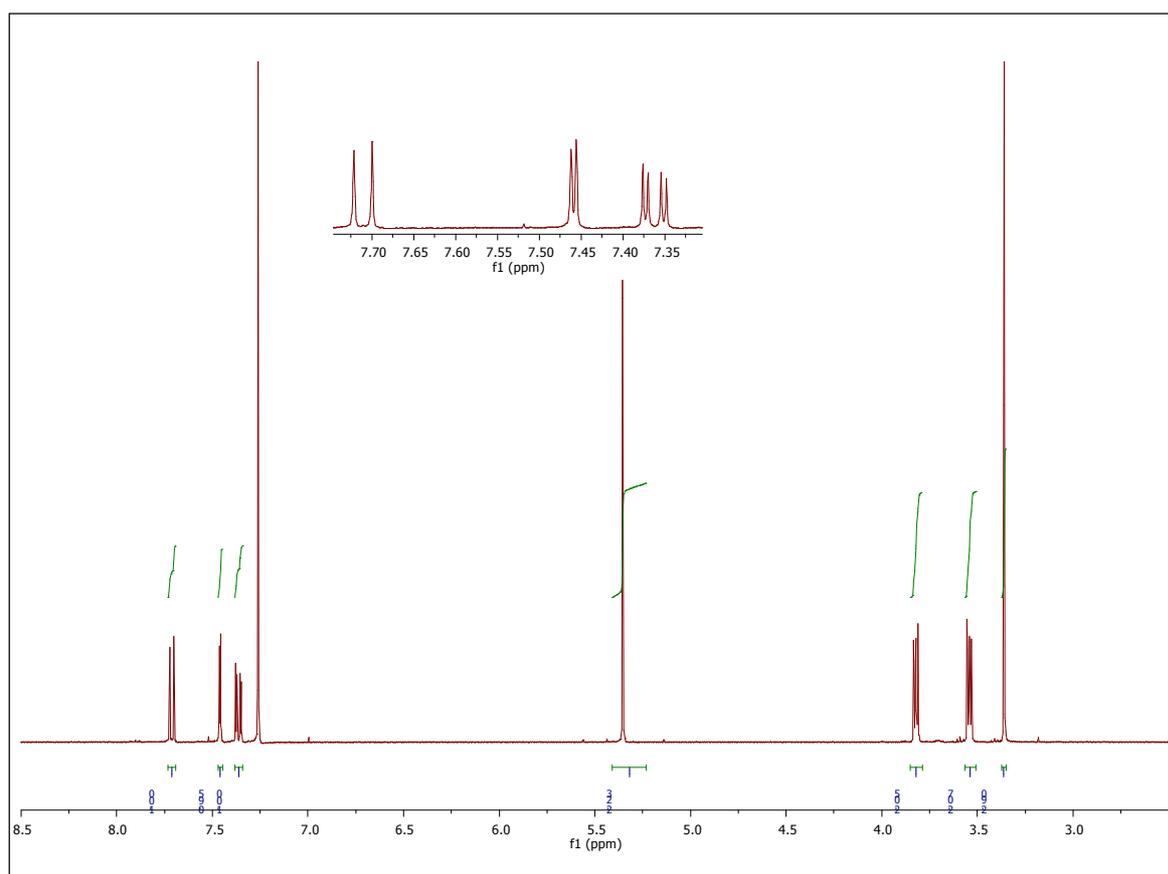


Figure 35: ¹H NMR of 4-(2-methoxyethoxymethoxy)phthalonitrile in CDCl₃ in 25 °C.

The reasons behind choosing MEM protecting group were the stability to strongly basic reaction conditions, it is easy to remove under acid conditions. Also, it confers high polarity to the intermediate, which helps to facilitate the separation of the symmetrical and unsymmetrical Pcs.^{37,38} The last reason was to avoid the deprotonation of phenolic hydroxy group during the base catalysed Pc forming reaction.^{38,39}

The preparation of the MEMO-ZnPc (**61**) was achieved by following the procedure described in the literature.⁴¹ A statistical condensation with a 3:1 stoichiometry was carried out, by reacting 3 equivalents of 4-(*tert*-butyl)phthalonitrile (**60**) and 1 equivalent of 4-(2-methoxyethoxymethoxy)phthalonitrile (**59**) with zinc acetate in *n*-hexanol at 155 °C for 18 h, in the presence of catalytic amounts of DBU. This resulted in the formation of a green compound suspected to be the required phthalocyanine. The solid was soluble in most common organic solvents. The purification of the crude green product was achieved by column chromatography through silica gel eluting with DCM/Pet.Ether to obtain the ZnPc-OMEM. The characterisation of the phthalocyanine (**61**) was attempted by ¹H-NMR and MALDI-MS. Thus, MALDI-MS gives the exact molecular ion peak at 848, as seen in figure 36.

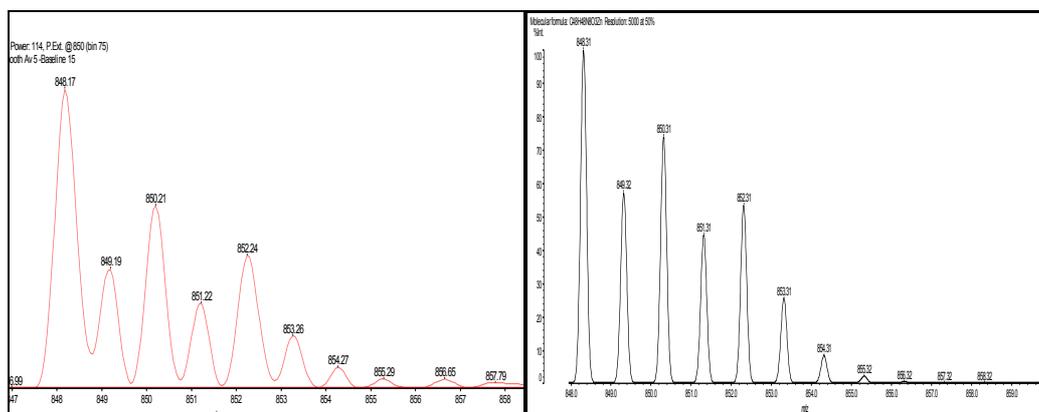


Figure 36: MALDI-MS spectrum of **61** (left) with its theoretical prediction.

The deprotection of ZnPc-OMEM (**61**) was achieved by refluxing the protected compound (**61**) in the presence of pyridinium *p*-toluenesulfonate (PPTS) to give the unsymmetrical Pc with hydroxy group (**55**). The product was only characterised by ^1H NMR spectroscopy, which agreed with the published data⁴⁰ and MALDI-MS (isotopic cluster 760) and was used directly for the next step.

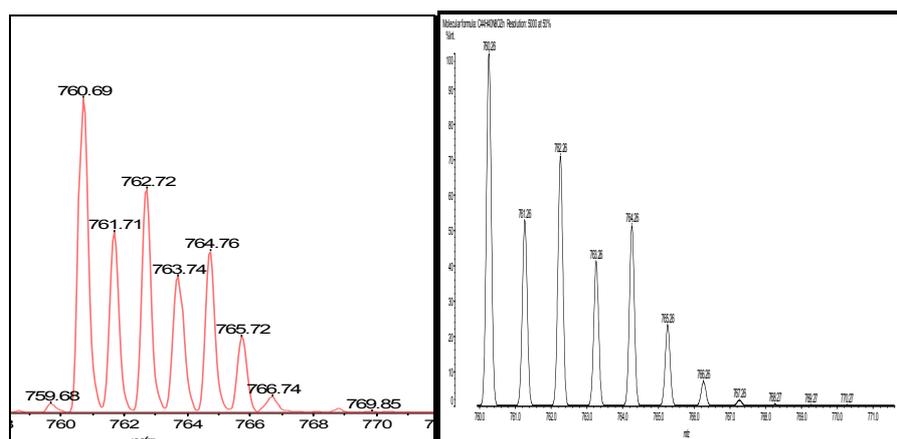


Figure 37: MALDI-MS spectrum of **55** (left) with its theoretical prediction.

Now since we had the ZnPc-OH in hand, the next step was forming the dimer by reacting the hydroxy Pc with the linker directly. This step involves the reaction of the unsymmetrical Pc starting material (**55**) with the commercially available 1,5-difluoro-2,4-dinitrobenzene (**56**) in acetone in presence of potassium carbonate. The reaction was heated for 18 h and monitored by TLC to ensure completion of the reaction. Then the crude product was purified by column chromatography to remove the excess starting material. The formation of the target Pc was confirmed with the MALDI-MS (isotopic cluster 1689).

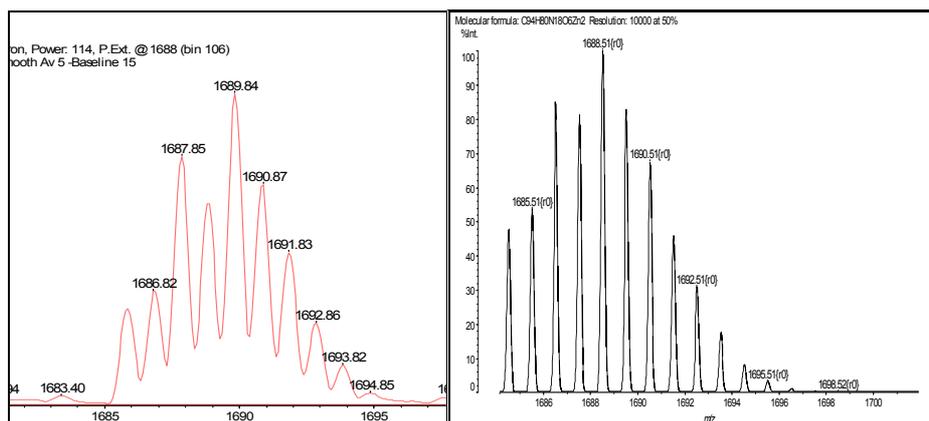


Figure 38: MALDI-MS spectrum of **57** (left) with its theoretical prediction.

The ^1H NMR spectrum was difficult to obtain. The spectrum of the dimer was complicated and gave broadened peaks due to possible intermolecular aggregation of the Pc as well as the presence of isomers. The phthalocyanine dimer was also not soluble in common NMR solvents such as chloroform, acetone or THF- d_8 . The spectra showed broad peaks, even with some drops of pyridine- d_5 to reduce the extensive aggregation of the molecules in solution.

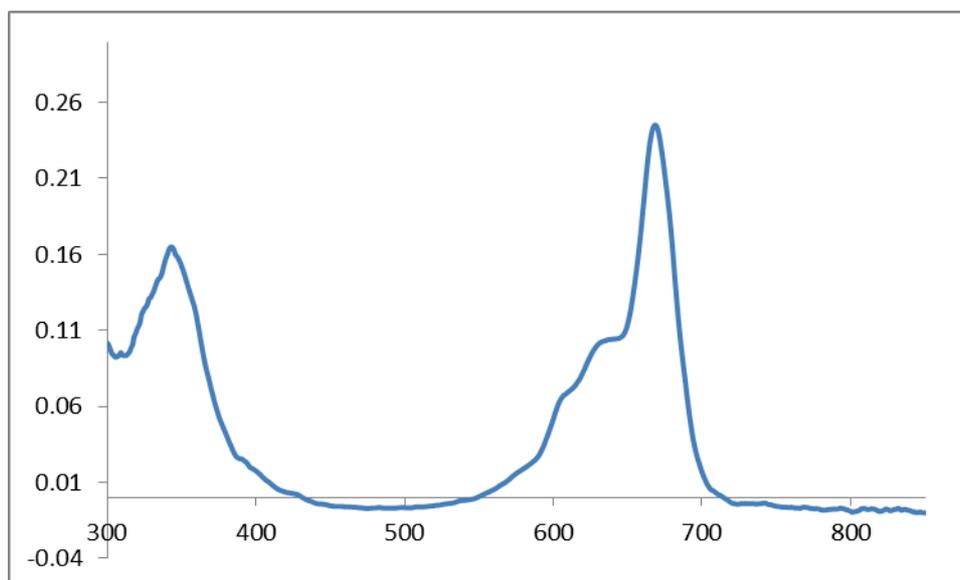


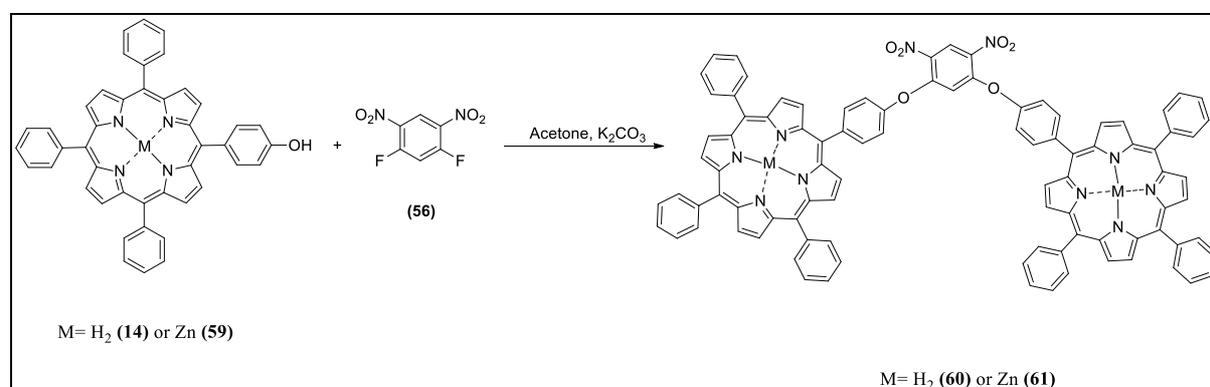
Figure 39: The UV-vis spectrum Pc-Pc dimer **57** in THF.

UV-Vis spectra of highly dilute solutions are typical of metallophthalocyanines. The UV-vis spectra of Pc-Pc **57** dimer showed the typical pattern with strong absorption at 669 nm for the Q-band with a shoulder at 629 nm, and 344 nm for the B-band. The nitrobenzene absorption (the bridge) overlaps with the Pc B-band which should appear around 320nm.

2.12 Synthesis of the *bis* and *tris*-porphyrins

2.12.1 Design and synthesis of dinitrobenzene-bridged bis-porphyrins system

The aim of this synthesis is the preparation of identical porphyrins linked to a rigid linker such as 1,5-difluoro-2,4-dinitrobenzene. Unsymmetrical monohydroxyporphyrins are appropriate precursors, which undergo chemical reactions to lead to the target molecule. All the syntheses of the target porphyrin derivatives in this section were achieved following Adler's procedure. The advantage of the Adler method is that the target porphyrin can be crystallised from the reaction mixture directly and pure porphyrin can be obtained by simple chromatography. The synthetic approach towards porphyrin dimers **60** is shown in scheme 44. The first step of this synthesis was obtaining the TPPOH by following Adler's procedure.



Scheme 44: Synthesis of the Pn-Pn dimer.

The target dimers were achieved from the nucleophilic aromatic substitution of functionalised 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin with 1,5-difluoro-2,4-dinitrobenzene. A mixture of 1 equivalent of 1,5-difluoro-2,4-dinitrobenzene, 3 equivalents of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin and an excess of K_2CO_3 were mixed in acetone. The reaction mixture was stirred at room temperature under air. TLC was used to follow the reaction and the reaction was stopped when most of the starting materials had been consumed. The required dimer was obtained as purple crystals in 60 % yield after purification by column chromatography and recrystallization from DCM/hexane. The 1H NMR spectrum showed all the required proton signals as shown in figure 40.

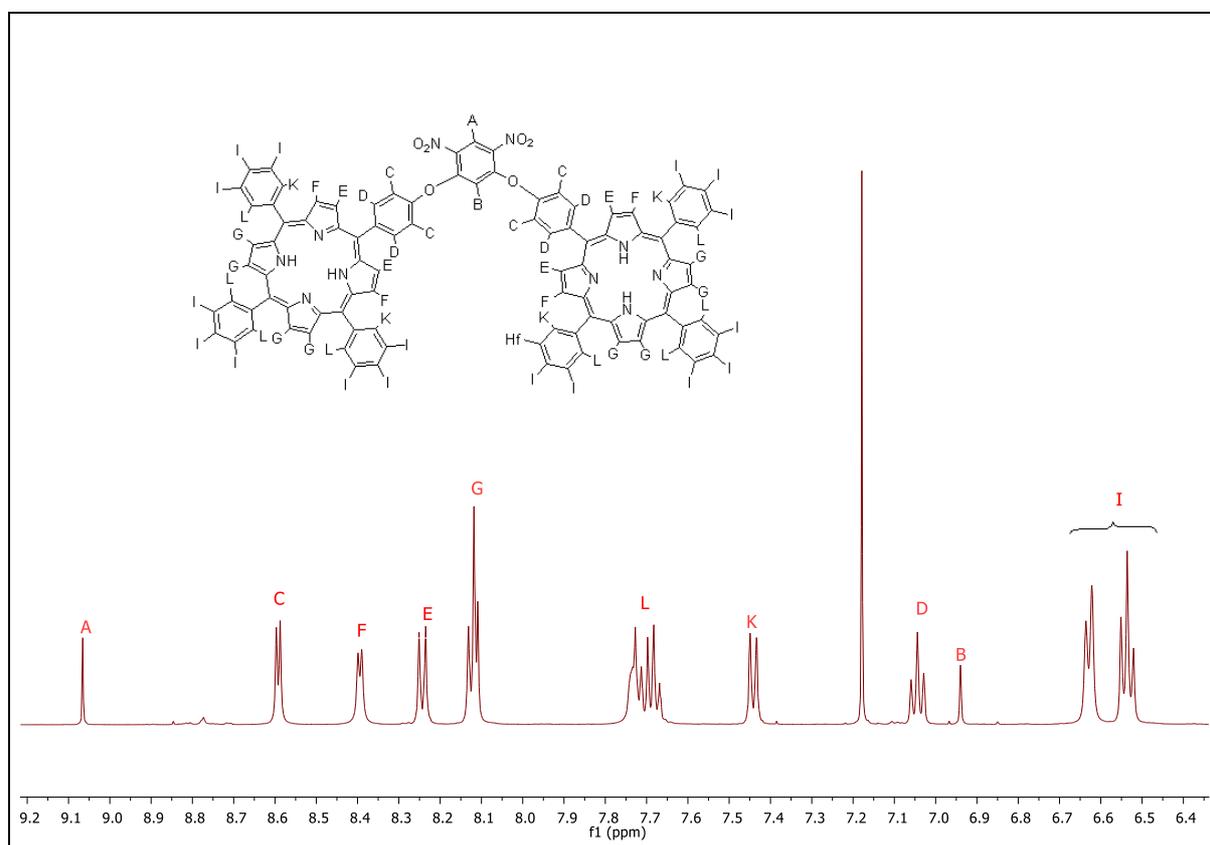


Figure 40: 1H NMR spectrum of aromatic area dinitrobenzene-bridged bis-porphyrins in $CDCl_3$ at 25 °C.

The dinitrobenzene-bridged bis-porphyrin afforded the required peak in the MALDI-MS at 1425 (figure 41).

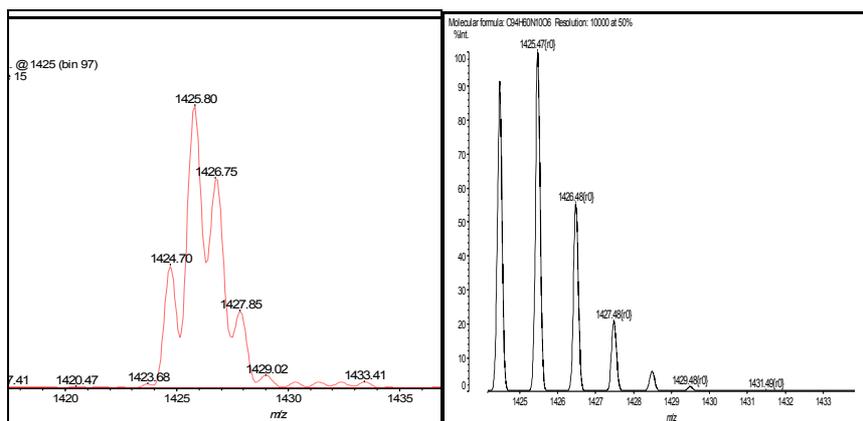


Figure 41: MALDI-MS spectrum of **60** (left) with its theoretical prediction.

The corresponding zinc-metallated dimer was made by replacing the starting material with the ZnTPP-OH. The reaction was repeated in same conditions.

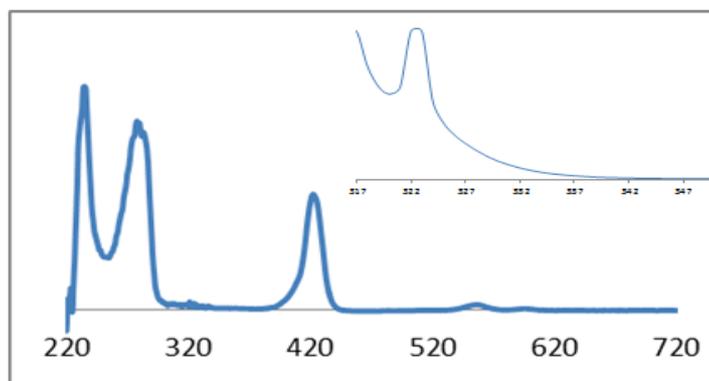
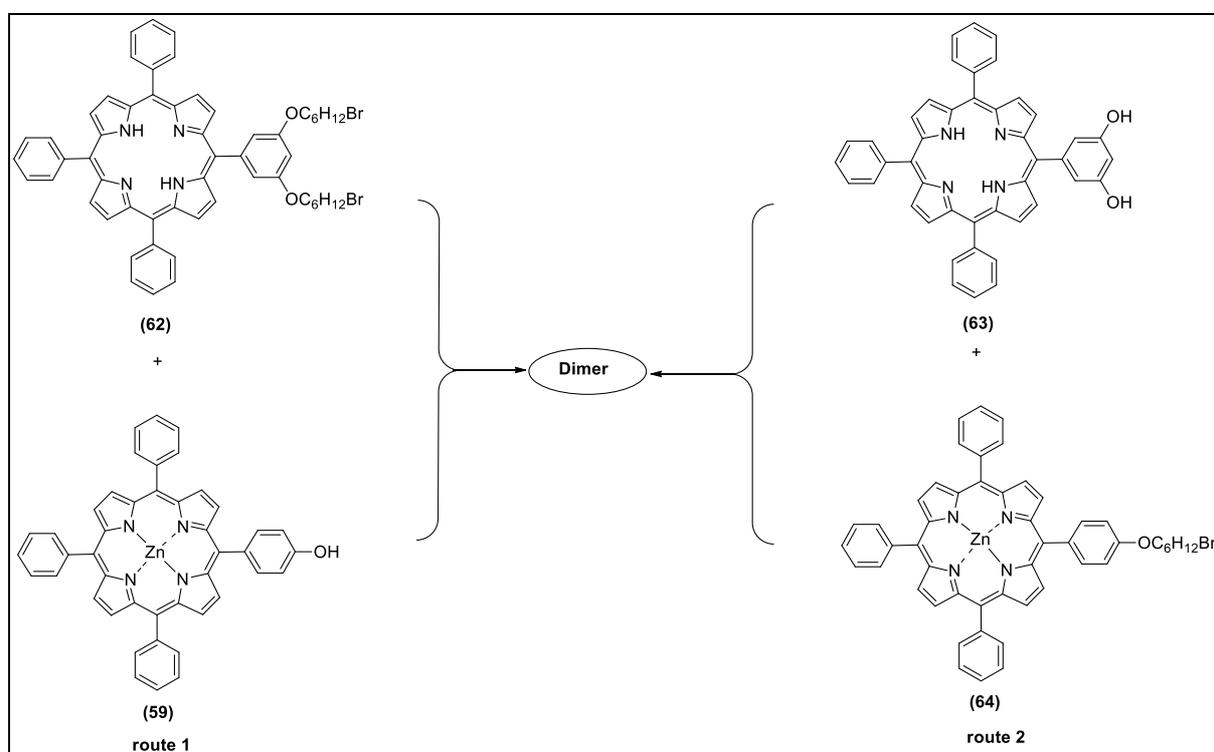


Figure 42: UV-Vis spectrum of H₂-porphyrin dimer (**60**) and the linker (**56**).

The UV comparison of the synthesised dimer (**60**) and the linker (**56**) was further confirmed evidence of synthesis the target. The visible spectra of target dimer shows two UV-active portions corresponding to the starting material (nitrobenzene) in the area between 200-320 nm and the porphyrin species with absorption at 420 nm (Soret band) and less intense signals, (the Q bands) at higher wavelengths starting from 543 to 625 nm (Figure 42).

2.13 Retrosynthesis of trimeric porphyrin

Attempts were made to synthesise a trimeric porphyrin by one route of the two initially considered (paths 1 and 2, scheme 45). The choice of the first approach was made as the immediate precursors to the aimed trimer porphyrin were readily available. The synthetic strategy employed here was to couple a core porphyrin bearing a 3,5-di(6-bromohexyloxy) phenyl substituent on one *meso* position. The synthesis of the porphyrin trimer can be accomplished via a nucleophilic substitution reaction in two ways, as proposed in scheme 45:

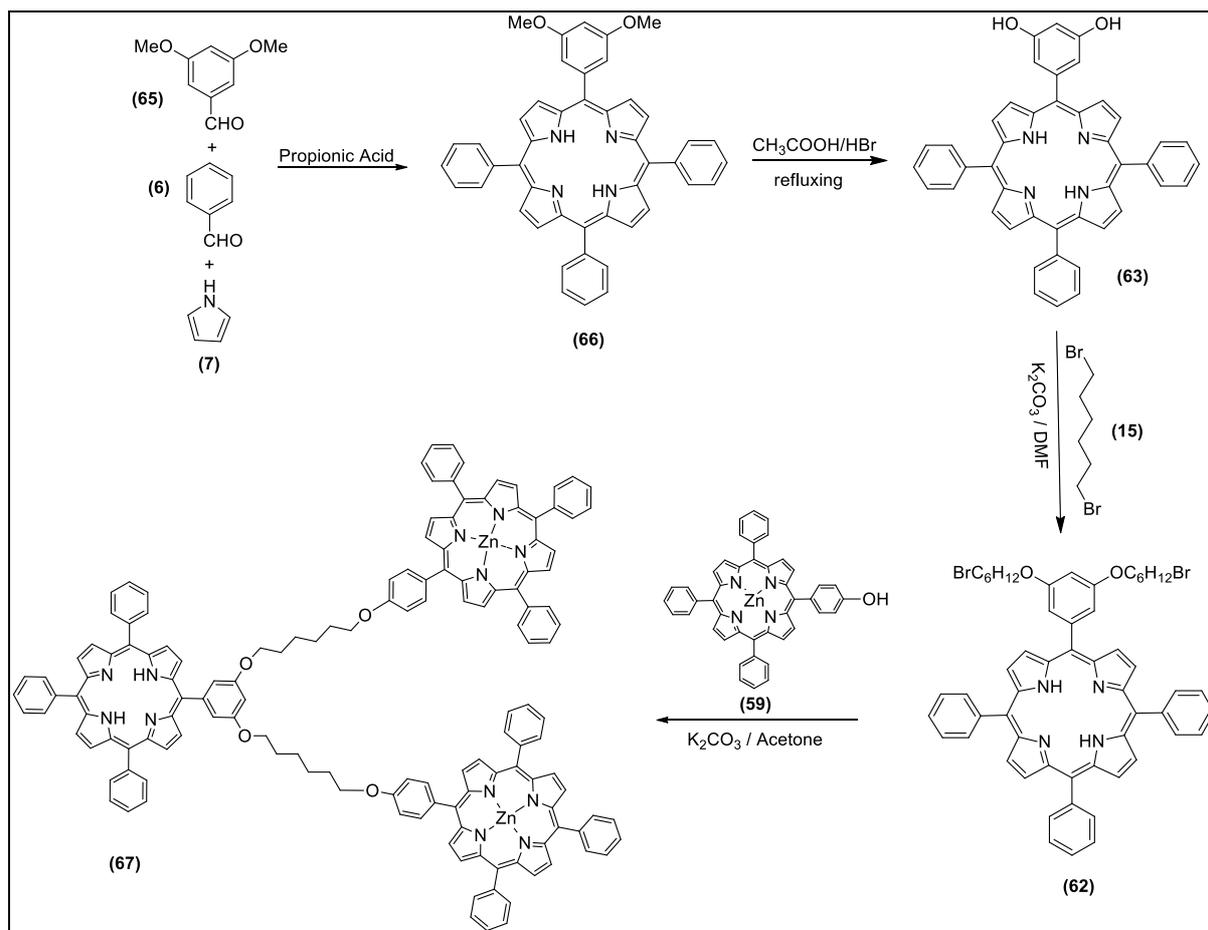


Scheme 45: Proposed synthesis of trimeric porphyrin (69).

The synthesis of the target trimeric porphyrin (67) requires a mixture of dibromoporphyrin (62) with functionalised metallated mono hydroxy porphyrin 59.

2.13.1 Synthesis of unsymmetrical porphyrins

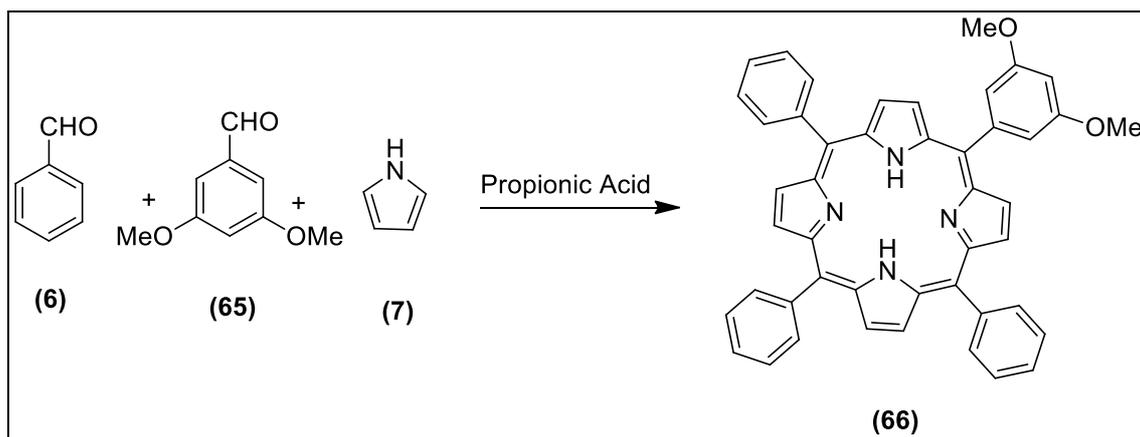
The synthetic routes attempted towards asymmetric porphyrins are diverse. The method which had been used in this section is a mixed condensation which involves reaction between two different aldehydes, and pyrrole, under Adler-Longo conditions. In the Adler-Longo procedure different solvents can be used. However, propionic acid is favoured to be used in our compounds because many aldehydes are soluble in it and the porphyrin product crystallises out easily with reasonable yield. In terms of producing a di-functional phenol on the porphyrin ring, suitable for linkage, two different aldehydes would be used; one bearing a functional group which can be transformed into hydroxy group and the rest facilitates solubility of the target compound. The yield of the porphyrin can be enhanced by using appropriate stoichiometry, while also considering the reactivities of the different aldehydes. And the total synthesis can be shown in scheme 46 as follows:



Scheme 46: Synthesis of the trimeric porphyrin (**67**).

2.13.2 Synthesis of 5-(3,5-methoxyphenyl)-triphenylporphyrin (**66**)

Following the synthetic strategy⁴¹ outlined in scheme 47, TPP (OMe)₂ (**66**) was synthesised using the Adler-Longo method. The advantage of the Adler-Longo method is that the target porphyrin can be crystallised from the reaction mixture followed by chromatography column to obtain the porphyrin.

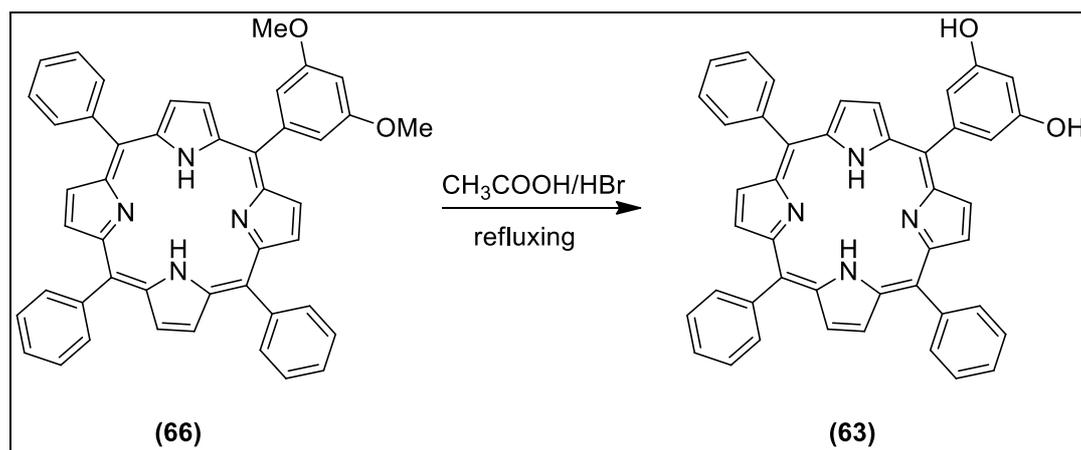


Scheme 47: Synthesis of 5-(3,5-methoxyphenyl)-triphenylporphyrin (**66**).

Benzaldehyde and 3,5-dimethoxybenzaldehyde were reacted with pyrrole in refluxing propionic acid for two hours. The reaction mixture was then placed into a refrigerator overnight and the porphyrin precipitate was filtered off and washed with methanol. The mixed porphyrin residue was subjected to flash column chromatography over silica gel. The isolated product provided satisfactory ^1H NMR spectra consistent with the structure of the product (**66**). The ^1H NMR spectrum shows the aromatic protons as a doublet at 8.95 ppm, singlet at 8.84 ppm, doublet of doublet at 8.21 ppm, multiplet at 7.76 ppm, doublet at 7.41 ppm and triplet at 6.90 ppm. In the case of the methoxy groups, the signals appear as a singlet at 3.96 ppm. The two hydrogens in the middle of porphyrin ring appear at -2.97 ppm.

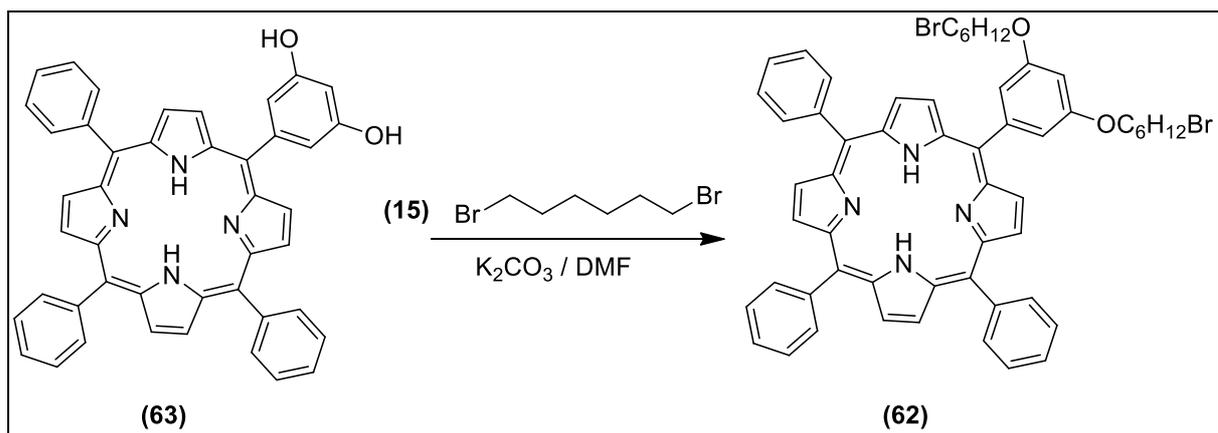
2.13.3 Synthesis of 5-(3,5-dihydroxyphenyl)-triphenylporphyrin (**63**)

The methoxy groups have the advantage of being removed for transformation to the corresponding hydroxy derivatives by reaction with BBr_3 or $\text{CH}_3\text{COOH}/\text{HBr}$.



Scheme 48: Hydrolysis of 5-(3,5-dimethoxyphenyl)-triphenylporphyrin (**66**).

The hydrolysis of 5-(3,5-methoxyphenyl)-triphenylporphyrin to obtain 5-(3,5-dihydroxyphenyl)-10,15,20-triphenylporphyrin was performed at 110 °C using CH₃COOH/HBr. The TPP(OMe)₂ **66** was dissolved in CH₃COOH/HBr (1:1v/v), the mixture turned to a dark green colour, and then heated for 24 h. The reaction was followed by TLC. It showed that there was a new product. MALDI-MS also confirmed formation of the product. Ammonia solution was added to the mixture until the colour turned back to the desired purple. The compound was purified by column chromatography and an 85% yield was obtained as purple crystals. The product provided a clean ¹HNMR spectrum, which shows the disappearance of the methoxy group and a hydroxy group at 5.12 ppm as a broad signal. The other proof was from the MALDI-MS where the peak appearing at 646.73 refer to the TPP(OH)₂ **63**.



Scheme 49: Synthesis of porphyrin (**62**)

Alkylation of porphyrin (**63**) to dibromoalkoxyporphyrin (**62**) was achieved by reacting dihydroxy porphyrin (**63**) with 1,6-dibromohexane in DMF in presence of potassium carbonate. The reaction was monitored using TLC and, after two hours, the reaction mixture still had a substantial amount of unreacted starting material. The reaction was left for 18 h at room temperature. The crude product was dissolved in DCM and then washed with water and the washings extracted with DCM several times. The crude product was purified by column chromatography eluting with DCM: petroleum ether, to isolate the product 5-(3,5-di(6-bromohexyloxy)phenyl)-triphenylporphyrin **62** in a yield of 56 % as a purple solid.³⁶ By looking at the ¹H NMR spectrum for the product porphyrin (**62**), we see, at ca. 9.0 and 8.8 ppm, signals corresponding to 8H for the porphyrin β-hydrogens. Because the phenyls are not equivalent broad signals are observed. At ca. 8.25 and 7.7 ppm we find two broad signals integrating to 6H and 9H respectively that correspond to the hydrogens on the three unsubstituted phenyl rings. Signals for hydrogens on the substituted phenyl rings appear at 7.42 ppm and 6.91 ppm. The alkyl chain characteristic signals of the methylene groups appear at 4.16 ppm 2x (-OCH₂-), 3.42 ppm 2x (-CH₂Br), 1.92 ppm and 1.56 ppm. The distinctive signal for hydrogens in the centre of the porphyrin is observed at ca. -2.74 ppm

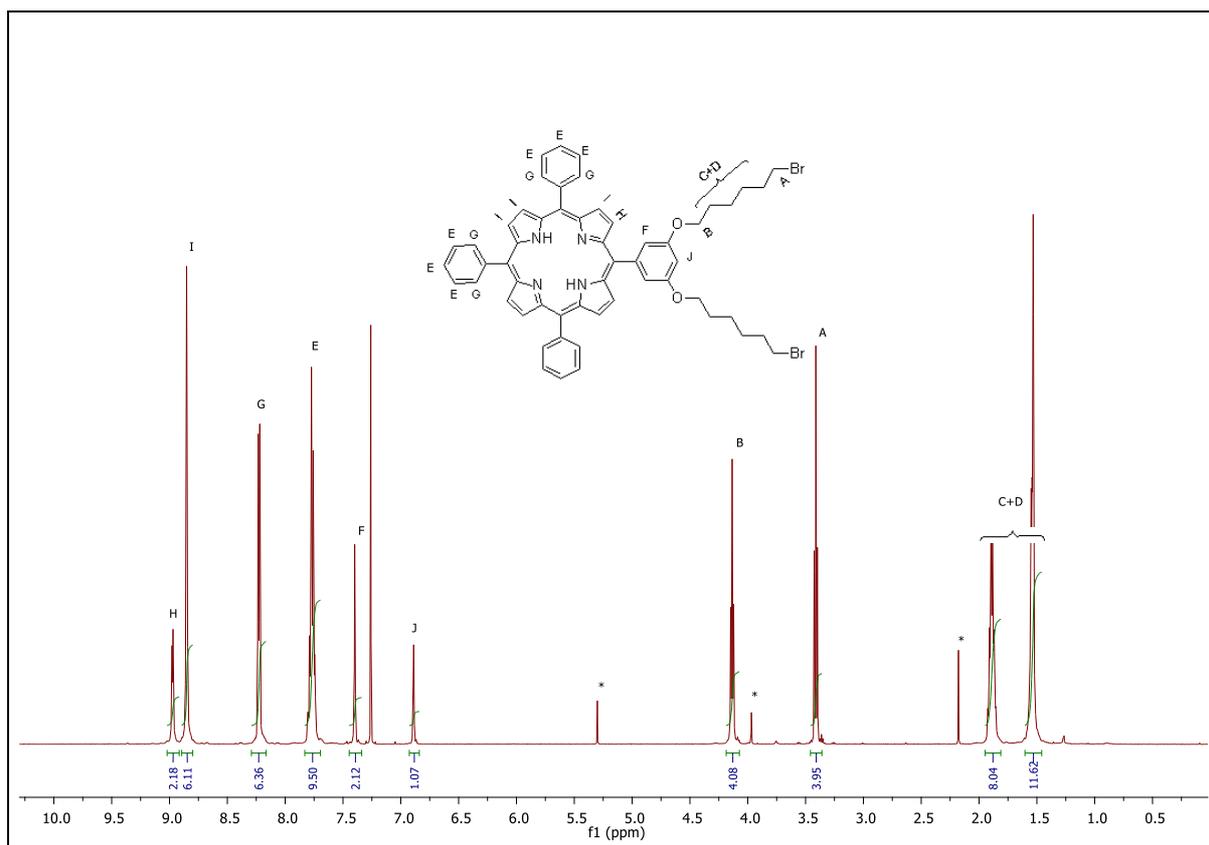


Figure 43: ¹H NMR spectrum of (62) in CDCl₃ at 25 °C.

The MALDI-MS of complex (62) showed a molecular ion peak at 972.25 which is consistent with predicted structure.

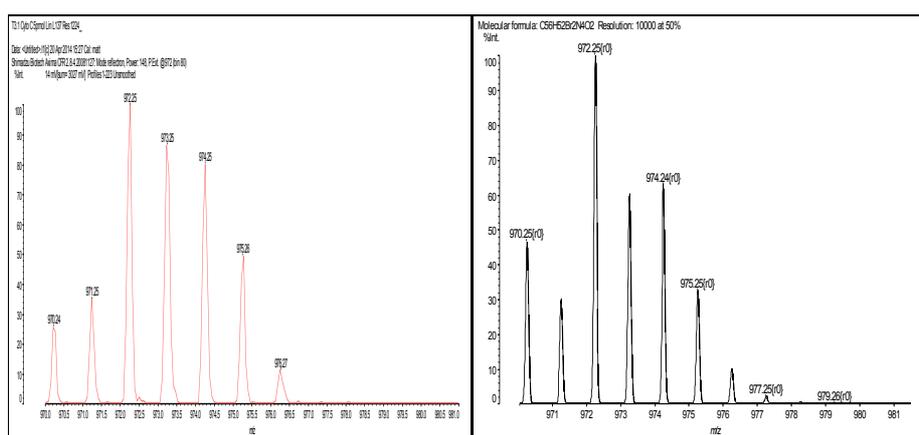
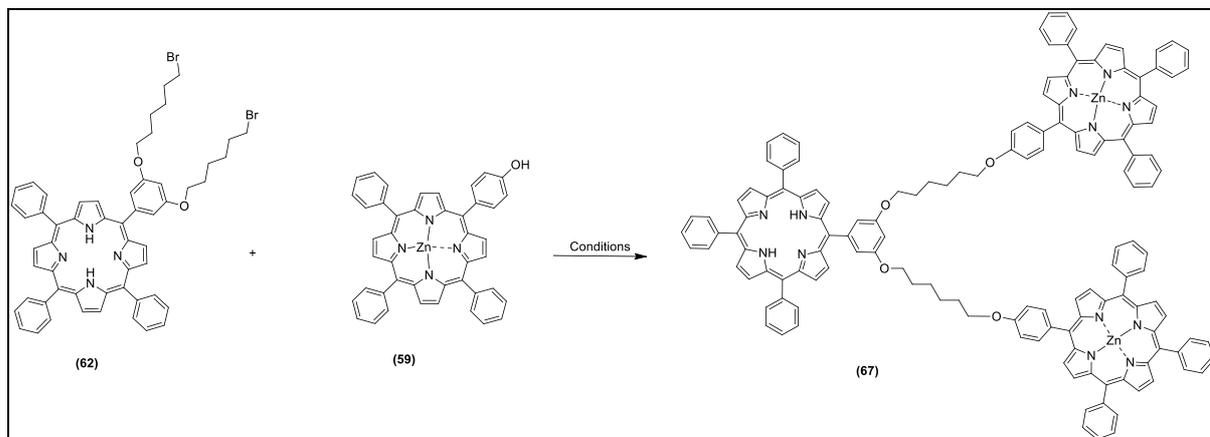


Figure 44: MALDI-MS spectrum of 62 (left) with its theoretical prediction.

2.13.4 Synthesis of Pn-Pn trimer



Scheme 50: Synthesis of trimeric porphyrin (67).

The synthesis of the target trimeric porphyrin **67** was achieved by reacting unsymmetrical porphyrin (**62**) with metallated hydroxy porphyrin (**59**) in acetone in the presence of potassium carbonate as shown in scheme 50. The reaction was monitored using TLC and, after two hours, the reaction mixture still had a substantial amount of unreacted starting material. The reaction was left for 48 h at room temperature. The crude reaction was worked up and the product was purified by column chromatography to isolate the trimeric porphyrin (**67**) in a yield of 60 % as a purple crystals. The MALDI-MS of the complex showed a molecular ion peak at 2199 which is consistent with predicted structure.

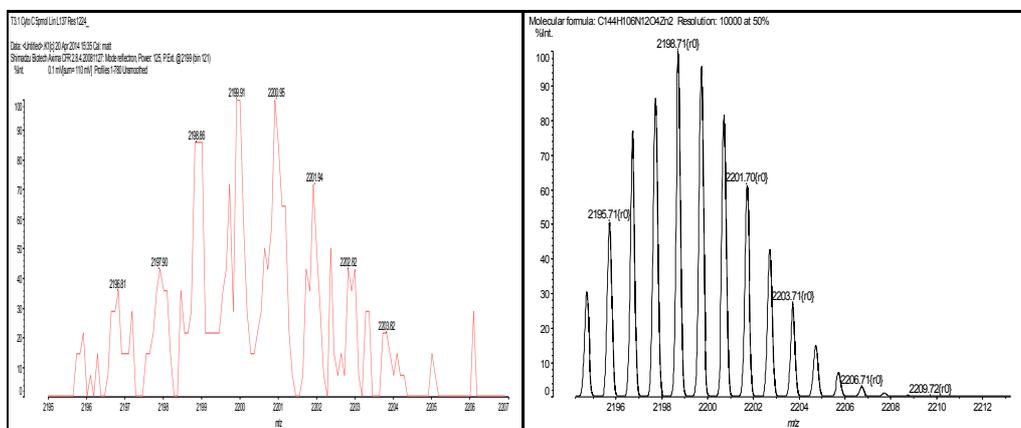


Figure 45: MALDI-MS spectrum of **65** (left) with its theoretical prediction.

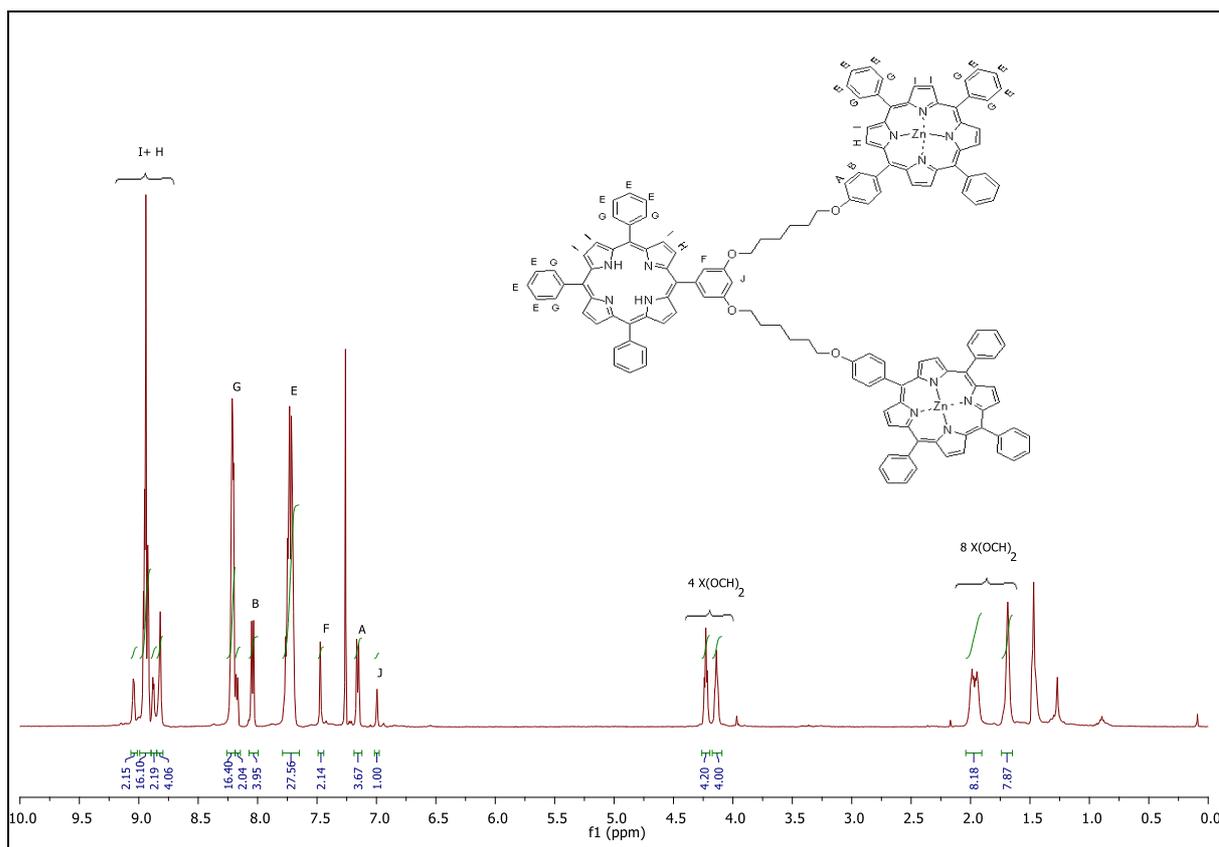


Figure 46: ^1H NMR spectrum of trimeric porphyrin (67) in CDCl_3 at 25°C .

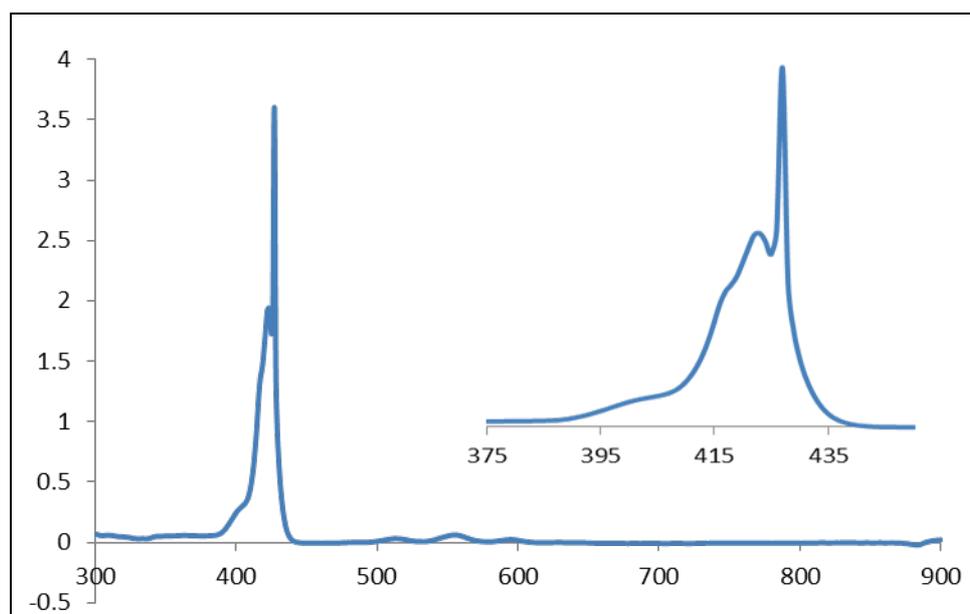


Figure 47: UV-Vis Spectrum of trimeric porphyrin (67).

The visible spectrum of **67** shows the metallated and metal-free porphyrins linked together with peaks at 420,511,548,590 and 640 nm which represent the Soret band and the weaker absorption of Q-bands in the longer wavelength region between 523 and 594nm (figure 47). The broadened signals possibly indicate some intramolecular aggregation.

2.14 Conclusion

The synthesis of identical and non-identical dimers from porphyrins and phthalocyanines were investigated and a number of systems were isolated and characterised. Flexible linkers (alkyl chains, ether linkages) and rigid spacers (alkynes, benzene) have been investigated. In agreement with previous literature, unsymmetrical porphyrins are easier to obtain than phthalocyanines, but a convenient synthesis of the latter has been used to, eventually, give a suitable monohydroxyphthalocyanine precursor. Mono- and dihydroxyporphyrins are easily obtained, and they have been employed to produce trimeric systems.

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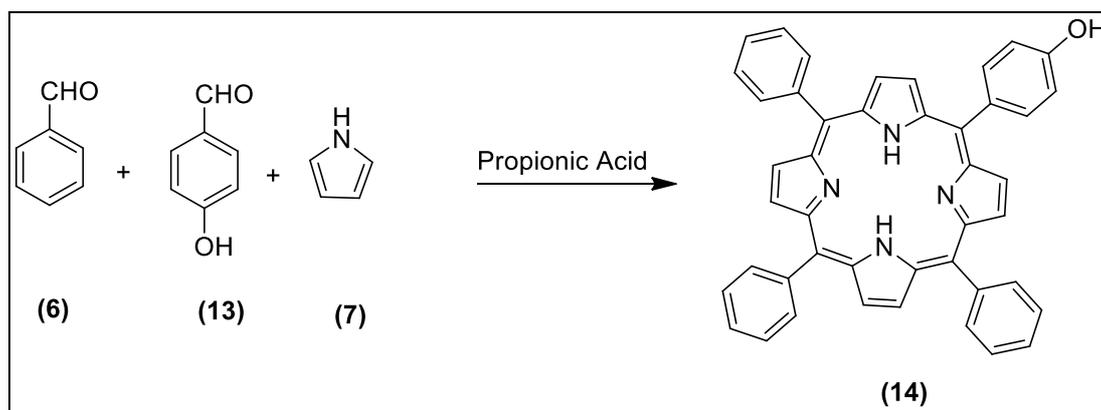
CHAPTER 3

Experimental

3.1 General procedures

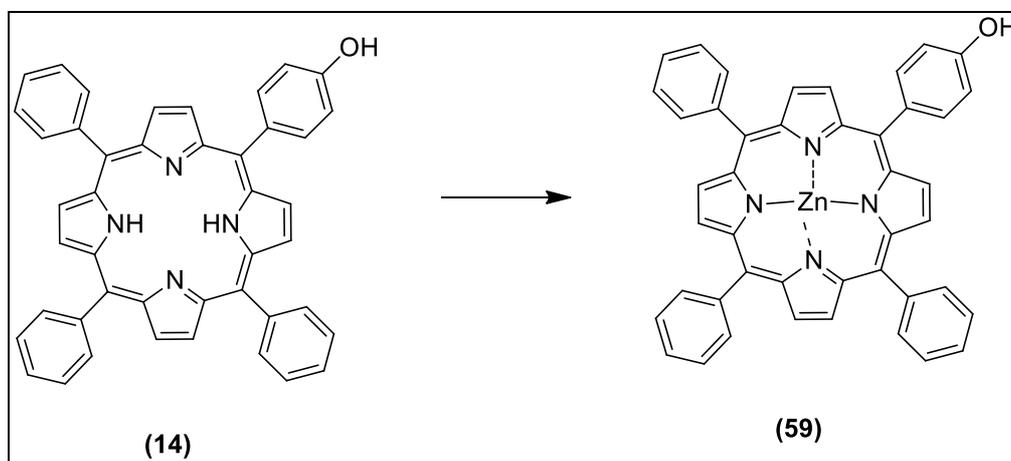
Reagents and solvents were purchased from commercial sources and used without further purification unless they are specified. Pyridine, toluene, triethylamine and DCM were dried over calcium hydride. THF was dried over sodium and benzophenone. IR spectra were recorded using a Perkin-Elmer Spectrum BX FT-IR spectrometer. ^1H (and ^{13}C -NMR) spectra were recorded at 500 (125.7) or 400 (100.6) MHz using a Bruker Ascend TM 500 or an Ultrashield Plus TM 400 spectrometer. The residual solvent peaks were used as references. ^1H and ^{13}C NMR signals are reported in ppm. MALDI-MS analyses were recorded on AXIMA-CFR plus equipment. UV spectra were recorded on HITACHI U300 equipment. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with Alugram® Sil G/UV254 (Macherey-Nagel). Column chromatography was carried out on silica gel Davisil® LC60A 40-63 micron (Grace GmbH & Co). MALDI-TOF mass spectra were obtained using a Shimadzu Biotech Axima instrument. Melting points were measured using a Reichert Thermovar microscope with a thermopar based temperature control. X-Ray crystallography data was run through WinGX (4) on Dell Optiplex GX620 PC at University of East Anglia. Size-exclusion chromatography was carried out over Bio-beads SX-3 using THF eluent.

3.2 Preparation of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin **14**



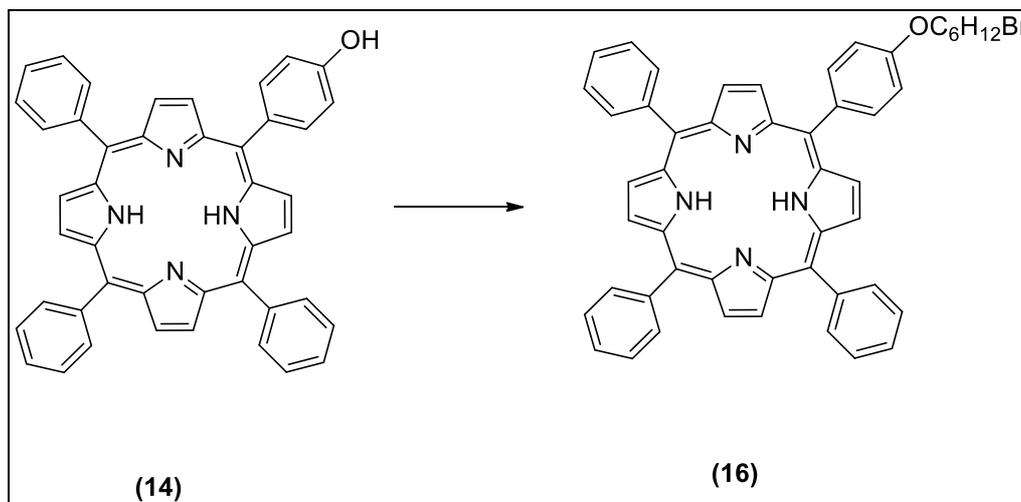
4-Hydroxybenzaldehyde **13** (3.05 g, 25.00 mmol) and benzaldehyde **6** (7.94 g, 75.00 mmol) were dissolved in propionic acid (250 mL) and to this was added pyrrole **7** (6.71 g, 100 mmol). This was refluxed in the dark for 30 min then cooled to room temperature. To this ethanol (150 mL) was added and the mixture left to crystallise overnight. The crystals were filtered off and purified by column chromatography on silica eluting with dichloromethane/petroleum ether (3:7) followed by THF/pet ether (1:1). The hydroxyphenylporphyrin was isolated as purple crystals (0.69 g, 4 %); Mp 290 °C; $^1\text{H NMR}$ (400 MHz, DMSO) δ 10.00 (s, 1H), 8.91 (s, 2H), 8.82 (s, 6H), 8.2 (d, $J = 7.5$ Hz, 6H), 8.01 (d, $J = 8.3$ Hz, 2H), 7.8-7.77 (m, 9H), 7.21 (d, $J = 8.3$ Hz, 2H), -2.92 (s, 2H); MALDI-MS: MALDI-MS 629 (cluster, $M^+ = 630$, isotopic distribution pattern corresponds to theoretical prediction). These data are consistent with literature values.³

3.3 Preparation of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrinatozinc **59**⁴



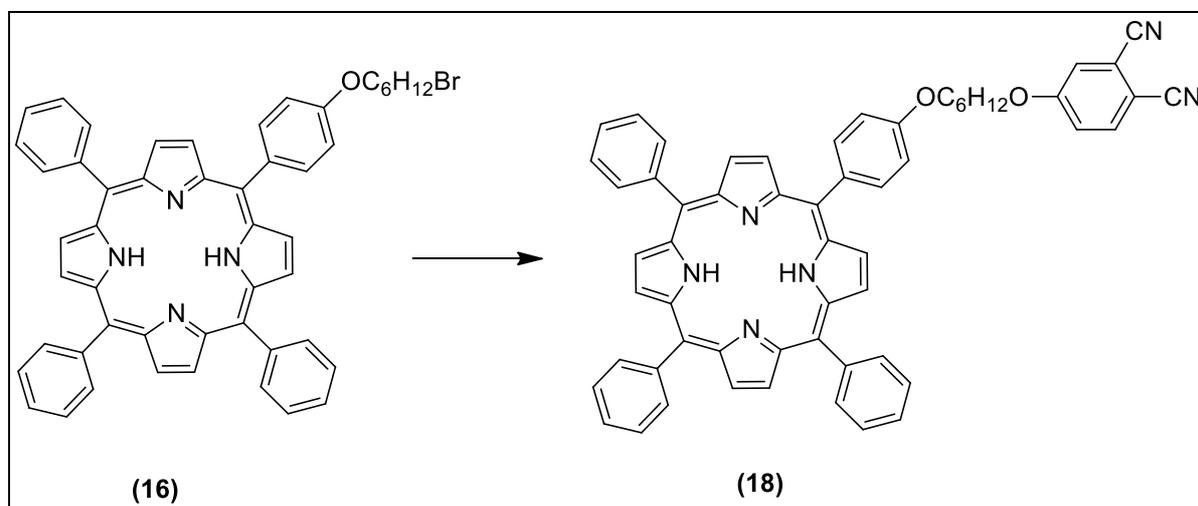
A solution of zinc acetate (0.27 g, 1.5 mol) in methanol (12 mL) was added to a solution of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin **14** (0.63 g, 1.00 mmol) in DCM (50 mL). The mixture was stirred at 40 °C for 2 h protected from light. The solution was washed with water twice and brine followed by an extraction with DCM. The solvent was removed under reduced pressure to give the product as a fine purple solid (0.57 g, 82 %); Mp 290 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.98 (2H, d, *J* = 4.6 Hz), 8.94 (6H, d, *J* = 5.4 Hz), 8.25 – 8.20 (6H, m), 8.08 (2H, d, *J* = 8.0 Hz), 7.80 – 7.71 (9H, m), 7.22 (2H, d, *J* = 8.0 Hz). MALDI-MS 692 (cluster, M⁺ = 693, isotopic distribution pattern corresponds to theoretical prediction). These data are consistent with literature values.⁴

3.4 Preparation of bromoalkoxy porphyrin **16**⁵



Hydroxyphenylporphyrin **14** (0.20 g, 0.32 mmol), 1,6-dibromohexane **15** (0.48 mL, 3.17 mmol) and potassium carbonate (0.44 g, 3.17 mmol) was added to dry DMF (40 mL) and the mixture stirred at rt for 48 h. The solvent was removed and the residue redissolved in DCM. This was washed with water and the washings extracted with DCM three times. The combined organic extracts were dried (MgSO₄) and the solvent removed in vacuo. The product was purified by column chromatography (eluting with DCM/petroleum ether, 1:1). Recrystallisation from hexane to give the titled compound as a purple solid (0.12 g, 47 %); Mp 173 °C (lit. 173 °C⁶); ¹H NMR (500 MHz, CDCl₃) δ 8.89 (d, *J* = 4.7 Hz, 2H), 8.84 (s, 6H), 8.24 – 8.19 (m, 6H), 8.12 (d, *J* = 5.4 Hz, 2H), 7.80 – 7.71 (m, 9H), 7.27 (d, *J* = 5.5 Hz, 2H), 4.26 (t, *J* = 6.3 Hz, 2H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.04 – 1.94 (m, 4H), 1.71 – 1.60 (m, 4H), -2.76 (s, 2H) ; UV-Vis (CH₂Cl₂)/(nm): 418, 516, 522, 590, 646; MALDI-MS 793 (cluster, M⁺ = 794, isotopic distribution pattern corresponds to theoretical prediction), these data are consistent with literature values.⁶

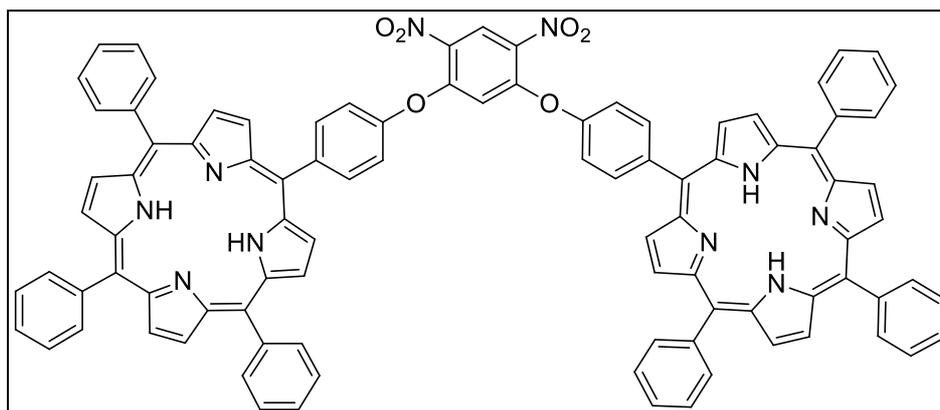
3.5 Preparation of (6-(3,4-dicyanophenoxy) hexyloxy)phenylporphyrin **18**



Bromoalkoxy porphyrin **16** (0.1 g, 0.13 mmol), 4-hydroxyphthalonitrile **17** (0.04 g, 0.3 mmol), potassium carbonate (0.04 g, 0.3 mmol) and potassium iodide (0.04 g, 0.2 mmol) were added to dry DMF (5 mL). This was placed under nitrogen and heated at 80 °C for 24 h. The mixture was cooled to room temperature and DCM was added, washed with water several times and the aqueous washings extracted with DCM. The organic extracts were then combined and the solvent evaporated. The crude product was purified column chromatography, eluting with toluene to give the titled compound as a purple solid (0.08 g, 72 %); Mp 129 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.91 (d, *J* = 4.7 Hz, 2H), 8.88 (s, 6H), 8.28 – 8.23 (m, 6H), 8.14 (d, *J* = 8.6 Hz, 2H), 7.84 – 7.73 (m, 9H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.08 (dd, *J* = 8.8, 2.6 Hz, 1H), 4.23 (t, *J* = 6.3 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.02 – 1.83 (m, 4H), 1.72 – 1.56 (m, 4H), -2.73 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 142.94, 140.33, 135.79, 134.70, 127.86, 126.83, 120.75, 119.96, 117.81, 112.85, 70.17, 29.62, 25.98, 25.98. UV-Vis (CH₂Cl₂) λ/(nm)(log ε): 399 (ε=1.4x10⁴), 418 (ε=8x10⁵), 517 (ε=4.3x10⁴), 549 (ε=3x10⁴), 590(ε=2.1x10⁴), 646(ε=2.1x10⁴); IR (KBr,

cm⁻¹): 3385, 2921, 2851, 2240, 1720, 1330, 1247, 800; MALDI-MS 856 (cluster, M⁺ = 857, isotopic distribution pattern corresponds to theoretical prediction).

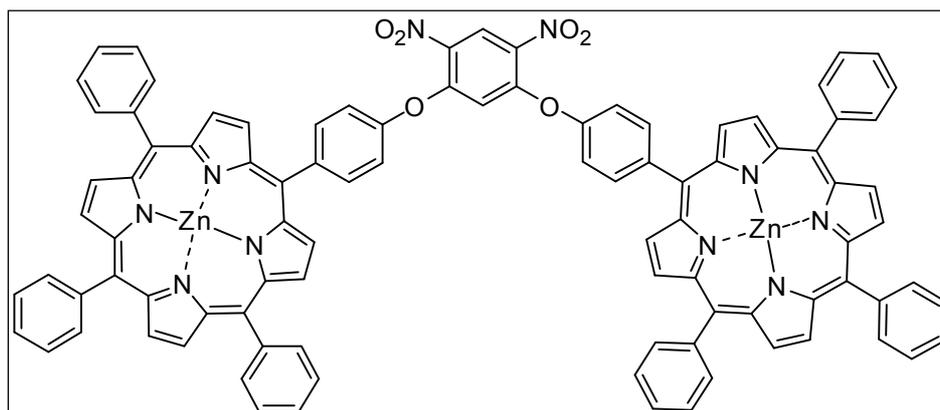
3.6 Preparation of dimer **60**⁷



1,5-Difluoro-2,4-dinitrobenzene **56** (0.015 g, 0.07 mmol), hydroxyphenylporphyrin **14** (0.1 g, 0.16 mmol) and potassium carbonate (0.010 g, 0.07 mmol) was added to acetone (30 mL) and the mixture stirred at room temp for 48 h. The solvent was removed and the residue redissolved in DCM. This was washed with water and the washings extracted with DCM. The combined organic extracts were dried (MgSO₄) and the solvent removed in vacuo. The product was purified by column chromatography (eluting with DCM). Recrystallisation from chloroform to give the titled dimer as a purple solid (0.05 g, 53 %); Mp 280 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.16 (s, 1H), 8.67 (d, *J* = 4.6 Hz, 4H), 8.47 (d, *J* = 4.4 Hz, 4H), 8.35 – 8.28 (m, 4H), 8.23 – 8.16 (m, 9H), 7.84 – 7.72 (m, 9H), 7.51 (t, *J* = 5.5 Hz, 4H), 7.13 (t, *J* = 7.7 Hz, 4H), 7.00 (s, 1H), 6.69 (d, *J* = 7.1 Hz, 8H), 6.61 (t, *J* = 7.6 Hz, 8H), -3.09 (4H, s); ¹³C NMR (126 MHz, CDCl₃) δ 157.52, 153.00, 142.21, 141.46, 141.00, 136.50, 134.72, 133.58, 133.07, 127.90, 127.01, 126.86, 126.52, 125.80, 120.45, 119.48, 117.22, 107.65, 105.01; UV-Vis (CH₂Cl₂)/nm (log ε): 406 (ε=4x10⁵), 418 (ε=4.5x10⁵), 516 (ε=4x10⁴), 549 (2x10⁴), 591 (1.5x10⁴), 647 (1.1x10⁴); IR (KBr, cm⁻¹): 3379, 2958, 2851, 1367, 1720, 1367, 1296, 1063.

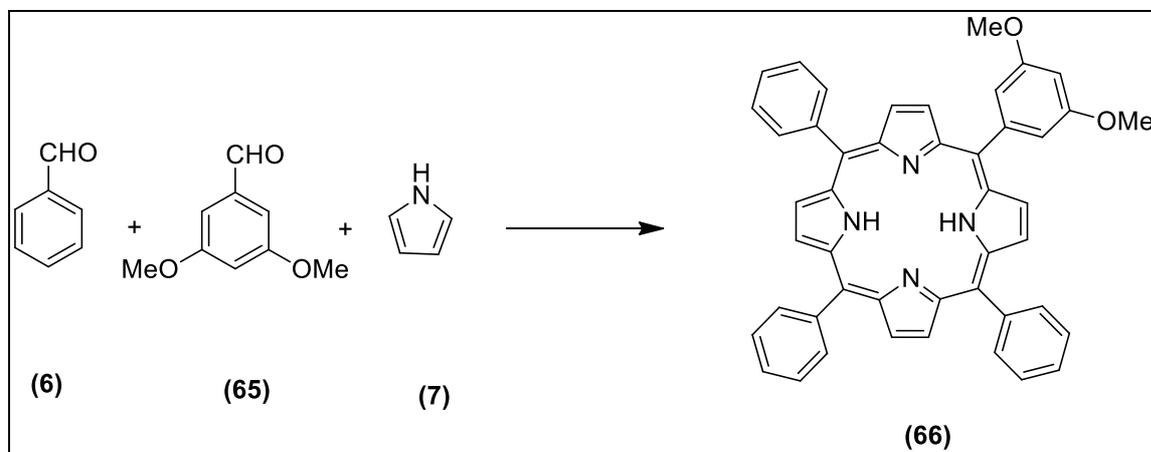
MALDI-MS 1425 (cluster, $M^+ = 1426$, isotopic distribution pattern corresponds to theoretical prediction).

3.7 Preparation of dimer 61



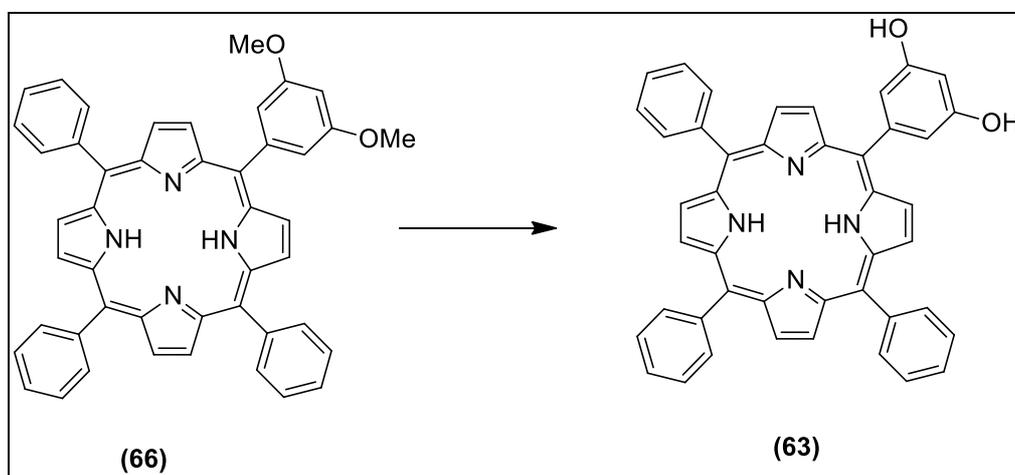
1,5-Difluoro-2,4-dinitrobenzene **56** (0.005 g, 0.02 mmol), hydroxyphenylphyrinatozinc **59** (0.04 g, 0.06 mmol) and potassium carbonate (0.005 g, 0.04 mmol) was added to acetone (6 mL) and the mixture stirred at room temp for 48 h. The solvent was removed and the residue redissolved in DCM. This was washed with water and the washings extracted with DCM. The combined organic extracts were dried ($MgSO_4$) and the solvent removed in vacuo. The product was purified by column chromatography (eluting with DCM). Recrystallisation from hexane gave titled dimer as a purple solid (0.018 g, 58%); Mp above 300 °C; 1H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.79 (d, $J = 4.6$ Hz, 4H), 8.69 (d, $J = 4.6$ Hz, 4H), 8.41 (dd, $J = 6.4, 4.9$ Hz, 9H), 8.23 – 8.17 (m, 4H), 8.01 (d, $J = 4.6$ Hz, 4H), 7.82 – 7.71 (m, 9H), 7.59 (d, $J = 8.4$ Hz, 4H), 7.14 (s, 1H), 7.05 – 6.97 (m, 8H), 6.74 (t, $J = 7.7$ Hz, 8H); UV-Vis (CH_2Cl_2)/nm ($\log \epsilon$): 415 ($\epsilon=5 \times 10^5$), 549 ($\epsilon=4 \times 10^4$), 591 ($\epsilon=1 \times 10^4$); MALDI-MS 1551 (cluster, $M^+ = 1552$, isotopic distribution pattern corresponds to theoretical prediction).

3.8 Preparation of 5-(3,5-dimethoxyphenyl)-10,15,20-triphenylporphyrin **66**⁸



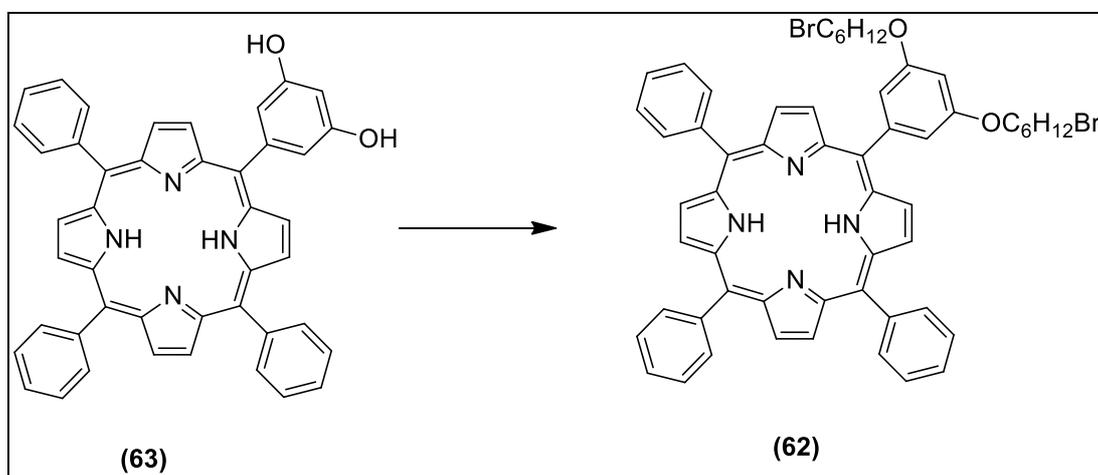
3,5-Dimethoxybenzaldehyde **65** (4.0 g, 25.00 mmol) and benzaldehyde **6** (7.7 g 72.00 mmol) were dissolved in propionic acid (250 mL), to this was added pyrrole **7** (6.71 g, 0.10 mol). This was refluxed in the dark for 30 min then cooled to room temperature. To this ethanol (150 mL) was added and the mixture left to crystallise overnight. The crystals were filtered off and purified by column chromatography on silica eluting with dichloromethane/petroleum ether (3:7) followed by THF/pet ether (1:1). The 5-(3,5-dimethoxyphenyl)-10,15,20-triphenylporphyrin was gained as purple crystals (0.98 g, 6 %); Mp >290 °C decomposed ; ¹H NMR (400 MHz, CDCl₃) δ 8.95 (d, *J* = 4.7 Hz, 2H), 8.84 (s, 6H), 8.21 (dd, *J* = 7.6, 1.7 Hz, 6H), 7.82 – 7.70 (m, 9H), 7.41 (d, *J* = 2.3 Hz, 2H), 6.90 (t, *J* = 2.3 Hz, 1H), 3.96 (s, 6H), -2.79 (s, 2H); MALDI-MS 674 (cluster, M⁺ = 675, isotopic distribution pattern corresponds to theoretical prediction).

3.9 Preparation of 5-(3,5-dihydroxyphenyl)-10,15,20-triphenylporphyrin **63**⁸



To solution (30 mL) of combination of HBr and CH₃COOH (1:1 / v:v) , a (0.95 g, 1.4 mmol) of 5,15-di(3,5-dimethoxyphenyl)-10,20-diphenylporphyrin **66** was added. The reaction mixture was then heated for 24 h on air. The mixture was poured into water and was extracted with ethyl acetate. The combined organic layers were washed with successively with brine and aqueous NaHCO₃ solution. The organic solution was then dried over Na₂SO₄ and evaporated to dryness, giving the titled porphyrin as purple product (0.8 g, 88 %); Mp 173 °C; ¹H NMR (500 MHz, Acetone) δ 9.06 (d, *J* = 4.3 Hz, 2H), 8.86 (s, 6H), 8.69 (s, 2H, s), 8.27– 8.24 (m, 6H), 7.89 – 7.80 (m, 9H), 7.33 (d, *J* = 2.2 Hz, 2H), 6.91 (t, *J* = 2.2 Hz, 1H), -2.69 (s, 2H); UV-Vis (CH₂Cl₂)/nm: 418, 516, 522, 590, 646; MALDI-MS 646 (cluster, M⁺ = 647, isotopic distribution pattern corresponds to theoretical prediction).

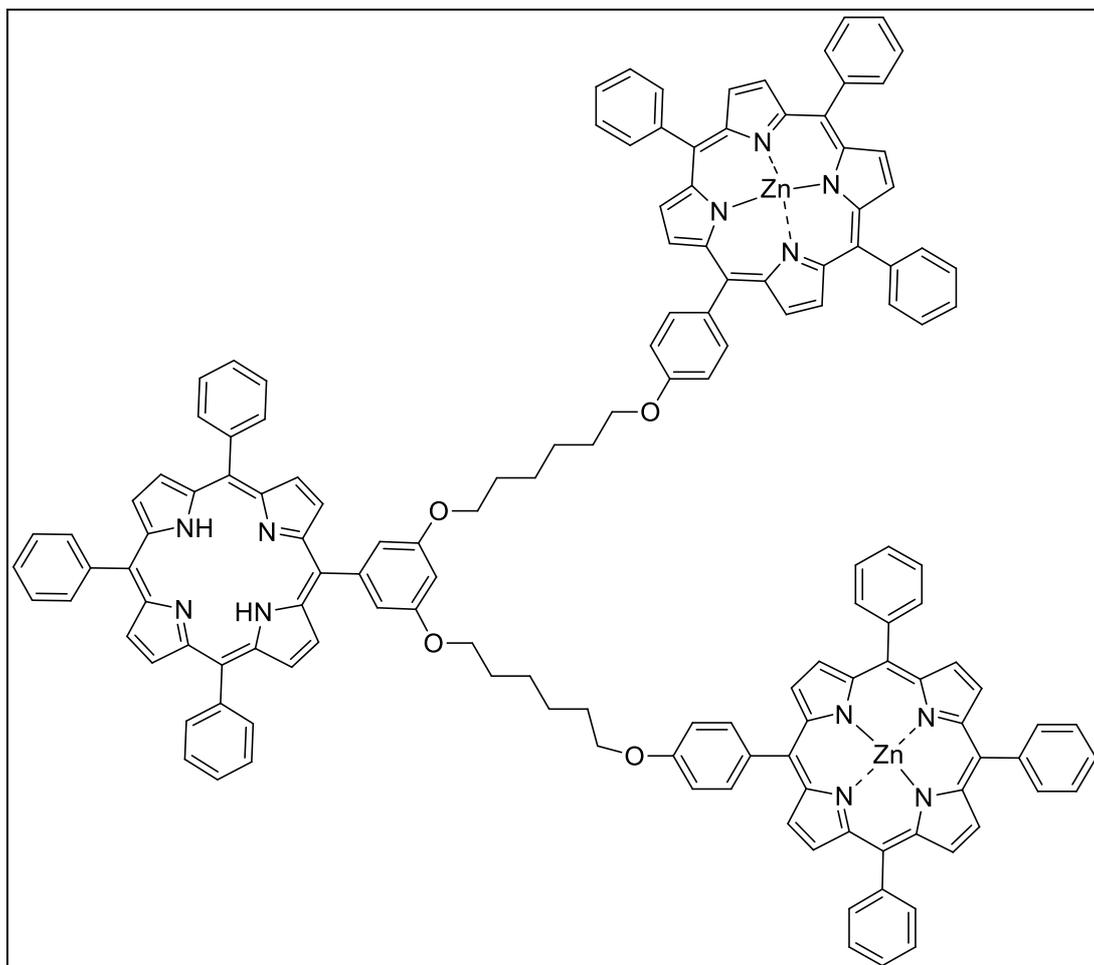
3.10 Preparation of 5-(3,5-bis((6-bromohexyl)oxy)phenyl)-10,15,20-triphenylporphyrin **62**⁵



5-(3,5-Dihydroxyphenyl)-10,15,20-triphenylporphyrin **63** (0.20 g, 0.31 mmol), 1,6-dibromohexane **15** (0.23 g, 0.93 mmol) and potassium carbonate (0.13 g, 0.93 mmol) was added to DMF (5 mL) and the mixture stirred at 80 °C for 72 h. The solvent was removed and the residue redissolved in DCM. This was washed with water and the washings extracted with DCM. The combined organic extracts were dried (MgSO₄) and the solvent removed in vacuo. The product was purified by column chromatography (eluting with hexane: acetone, 1:1). Recrystallisation from chloroform to give the titled compound as a purple solid. (0.142 g, 47 %); Mp 167 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.97 (d, *J* = 4.8 Hz, 2H), 8.85 (d, *J* = 17.5 Hz, 6H), 8.23 (d, *J* = 6.4 Hz, 6H), 7.80 – 7.72 (m, 9H), 7.40 (d, *J* = 2.1 Hz, 2H), 6.89 (t, *J* = 2.1 Hz, 1H), 4.13 (t, *J* = 6.4 Hz, 4H), 3.41 (t, *J* = 6.8 Hz, 4H), 1.95 – 1.81 (m, 8H), 1.62 – 1.47 (m, 8H), -2.77 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 158.39, 144.12, 142.31, 134.69, 127.86, 126.84, 120.31, 120.02, 114.61, 101.25, 68.24, 33.92, 32.83, 29.33, 28.10, 25.51; UV-Vis (CH₂Cl₂)/nm (log ε): 402 (ε=9.5x10⁴), 418 (ε=5x10⁴), 515 (ε=3x10⁴), 550 (1.5x10⁴), 592 (ε=1.5x10⁴), 643 (ε=1.5x10⁴); IR (KBr, cm⁻¹): 3392, 2958, 1647, 1343, 1186,

1063, 1035, 985, 922, 563; MALDI-MS 972 (cluster, $M^+ = 973$, isotopic distribution pattern corresponds to theoretical prediction).

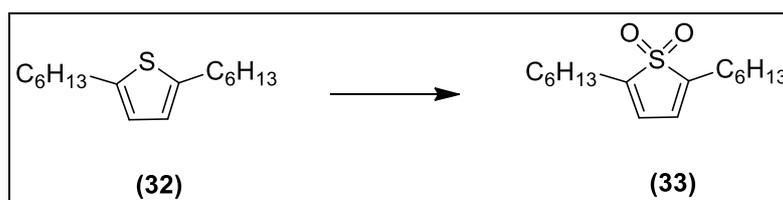
3.11 Preparation of trimer 67.



5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrinatozinc **59** (0.036 g, 0.052 mmol), *bis*-bromoalkoxy porphyrin **60** (0.04 g, 0.041 mmol), K_2CO_3 (0.1 g, 0.725 mmol) were all added to 6 mL acetone and stirred at room temperature in an air atmosphere for 3 days. DCM was then added and the mixture washed with water. The aqueous washings were extracted with DCM and the organic extracts combined, dried ($MgSO_4$) and the solvent removed in vacuo. The residue was then purified by column chromatography, the remaining starting material was eluted with DCM/Pet (1:1) and the product was eluted with toluene. The trimer **67**

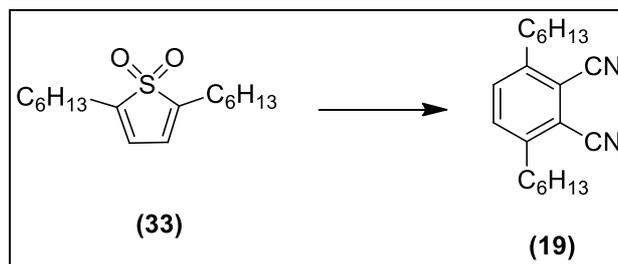
bulb distillation; the resulting orange oil of 2,5-dihexylthiophene (26.13 g, 74 %) was used without further purification. ^1H NMR (500 MHz, CDCl_3) δ 6.57 (s, 2H), 2.75 (t, $J = 7.7$ Hz, 4H), 1.65 (m, 4H), 1.30 (m, 12H), 0.90 (t, $J = 6.7$ Hz, 6H).

3.13 Preparation of 2, 5-dihexylthiophene-1,1-dioxide **33**⁹



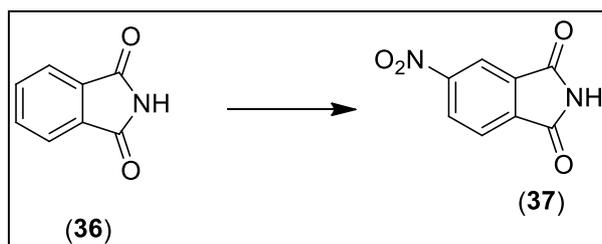
2,5-Dihexylthiophene **32** (25.25g, 0.1 mol) was placed into two liter round –bottom-three-neck flask fitted with an efficient stirrer bar and dry-ice condenser. Dichloromethane (350 mL), water (450 mL) acetone (350 mL) and NaHCO_3 (140 g) were added. The mixture was cooled to 5-10 $^\circ\text{C}$ and solid oxone (140 g) was added slowly in portions over 1.5-2 hrs while maintaining the temperature between 5-10 $^\circ\text{C}$. After addition was complete, the mixture was stirred a further 1 hr at this temperature. Then it left to warm gradually to room temperature and stirred overnight. Water was added (as necessary to dissolve most of the solid) and extracted with DCM. Organic layer dried over MgSO_4 , filtered and solvent removed under reduced pressure leaving yellow oil. Upon cooling, the oil solidifies and was recrystallised from ethanol (20 g, 70%). Mp 46-47 $^\circ\text{C}$ (lit. 47 $^\circ\text{C}^{10}$); ^1H NMR (400 MHz, CDCl_3) 6.21 (s, 2H), 2.50 (t, $J=7.6$, 4H), 1.4 (m, 16H), 0.90 (t, $J = 6.7$, 6H).

3.14 Preparation of 3,6-dihexylphthalonitrile **19**¹⁰



2,5-Dihexylthiophene-1,1-dioxide **33** (2 g, 7.0 mmol) and fumaronitrile (1 g, 13.8 mmol) in chloroform (5 mL) were heated in a sealed tube at 150 °C for 2 days. The contents of tube were evaporated to dryness and chromatographed over silica (DCM: Pet. Ether (2:3)) as eluant to afford the titled compound as 1.2 g, 60%. Mp 38-39 °C (lit. 38 °C¹⁰); ¹HNMR (500 MHz, CDCl₃) 7.43 (s, 2H), 2.81 (t, *J* = 7.2, 4H), 1.70 – 1.58 (m, 4H), 1.42 – 1.26 (m, 12H), 0.85 (t, *J* = 6.8 Hz, 6H).

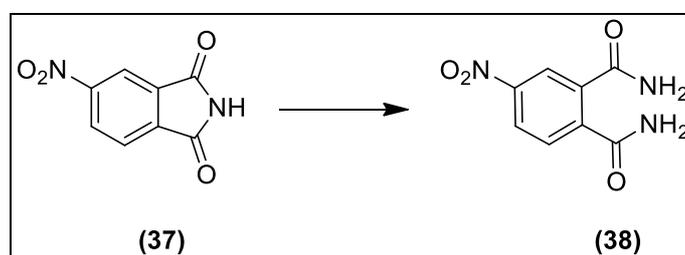
3.15 Preparation of 4-nitrophthalimide **37**¹¹



A 100 mL solution of concentrated H₂SO₄ and HNO₃ (6:1 v/v) was cooled to 15 °C using an ice bath. Thereafter phthalimide **36** (30.0 g, 0.20 mol) was added portion wise to the acid solution while stirring maintaining the temperature between 10 and 15 °C. The temperature was increased to 35 °C and the mixture stirred at that temperature for 1 h. After cooling to 0 °C, the yellow reaction mixture was poured onto crushed ice (500g) while stirring to yield a

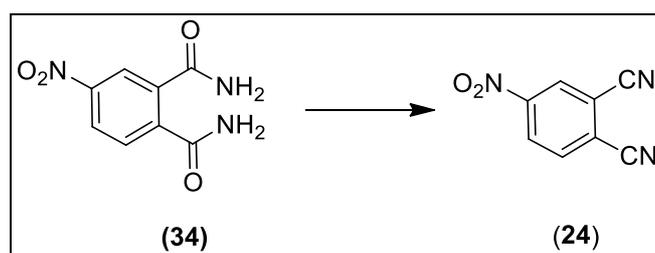
beige suspension. The mixture was filtered and the solid mass was thoroughly washed with cool water to gain the titled compound (30 g, 78 %). M.p.197 °C (lit. 195 °C¹²); ¹H NMR (500 MHz, DMSO) δ 11.83 (s, 1H), 8.61 (dd, $J = 8.1, 2.0$ Hz, 1H), 8.44 (d, $J = 2.0$ Hz, 1H), 8.08 (d, $J = 8.1$ Hz, 1H).

3.16 Preparation of 4-nitrophthalamide **38**¹¹



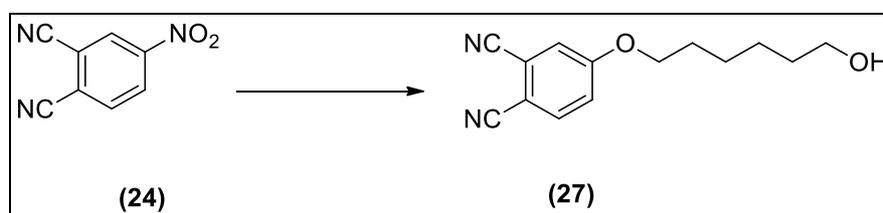
4-Nitrophthalimide **37** (21.0 g, 0.11 mol) was stirred in 25% ammonium solution (138 mL) for 24 h. The mixture was filtered and washed with cooled water until excess ammonia was not detected. The title compound was dried at 110 °C to gain the titled compound (20 g, 87 %). H NMR (500 MHz, DMSO) δ 8.32 (dd, $J = 8.3, 2.4$ Hz, 1H), 8.29 (d, $J = 2.2$ Hz, 1H), 8.04 (s, 1H), 7.98 (s, 1H), 7.71 (d, $J = 8.3$ Hz, 1H), 7.61 (s, 1H).

3.17 Preparation of 4-nitrophthalonitrile **24**¹¹



Dry DMF (167 mL) was poured in a three necked flask under argon and cooled to 0 °C using an ice bath. Maintaining this temperature, thionyl chloride (17 mL) was added drop by drop while stirring, thereafter the solution was left to reach room temperature and stirring was continued for 30 minutes. The solution was again cooled to 0 °C followed by the slow addition of 4-nitrophthalonitrile **34** (20 g, 0.1 mol) with stirring. The mixture was stirring for 3 hours at room temperature; thereafter the mixture was poured onto crushed ice (200 g), filtered and washed with cooled water. The pale yellow title compound was dried at 110 °C to gain the titled compound (14.5 g, 84 %). Mp 143 °C (lit. 141 °C¹³); ¹HNMR (500 MHz, DMSO) 9.11 (s, 1H), 8.75 (d, *J* = 7.3 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (126 MHz, DMSO) δ 149.81, 135.70, 128.77, 120.29, 116.65, 114.99, 114.68.

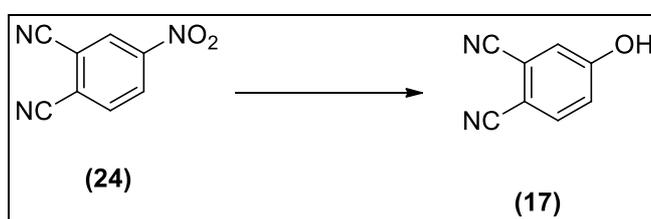
3.18 Preparation of 4-(6-hydroxyhexyloxy)phthalonitrile **27**¹⁴



A mixture of 4-nitrophthalonitrile **24** (1 g, 5.77 mmol), 1,6-hexanediol **25** (2 g, 8.23 mmol) and potassium carbonate (1.11 g, 8.08 mmol) was added to dry DMF (20 mL) and the mixture stirred at room temp for 24 h. The solvent was removed and the residue redissolved in DCM (50 mL). This was washed with water (100 mL) and the washings extracted with DCM (3 x 50 mL). The combined organic extracts were dried (MgSO₄) and the solvent removed in vacuo. The product was purified by column chromatography (eluting with EtOAc: petroleum ether, 1:4). The light yellow solid was gained as (1.0 g, 70 %). Mp 65 °C

(lit. 65 °C¹⁴); ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 2.6 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.6 Hz, 1H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.67 (t, *J* = 6.5 Hz, 2H), 1.84 (q, *J* = 6.5, 2H), 1.64 – 1.41 (6H, m), 1.31 (1H, br). These data are consistent with literature values.¹⁴

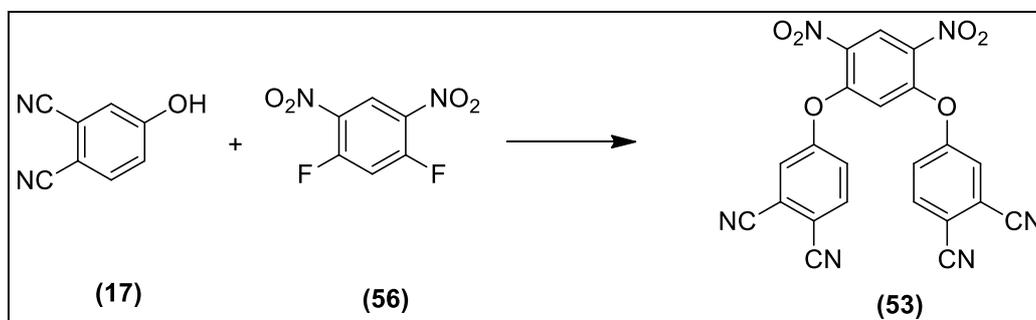
3.19 Preparation of 4-hydroxyphthalonitrile **17**¹⁵



A mixture of 4-nitro-2,3-dicyanobenzonitrile **24** (1.00 g, 5.78 mmol), sodium nitrite (0.44 g, 6.36 mmol) and freshly ground anhydrous potassium carbonate (0.87 g, 6.36 mmol) was dissolved in dry DMSO (30 mL) and heated to 120 °C under an atmosphere of argon for 24 hours. After the reaction had cooled down to room temperature, it was poured into water (150 mL) and the precipitate was removed by filtration. The mother liquor was acidified with concentrated HCl (7 mL) and cooled in the fridge for 24 h. The resultant precipitate was collected and oven dried to give the titled compound (0.60 g, 72 %). Mp 210-211.5 °C (lit. 208-210 °C¹³); ¹H NMR (500 MHz, DMSO) 11.45 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.21 (dd, *J* = 8.7 and 2.5 Hz, 1H). These data are consistent with literature values.¹⁶

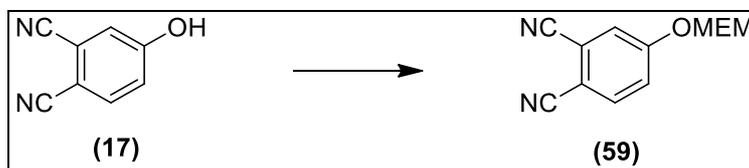
3.20 Preparation of 4,4'-((4,6-dinitro-1,3-henylene)bis(oxy))diphthalonitrile

53



1,5-difluoro-2,4-dinitrobenzene **56** (0.2 g, 1 mmol), 4-hydroxyphthalonitrile **17** (0.3 g, 2.1 mmol) and potassium carbonate (0.274 g, 2.0 mmol) was added to acetone (7 mL) and the mixture stirred at room temperature for 24 h. The solvent was removed and the residue redissolved in DCM. This was washed with water and the washings extracted with DCM three times. The combined organic extracts were dried (MgSO₄) and the solvent removed under reduced pressure. The product was purified by column chromatography (eluting with DCM). Recrystallisation from acetone to give titled compound as yellow crystals solid in (0.3 g, 66.3 %). Mp 197 °C; ¹H NMR (500 MHz, Acetone) δ 9.04 (s, 1H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 2.5 Hz, 2H), 7.80 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.73 (s, 1H); ¹³C NMR (126 MHz, Acetone) δ 160.10, 153.48, 139.12, 137.36, 126.49, 124.56, 124.31, 118.82, 117.81, 116.11, 115.74, 112.56; (KBr, cm⁻¹): 3047, 2240, 1630, 1536.

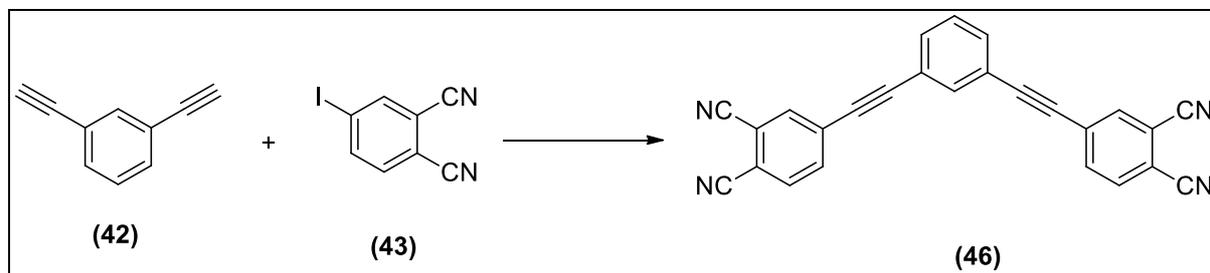
3.21 Preapration of 4-(2-methoxyethoxymethyl) phthalonitrile **59**¹⁷



A stirred solution of 4-hydroxyphthalonitrile **17** (2 g, 13.88 mmol) in dry THF (20 mL) was cooled to 0 °C using an ice bath, and a 2.6 mL of *n*-BuLi (2.5 M solution in Hexanes) was added. To the resulting red solution, MEM chloride (2.06 g, 166 mmol) was added, and the reaction mixture was stirred under a nitrogen atmosphere for 48 h. The resulting brown reaction mixture was then added to aqueous ammonia (30%, 150 mL) and the product extracted with THF (3x50 mL). The solvent was removed under reduced pressure and the residue was redissolved in DCM and washed with water (2 x 100 mL), dried over MgSO₄ and the solvent evaporated under reduced pressure. The resulting solid was purified by column chromatography over silica gel (eluent: DCM) to yield the titled compound as white crystals (1 g, 31%) ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.36 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.35 (s, 2H), 3.84 – 3.79 (m, 2H), 3.56 – 3.52 (m, 2H), 3.36 (s, 3H). These data are consistent with literature values.¹⁶

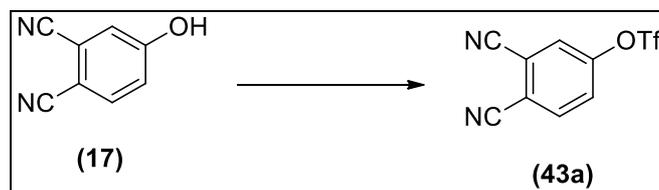
3.22 Preparation of 4,4'-(1,3-phenylenebis(ethyne-2,1-diyl))diphthalonitrile

46¹⁸



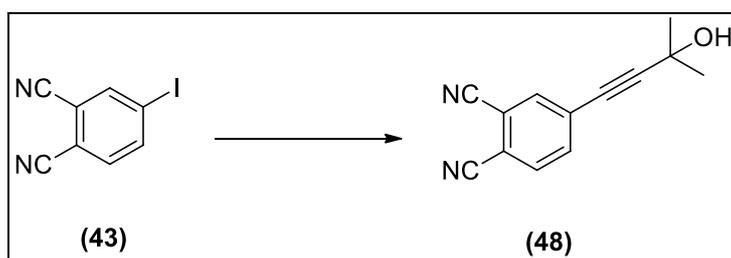
Following a modification to the procedure in literature,¹⁶ bis[triphenylphosphine]palladium dichloride (0.005 g, 7×10^{-5} mol) and copper(I) iodide (0.001g, 5×10^{-6} mol) were added successively to 4-iodophthalonitrile **43** (0.2 g, 0.8 mmol) and 1,3-diethynylbenzene **42** (0.05 g, 0.36 mmol) in freshly distilled TEA and THF (2+6 mL) at room temperature under argon atmosphere. After stirring at room temperature for 6 h, the reaction was complete as checked by TLC (silica gel, DCM). The solvent was evaporated, then water was added and the residue was extracted with Et₂O. The combined organic layers were washed with water, dried over Na₂SO₄, and the solvent removed under reduced pressure. The resulting residue was purified by column chromatography to give the titled product as white solid (0.08, 60%). Mp 239 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 1.0 Hz, 2H), 7.85 – 7.80 (m, 4H), 7.74 (t, *J* = 1.3 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 136.19, 135.76, 135.24, 133.73, 133.13, 129.27, 128.90, 122.27, 116.56, 115.20, 114.82, 95.08, 86.81; (KBr, cm⁻¹): 3047, 2240, 2245, 1630, 1599.

3.23 Preparation of 4-(trifluoromethanesulfonyloxy)phthalonitrile **43 a**



4-Hydroxyphthalonitrile **17** (1.0 g, 0.007mmol) was added to dry dichloromethane (10 mL) and 2,6-lutidine (3mL) at -20 °C. Trifluoromethanesulphonic acid anhydride (2.10 mL, 0.01 mol) was slowly added to the solution and the mixture allowed warming to room temperature overnight. Dilute hydrochloric acid was added and the mixture extracted with dichloromethane (3x 150 mL). The solvent was removed in vacuo and the residue purified by column chromatography eluting with dichloromethane to give the pure title compound as an oil yellow product (0.84 g, 44 %). ¹H NMR (500 MHz, DMSO) δ 7.79 (dd, $J = 9.6, 5.8$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 1H).

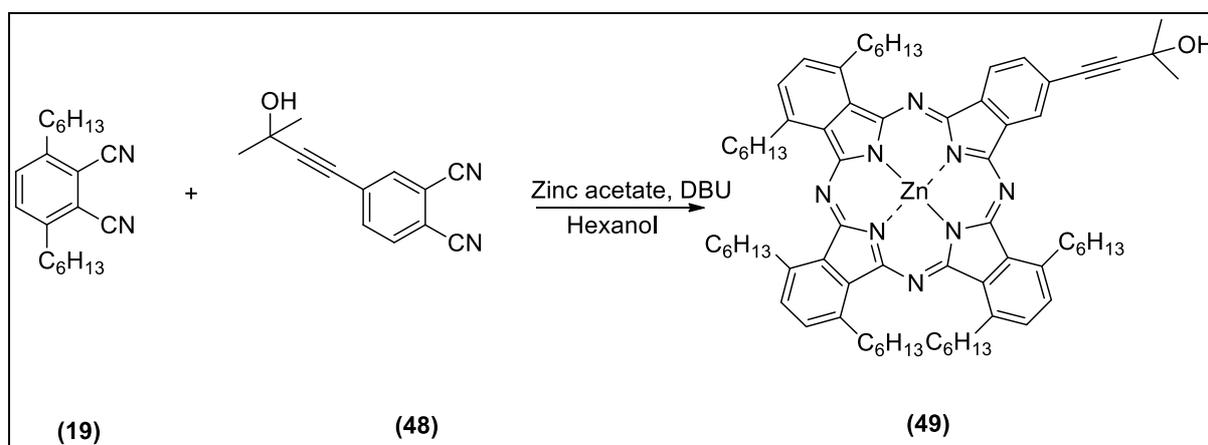
3.24 Preparation of 4-(3-Hydroxy-3-methyl-1-butynyl) phthalonitrile **48**¹⁸



Bis[triphenylphosphine]palladium dichloride (0.02 g) and copper(I) iodide (0.01 g) were added successively to 4-iodophthalonitrile **43** (0.2 g, 0.8 mmol) and 2-methylbut-3-yn-2-ol (0.13 g, 0.001 mmol) in freshly distilled TEA and THF (2+6 mL) at room temperature under argon atmosphere. After stirring at room temperature for 6 h, the reaction was complete as

checked by TLC (silica gel, DCM). The solvent was evaporated, then water was added and the residue was extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with water (3 x 30 mL), dried over Na₂SO₄, and the solvent removed under reduced pressure. The resulting residue was purified by column chromatography (silica: hexane/ethyl acetate 3:2) to give the desired product as an oil which upon cooling became a white solid. ¹H NMR (500 MHz, DMSO) δ 8.18 (d, *J* = 1.6 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, *J* = 8.2 and 1.7 Hz, 1H), 5.65 (s, 1H), 1.49 (s, 6H). These data are consistent with literature values.¹⁶

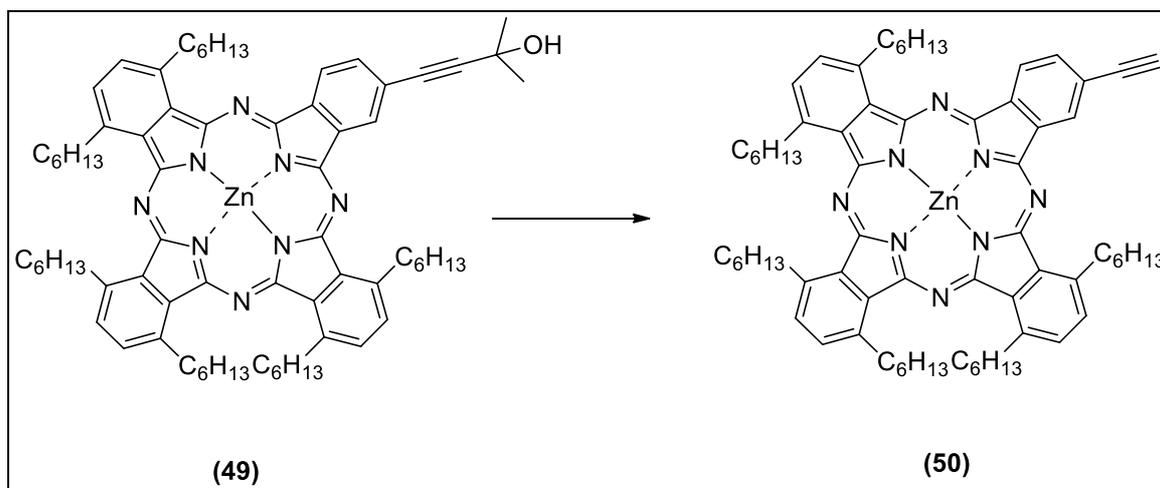
3.25 Preparation of 1,4,8,11,15,18-hexakis(hexyl)-23-(3-hydroxy-3-methyl-1-butynyl)-phthalocyaninatozinc(II) **49**



3,6-Dihexylphthalonitrile **19** (0.92 g, 3.1 mmol) and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile **48** (0.22 g, 1.0 mmol) was refluxing in *n*-hexanol (10 mL) for 24 h under an argon atmosphere in the presence of zinc acetate dehydrate (excess) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The resulting green crud product was the purified by column chromatography eluting with DCM/ EtOH (30:1) to give the desired product as the second green fraction in (0.23, 18 %) as green-blue product. Mp > 300 °C;

^1H NMR (500 MHz, THF- d_8) δ 9.42 (s, 1H), 9.30 (d, $J = 7.8$, 1H), 8.16 (dd, $J = 7.8$ and 1.3, 1H), 7.91 (s, 2H), 7.87 (s, 2H), 7.84 (q, $J = 7.5$, 2H), 4.75 (s, 1H), 4.61 (m, 4H), 4.58 – 4.51 (m, 6H), 4.50 – 4.45 (m, 2H), 2.42 (s, 6H), 2.14 – 1.74 (m, 6H), 1.66 – 1.54 (m, 6H), 1.49 – 1.17 (m, 36H), 1.00 – 0.86 (m, 9H), 0.86 – 0.70 (m, 9H); ^{13}C NMR Could not be obtained due to the intensive aggregations; UV-Vis (THF)/nm: 697 and 628; IR (KBr/ cm^{-1}): 3338, 2958, 2889, 1721, 1644, 1189, 1120, 965, 925, 850, 755; MALDI-MS 1162 (cluster, $\text{M}^+ = 1163$, isotopic distribution pattern corresponds to theoretical prediction).

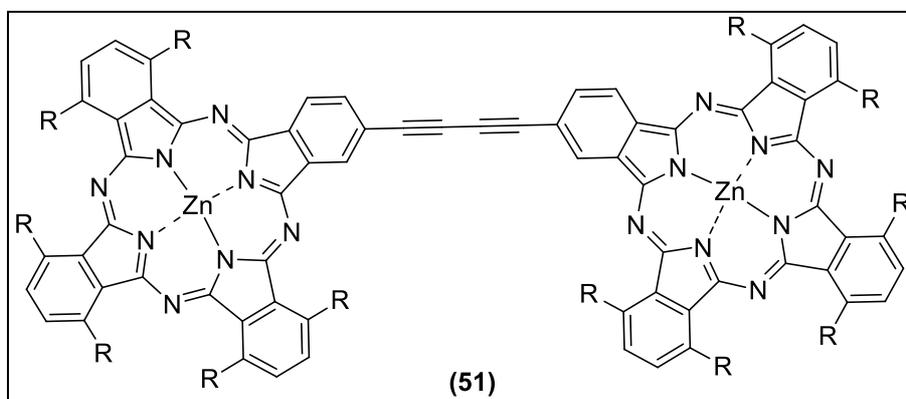
3.26 Preparation of 1,4,8,11,15,18-hexakis(hexyl)-23-ethynyl-phthalocyaninatozinc(II) **50**



A mixture of 1,4,8,11,15,18-hexakis(hexyl)-23-(3-hydroxy-3-methyl-1-butynyl)-phthalocyaninatozinc (II) **49** (0.23g, 0.2 mmol) and sodium hydroxide (0.2 g, 5 mmol) in dry toluene (5 mL) was refluxed for 6h under argon. After cooling to rt, the solvent was removed and the residue was suspended in DCM and washed water. The organic layer then dried and the solvent evaporated. The resulting greenish-blue product was purified by column

chromatography. The fraction was collected using DCM/EtOH (100: 1) to yield 1, 4, 8, 11, 15,18-hexakis (hexyl)-23-ethynyl-phthalocyaninatozinc (II) (0.15 g, 68 %); Mp 283 °C; ^1H NMR (500 MHz, THF) δ 9.37 (s, 1H), 9.15 (d, $J = 7.7$ Hz, 1H), 8.15 (d, $J = 7.6$ Hz, 1H), 7.88 (s, 2H), 7.80 – 7.68 (m, 4H), 4.56 (t, $J = 7.2$ Hz, 4H), 4.46 (dd, $J = 14.6, 7.3$ Hz, 4H), 4.42 – 4.36 (m, 2H), 4.34 – 4.28 (m, 2H), 3.94 (s, 1H), 2.39 – 2.13 (m, 12H), 1.52 – 1.23 (m, 36H), 0.99 – 0.86 (m, 9H), 0.86 – 0.77 (m, 9H); ^{13}C NMR Could not be obtained due to the intensive aggregations; UV-Vis (THF)/nm: 697; IR (KBr/ cm^{-1}): 3390, 2981, 2869, 1235, 11082, 965, 925, 850, 755; MALDI-MS 1106 (cluster, $M^+ = 1107$, isotopic distribution pattern corresponds to theoretical prediction).

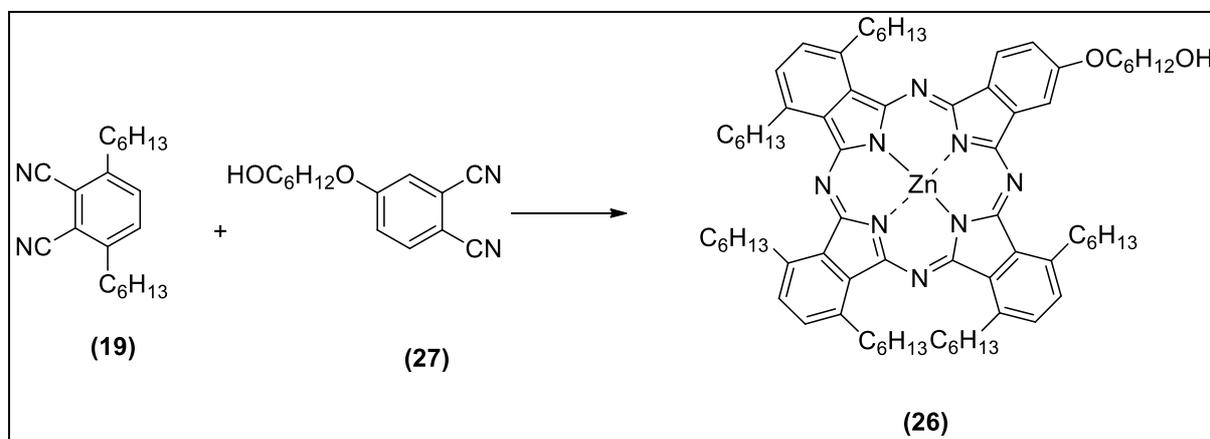
3.27 Preparation of *bis*[(23-ethynyl-1,4,8,11,15,18-hexakis(hexyl)phthalocyaninato)zinc(II)]butadiyne **51**



A mixture of 1,4,8,11,15,18-hexakis(hexyl)-23-ethynyl-phthalocyaninatozinc (II) **50** (30 mg, 0.03 mmol), copper(II) acetate monohydrate (14 mg, 0.80 mmol) and copper chloride (7 mg, 0.05 mmol) in dry pyridine (4 mL) was heated at 55-60 °C for 24 h under argon. After cooling to rt, the solvent was removed and the residue was suspended in DCM and washed with water and then EDTA. The organic layer then dried and the solvent evaporated. The resulting

greenish-blue product was purified by column chromatography. The fraction was collected using DCM/EtOH (100:1) and then re-column using size-exclusion chromatography using THF as elute to give the titled compound as (0.02 g, 30 %). Mp > 300 °C, ¹H NMR (500 MHz, THF-d₈) δ 9.29 (2H, s), 8.51 (2H, s), 8.21 (2H, s), 7.88 (4H, s), 7.68 (4H, s), 7.20 (2H, s), 7.05 (2H, s), 4.26 (24H, m), 2.28(24H,m), 1.38(72H, m), 0.91(36H, m),¹³C NMR Could not be obtained due to the intensive aggregations; UV-Vis (THF)/nm: 719, 685, 623; MALDI-MS 2211 (cluster, M⁺ = 2212, isotopic distribution pattern corresponds to theoretical prediction).

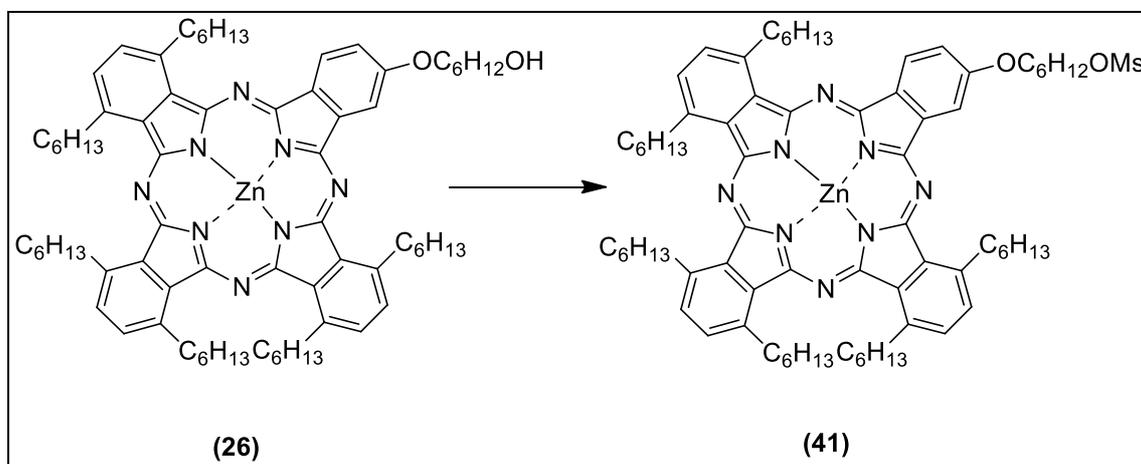
3.28 Preparation of 1,4,8,11,15,18-hexakis(hexyl)-23-(6-hydroxyhexyloxy)phthalocyaninatozinc(II) **26**



3,6-Dihexylphthalonitrile **19** (0.71 g, 2.4 mmol) and 4-(6-hydroxyhexyloxy) phthalonitrile **27** (0.18 g, 0.7 mmol) was refluxing in *n*-hexanol (5 mL) for 24 h under an argon atmosphere in the presence of zinc acetate dehydrate (excess) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The resulting green crude product was the purified

by column chromatography eluting with toluene/ EtOAc to give the titled product as green-blue product in (0.32, 38 %). Mp > 300 °C; ^1H NMR (500 MHz, THF) δ 8.96 (d, $J = 8.2$ Hz, 1H), 8.56 (d, $J = 1.9$ Hz, 1H), 7.87 (s, 1H), 7.79 – 7.67 (m, 4H), 7.56 (dd, $J = 8.2, 2.1$ Hz, 1H), 7.39 (s, 1H), 4.59 (dd, $J = 12.9, 7.1$ Hz, 4H), 4.53 – 4.26 (m, 12H), 2.35 – 2.18 (m, 12H), 2.12 – 2.06 (m, 2H), 1.94 – 1.81 (m, 6H) 1.55 – 1.16 (m, 36H), 0.95 – 0.86 (m, 6H), 0.86 – 0.79 (m, 12H); ^{13}C NMR Could not be obtained due to the intensive aggregations; UV-Vis (THF)/nm: 701 and 621; IR (KBr/ cm^{-1}): 3390, 2965, 1720, 102, 1035, 985, 922, 849; MALDI-MS 1197 (cluster, $\text{M}^+ = 1198$, isotopic distribution pattern corresponds to theoretical prediction).

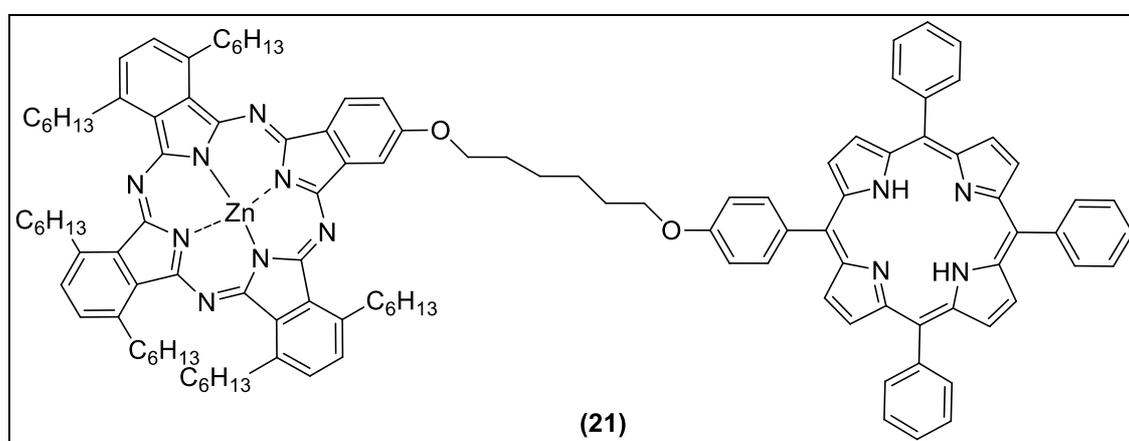
3.29 Preparation of 1,4,8,11,15,18-hexakis(hexyl)-23-(6-methanesulfonate-hexyloxy)phthalocyaninatozinc(II) 41



A mixture of 1,4,8,11,15,18-hexakis(hexyl)-23-(6-hydroxyhexyloxy)phthalocyaninatozinc(II) **26** (0.09g, 0.08 mmol) and methanesulfonyl chloride (0.01 g, 0.09 mmol) in dry pyridine (4 mL) was stirred at 0 °C for 24 h under argon. After cooling to rt, the solvent was removed and the residue was suspended in DCM and washed water. The organic layer then dried and

the solvent evaporated. The resulting greenish-blue product was purified by column chromatography. The fraction was collected using toluene/ EtOAc to give the tilted compound as bluish green solid (0.08 g, 87 %). Mp 283 °C; ^1H NMR (400 MHz, THF) δ 9.18 (d, $J = 7.8$ Hz, 1H), 8.77 (s, 1H), 7.90 (s, 2H), 7.88 – 7.79 (m, 4H), 7.69 (d, $J = 6.9$ Hz, 1H), 4.64 (t, $J = 6.6$ Hz, 4H), 4.60 – 4.41 (m, 10H), 4.31 – 4.25 (m, 2H), 3.03 (s, 3H), 2.43 – 2.17 (m, 12H), 2.17 – 2.05 (m, 2H), 1.96 – 1.86 (m, 6H), 1.60 – 1.21 (m, 36H), 0.97 – 0.89 (m, 6H), 0.86 – 0.77 (m, 12H); ^{13}C NMR Could not be obtained due to the intensive aggregations; UV-Vis (THF)/nm: 792 and 624 ; IR (KBr/ cm^{-1}): 2957, 2887, 1645, 1716, 1442, 1344, 1036, 985, 924, 851; MALDI-MS 1274 (cluster, $\text{M}^+ = 1275$, isotopic distribution pattern corresponds to theoretical prediction).

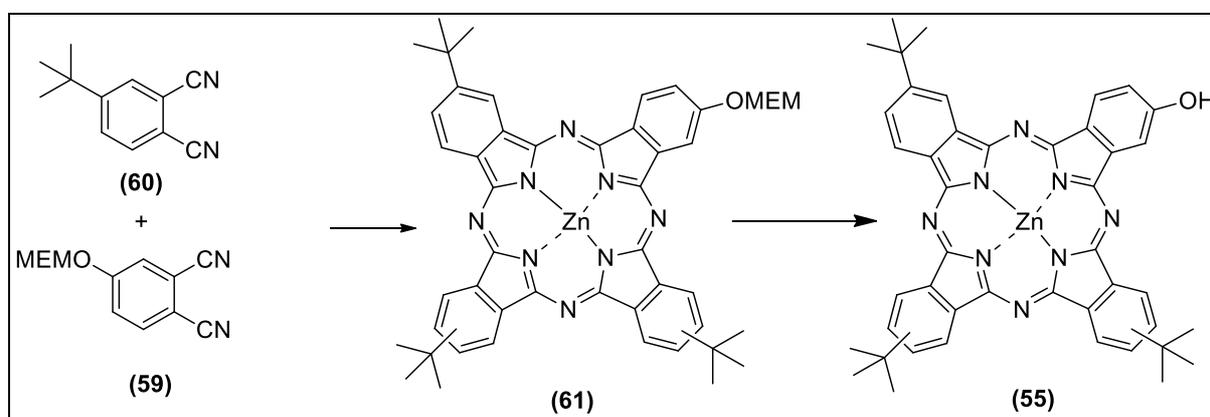
3.30 Preparation of dimer 21



A mixture of 1,4,8,11,15,18-hexakis(hexyl)-23-(6-methanesulfonate-hexyloxy) phthalocyaninatozinc(II) **41** (0.113 g, 0.1 mmol), 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin **14** (0.17 g, 0.3 mmol) and CsCO_3 (0.5 g, 1.5 mmol) in dry DMF (4 mL) was heated at 85-80 °C for 24h under argon for 48h. After cooling to rt, the solvent was removed and the residue was suspended in DCM and washed water. The organic layer then

dried and the solvent evaporated. The resulting bluish green product was purified by column chromatography. The fraction was collected using toluene/EtOAc to give the titled compound (0.085, 53 %). Mp > 300 °C; ¹H NMR (500 MHz, THF) δ 9.13 (d, *J* = 8.2 Hz, 1H), 8.90 (d, *J* = 4.3 Hz, 2H), 8.80 (s, 6H), 8.75 (s, 1H), 8.22 – 8.17 (m, 6H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.89 (s, 2H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 3.2 Hz, 2H), 7.77 – 7.74 (m, 9H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.67 – 4.61 (m, 4H), 4.61 – 4.51 (m, 6H), 4.48 – 4.36 (m, 6H), 2.27 – 2.20 (m, 12H), 2.18 – 2.14 (m, 2H), 2.01 – 1.92 (m, 6H), 1.61 – 1.24 (m, 36H), 0.94 – 0.85 (m, 6H), 0.85 – 0.79 (m, 12H), -2.68 (s, 2H); ¹³C NMR Could not be obtained due to the intensive aggregations; UV-Vis (THF)/nm: 418, 511, 624, 691; IR (KBr/cm⁻¹): 3338, 2957, 2888, 1719, 1647, 1064, 966, 924, 849; MALDI-MS 1812 (cluster, M+ = 1813, isotopic distribution pattern corresponds to theoretical prediction).

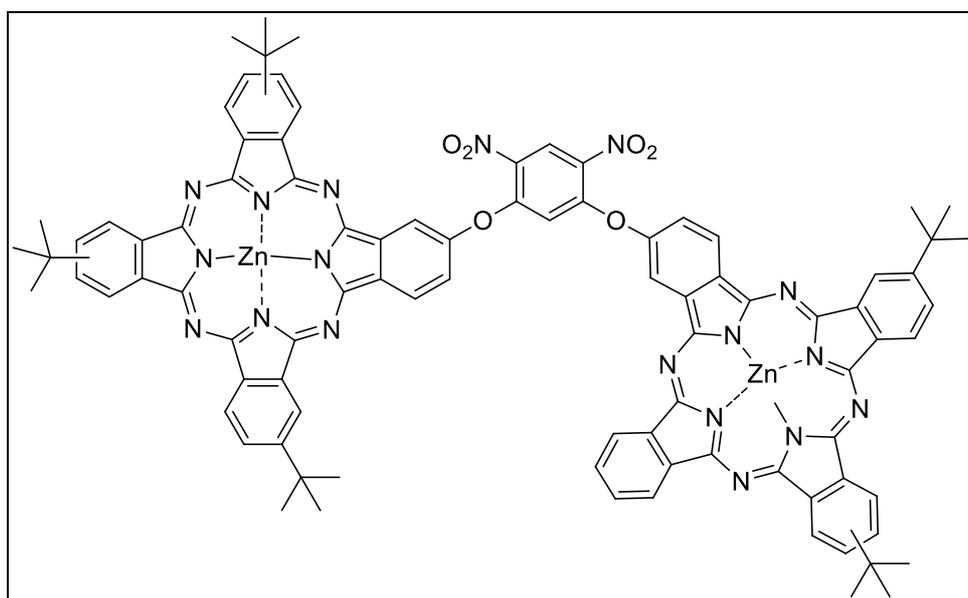
3.31 Preparation of hydroxyphthalocyanine **55**¹⁹



4-(*Tert*-butyl)phthalonitrile **60** (0.24 g, 1.3 mmol) and 4-((2-methoxyethoxy)methoxy)phthalonitrile **59** (0.1 g, 0.4 mmol) was refluxing in *n*-hexanol (5 mL) for 24 h under an argon atmosphere in the presence of zinc acetate dehydrate (excess) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The resulting green crud product was the purified by column chromatography eluting with hexan/DCM to give the

titled product as green-blue product in (0.09, 24 %); MALDI-MS: 850 and this used directly without further purification. The MEMO-Pc **61** was then dissolved in 1-butanol in presence of pyridinium *p*-toluenesulfonate (0.165g, 0.7 mmol). This mixture was refluxed under argon atmosphere for 5 h. After cooling to rt, the resulting precipitate was filtered off and washed with methanol. The resulting green crud product was purified by column chromatography eluting with pet. ether / DCM to give the titled product as green-blue product in (0.04 g, 47 %). ^1H NMR (500 MHz, CDCl_3) δ 8.28 – 8.20 (m, 9H), 8.28 – 8.20 (m, 3H), 1.85 (s, 27H); MALDI-MS 760 (cluster, $M^+ = 761$, isotopic distribution pattern corresponds to theoretical prediction). These data are consistent with literature values.

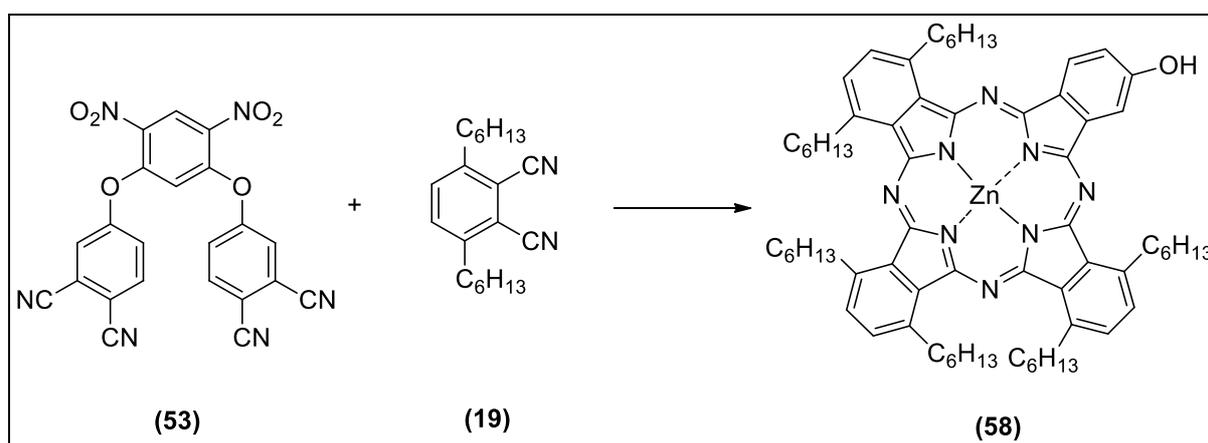
3.32 Preparation of dimer **57**



To a solution of hydroxy-phthalocyanine **55** (0.04 g, 0.05 mmol) in acetone (5 mL) was added K_2CO_3 (0.04 g, 0.3 mmol) under a nitrogen atmosphere. After stirring at RT for 30 min, 1,5-difluoro-2,4-dinitrobenzene **46** (0.005g, 0.02mmol) was added and the mixture was heated to 50 °C for overnight. The reaction mixture was dissolved in DCM and washed with water

dried (MgSO₄) and concentrated under reduced pressure. The product was purified by column chromatography over silica gel to give the titled product (0.015 g, 37 %). Mp above 300 °C; UV-Vis (THF)/nm: 669, 633, 349; IR (KBr, cm⁻¹): 3392, 2958, 1718, 1442, 1344, 1367; MALDI-MS 1689 (cluster, M⁺ = 1690, isotopic distribution pattern corresponds to theoretical prediction). ¹H & ¹³C NMR could not be obtained due to the intensive aggregations, diffrents solvents and conditions had been used.

3.33 Synthesis of 1,4,8,11,15,18-hexakis (hexyl)-23-hydroxyphthalocyaninatozinc(II) (58)



3,6-Dihexylphthalonitrile **19** (0.2 g, 0.7 mmol) and 4,4'-((4,6-dinitro-1,3-phenylene)bis(oxy))diphthalonitrile **53** (0.05 g, 0.11 mmol) was refluxing in *n*-hexanol (5 mL) for 24 h under an argon atmosphere in the presence of zinc acetate dehydrate (excess) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The resulting green crud product was the purified by column chromatography eluting with toluene/ EtOAc to give the titled product as green-blue product in (0.015, 12 %). Mp > 300 °C; ¹H NMR (500 MHz, THF) δ 9.31 (1H, s), 9.15 (1H, d, *J* = 8.0 Hz), 8.72 (1H, s), 7.87 (2H, s), 7.83 – 7.76 (4H, m), 7.58 (1H, d, *J* = 6.5 Hz), 4.52 (12H, m), 2.31- 2.18 (6H, m), 1.64 (6H, s), 1.41 – 1.20 (36H, m), 0.97 – 0.77 (18H, m); ¹³C NMR Could not be obtained due to the intensive aggregations;

MALDI-MS 1196 (cluster, $M^+ = 1197$, isotopic distribution pattern corresponds to theoretical prediction).

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APPENDIX

Crystal data and structure refinement for 1,5-(NO₂)₂,2,4-(OC₆H₃(CN)₂-3',4')₂-C₆H₂

Identification code	ateyah2		
Elemental formula	C22 H8 N6 O6		
Formula weight	452.34		
Crystal system, space group	Monoclinic, P2 ₁ /n		
Unit cell dimensions	a = 15.3939 (6) Å	α = 90 °	
	b = 7.3053 (3) Å	β =	
91.567 (3) °			
	c = 16.8282 (6) Å	γ = 90 °	
Volume	1891.74 (13) Å ³		
Z, Calculated density	4, 1.588 Mg/m ³		
F(000)	920		
Absorption coefficient	0.121 mm ⁻¹		
Temperature	140 (1) K		
Wavelength	0.71073 Å		
Crystal colour, shape	pale yellow plate		
Crystal size	0.08 x 0.03 x 0.010 mm		
Crystal mounting:	on a glass fibre, in oil, fixed in cold N ₂ stream		
On the diffractometer:			
Theta range for data collection	3.04 to 25.00 °		
Limiting indices	-18<=h<=18, -8<=k<=8, -20<=l<=20		
Completeness to theta = 25.00	99.9 %		
Absorption correction equivalents	Semi-empirical from		
Max. and min. transmission	1.00000 and 0.96254		
Reflections collected (not including absences)	23318		
No. of unique reflections	3333 [R(int) for		
equivalents = 0.085]			

No. of 'observed' reflections ($I > 2\sigma_I$) 2315

Structure determined by: direct methods, in SHELXS

Refinement: Full-matrix least-squares on F^2 , in SHELXL

Data / restraints / parameters 3333 / 0 / 339

Goodness-of-fit on F^2 1.039

Final R indices ('observed' data) $R_1 = 0.051$, $wR_2 = 0.078$

Final R indices (all data) $R_1 = 0.088$, $wR_2 = 0.087$

Reflections weighted:
 $w = [\sigma^2(F_o^2) + (0.0277P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2) / 3$

Largest diff. peak and hole 0.20 and -0.21 e. \AA^{-3}

Location of largest difference peak near N(631)

Table 1. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. E.s.ds are in parentheses.

	x	y	z	$U(\text{eq})$
C(1)	57921(15)	80960(30)	20185(14)	199(6)
C(2)	53242(14)	70430(30)	14712(13)	193(5)
C(3)	53716(15)	51420(30)	15288(13)	190(6)
C(4)	59101(15)	43390(30)	20993(14)	212(6)
C(5)	63902(15)	54040(30)	26216(13)	189(6)
C(6)	63195(14)	73110(30)	26008(13)	182(5)
O(2)	48760(10)	79270(20)	8682(9)	232(4)
C(21)	40277(15)	84420(30)	9919(14)	196(6)
C(22)	36351(16)	81230(30)	17038(15)	200(6)
C(23)	27956(15)	87490(30)	18027(13)	198(6)
C(24)	23554(15)	96720(30)	11806(14)	202(6)
C(25)	27591(17)	99350(30)	4637(15)	241(6)
C(26)	35984(16)	93300(30)	3719(15)	220(6)
C(231)	23842(15)	85750(30)	25549(14)	227(6)
N(231)	20400(14)	84930(30)	31519(13)	314(5)
C(241)	15022(17)	103470(30)	13437(14)	237(6)
N(241)	8405(14)	108520(30)	15378(13)	352(6)
N(3)	48709(13)	39120(30)	9940(12)	267(5)
O(31)	42934(11)	45680(20)	5668(10)	315(4)
O(32)	50654(12)	22850(20)	10111(10)	379(5)
N(5)	70039(13)	44320(30)	31619(12)	261(5)
O(51)	75237(12)	53490(20)	35598(10)	360(5)
O(52)	69727(11)	27530(20)	31646(10)	344(5)

O (6)	67834 (10)	84920 (20)	30921 (9)	239 (4)
C (61)	65818 (15)	85760 (30)	38875 (13)	195 (6)
C (62)	58248 (15)	78330 (30)	41665 (14)	196 (6)
C (63)	56391 (14)	80280 (30)	49640 (13)	178 (5)
C (64)	62098 (15)	89880 (30)	54776 (13)	197 (6)
C (65)	69742 (16)	97010 (30)	51824 (15)	224 (6)
C (66)	71587 (16)	94970 (30)	43899 (14)	217 (6)
C (631)	48516 (16)	72390 (30)	52597 (13)	215 (6)
N (631)	42304 (14)	65950 (30)	54914 (12)	308 (5)
C (641)	59660 (16)	92050 (30)	62918 (16)	250 (6)
N (641)	57146 (15)	93360 (30)	69278 (13)	365 (6)

Table 2. Molecular dimensions. Bond lengths are in Ångstroms, angles in degrees. E.s.ds are in parentheses.

C (1) -C (6)	1.380 (3)	C (25) -H (25)	0.96 (2)
C (1) -C (2)	1.387 (3)	C (26) -H (26)	0.96 (2)
C (1) -H (1)	0.963 (19)	C (231) -N (231)	1.150 (3)
C (2) -O (2)	1.373 (3)	C (241) -N (241)	1.139 (3)
C (2) -C (3)	1.394 (3)	N (3) -O (31)	1.226 (2)
C (3) -C (4)	1.382 (3)	N (3) -O (32)	1.226 (2)
C (3) -N (3)	1.474 (3)	N (5) -O (52)	1.227 (2)
C (4) -C (5)	1.374 (3)	N (5) -O (51)	1.228 (2)
C (4) -H (4)	0.95 (2)	O (6) -C (61)	1.384 (3)
C (5) -C (6)	1.397 (3)	C (61) -C (62)	1.379 (3)
C (5) -N (5)	1.476 (3)	C (61) -C (66)	1.384 (3)
C (6) -O (6)	1.381 (3)	C (62) -C (63)	1.387 (3)
O (2) -C (21)	1.380 (3)	C (62) -H (62)	0.95 (2)
C (21) -C (22)	1.376 (3)	C (63) -C (64)	1.403 (3)
C (21) -C (26)	1.381 (3)	C (63) -C (631)	1.443 (3)
C (22) -C (23)	1.385 (3)	C (64) -C (65)	1.391 (3)
C (22) -H (22)	0.92 (2)	C (64) -C (641)	1.439 (3)
C (23) -C (24)	1.404 (3)	C (65) -C (66)	1.379 (3)
C (23) -C (231)	1.436 (3)	C (65) -H (65)	0.94 (2)
C (24) -C (25)	1.386 (3)	C (66) -H (66)	0.95 (2)
C (24) -C (241)	1.437 (3)	C (631) -N (631)	1.144 (3)
C (25) -C (26)	1.378 (3)	C (641) -N (641)	1.152 (3)
C (6) -C (1) -C (2)	121.7 (2)	C (25) -C (24) -C (23)	119.8 (2)
C (6) -C (1) -H (1)	118.1 (12)	C (25) -C (24) -C (241)	123.6 (2)
C (2) -C (1) -H (1)	120.2 (12)	C (23) -C (24) -C (241)	116.6 (2)
O (2) -C (2) -C (1)	118.1 (2)	C (26) -C (25) -C (24)	119.8 (2)
O (2) -C (2) -C (3)	123.0 (2)	C (26) -C (25) -H (25)	118.2 (13)
C (1) -C (2) -C (3)	118.8 (2)	C (24) -C (25) -H (25)	122.0 (13)
C (4) -C (3) -C (2)	120.0 (2)	C (25) -C (26) -C (21)	119.8 (2)
C (4) -C (3) -N (3)	117.4 (2)	C (25) -C (26) -H (26)	121.0 (13)
C (2) -C (3) -N (3)	122.6 (2)	C (21) -C (26) -H (26)	119.2 (13)
C (5) -C (4) -C (3)	120.4 (2)	N (231) -C (231) -C (23)	177.6 (3)
C (5) -C (4) -H (4)	121.1 (14)	N (241) -C (241) -C (24)	174.3 (3)
C (3) -C (4) -H (4)	118.5 (14)	O (31) -N (3) -O (32)	124.5 (2)
C (4) -C (5) -C (6)	120.5 (2)	O (31) -N (3) -C (3)	118.6 (2)
C (4) -C (5) -N (5)	116.5 (2)	O (32) -N (3) -C (3)	117.0 (2)
C (6) -C (5) -N (5)	122.9 (2)	O (52) -N (5) -O (51)	124.6 (2)
C (1) -C (6) -O (6)	116.7 (2)	O (52) -N (5) -C (5)	117.3 (2)
C (1) -C (6) -C (5)	118.4 (2)	O (51) -N (5) -C (5)	118.0 (2)
O (6) -C (6) -C (5)	124.7 (2)	C (6) -O (6) -C (61)	118.73 (17)
C (2) -O (2) -C (21)	118.38 (17)	C (62) -C (61) -O (6)	121.7 (2)
C (22) -C (21) -O (2)	121.7 (2)	C (62) -C (61) -C (66)	121.2 (2)
C (22) -C (21) -C (26)	121.6 (2)	O (6) -C (61) -C (66)	117.1 (2)
O (2) -C (21) -C (26)	116.7 (2)	C (61) -C (62) -C (63)	119.1 (2)
C (21) -C (22) -C (23)	118.8 (2)	C (61) -C (62) -H (62)	122.7 (13)
C (21) -C (22) -H (22)	122.4 (13)	C (63) -C (62) -H (62)	118.1 (13)
C (23) -C (22) -H (22)	118.8 (13)	C (62) -C (63) -C (64)	120.4 (2)
C (22) -C (23) -C (24)	120.1 (2)	C (62) -C (63) -C (631)	119.3 (2)
C (22) -C (23) -C (231)	120.8 (2)	C (64) -C (63) -C (631)	120.3 (2)
C (24) -C (23) -C (231)	118.9 (2)	C (65) -C (64) -C (63)	119.2 (2)

C(65)-C(64)-C(641)	122.9(2)	C(65)-C(66)-C(61)	119.8(2)
C(63)-C(64)-C(641)	117.8(2)	C(65)-C(66)-H(66)	120.5(12)
C(66)-C(65)-C(64)	120.2(2)	C(61)-C(66)-H(66)	119.7(12)
C(66)-C(65)-H(65)	119.1(13)	N(631)-C(631)-C(63)	179.3(3)
C(64)-C(65)-H(65)	120.7(13)	N(641)-C(641)-C(64)	175.3(3)

Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for the expression:

$$\exp \{-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12})\}$$

E.s.ds are in parentheses.

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(1)	199(14)	167(13)	235(15)	1(11)	63(11)	2(11)
C(2)	163(13)	246(14)	172(14)	31(11)	52(11)	29(11)
C(3)	175(13)	239(14)	159(14)	-43(11)	52(11)	-35(11)
C(4)	221(14)	208(14)	210(15)	-3(11)	62(12)	40(12)
C(5)	154(13)	254(14)	163(14)	45(11)	63(11)	41(11)
C(6)	150(13)	222(13)	177(14)	-3(11)	57(11)	-37(11)
O(2)	210(9)	298(10)	190(10)	37(7)	20(8)	55(8)
C(21)	175(13)	192(13)	218(14)	-36(11)	-16(11)	24(11)
C(22)	195(14)	212(13)	191(15)	13(11)	-33(12)	32(11)
C(23)	214(14)	176(13)	203(14)	-19(11)	-4(11)	-8(11)
C(24)	185(14)	205(13)	215(15)	-47(11)	-20(12)	24(11)
C(25)	261(16)	238(14)	221(16)	-1(12)	-44(13)	39(12)
C(26)	256(15)	235(14)	171(15)	0(11)	15(12)	-3(12)
C(231)	174(14)	257(14)	246(16)	-15(12)	-34(12)	33(11)
N(231)	282(13)	380(14)	281(14)	5(11)	36(11)	61(11)
C(241)	245(15)	262(14)	199(14)	-23(11)	-53(12)	31(13)
N(241)	265(14)	459(15)	330(14)	-59(11)	-55(11)	111(12)
N(3)	281(13)	296(13)	229(13)	-45(10)	72(11)	-61(11)
O(31)	249(10)	413(11)	281(11)	-41(9)	-34(9)	-25(9)
O(32)	537(13)	215(10)	383(12)	-78(8)	18(10)	-3(10)
N(5)	235(13)	377(14)	177(13)	45(10)	100(10)	109(11)
O(51)	295(11)	513(12)	267(11)	-69(9)	-70(9)	88(10)
O(52)	370(11)	319(11)	348(11)	131(9)	108(9)	130(9)
O(6)	232(10)	312(10)	173(9)	-11(8)	30(8)	-89(8)
C(61)	204(14)	190(13)	191(14)	-8(11)	6(11)	8(11)
C(62)	160(14)	205(13)	223(15)	-12(11)	-3(12)	-12(11)
C(63)	157(13)	170(13)	207(14)	23(10)	20(11)	15(11)
C(64)	234(14)	163(13)	193(14)	1(10)	-2(11)	37(11)
C(65)	228(15)	215(14)	226(15)	-25(11)	-49(12)	-12(12)
C(66)	171(14)	226(14)	255(16)	34(11)	20(12)	-32(12)
C(631)	262(15)	198(14)	186(14)	-3(11)	34(12)	33(12)
N(631)	303(14)	312(13)	313(14)	-1(10)	89(11)	2(11)
C(641)	251(15)	218(14)	276(17)	-28(12)	-47(13)	20(12)
N(641)	411(15)	421(14)	265(14)	-73(11)	20(12)	-23(12)

Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). All hydrogen atoms were located in a difference map and were refined freely.

	x	y	z	U(iso)
H(1)	5752(13)	9410(30)	2002(11)	16(6)
H(22)	3917(13)	7540(30)	2123(12)	22(6)
H(25)	2473(14)	10550(30)	23(13)	23(6)
H(26)	3892(14)	9520(30)	-117(13)	17(6)
H(4)	5943(15)	3040(30)	2118(13)	35(7)
H(62)	5419(14)	7190(30)	3833(12)	23(6)
H(65)	7371(14)	10320(30)	5518(12)	17(6)
H(66)	7688(13)	9950(20)	4190(11)	10(6)

Table 5. Torsion angles, in degrees. E.s.ds are in parentheses.

C(6)-C(1)-C(2)-O(2)	-174.3(2)	C(22)-C(23)-C(231)-N(231)	146(6)
C(6)-C(1)-C(2)-C(3)	1.9(3)	C(24)-C(23)-C(231)-N(231)	-30(6)
O(2)-C(2)-C(3)-C(4)	172.9(2)	C(25)-C(24)-C(241)-N(241)	-166(3)
C(1)-C(2)-C(3)-C(4)	-3.1(3)	C(23)-C(24)-C(241)-N(241)	12(3)
O(2)-C(2)-C(3)-N(3)	-6.5(3)	C(4)-C(3)-N(3)-O(31)	169.0(2)
C(1)-C(2)-C(3)-N(3)	177.5(2)	C(2)-C(3)-N(3)-O(31)	-11.7(3)
C(2)-C(3)-C(4)-C(5)	1.1(3)	C(4)-C(3)-N(3)-O(32)	-10.9(3)
N(3)-C(3)-C(4)-C(5)	-179.5(2)	C(2)-C(3)-N(3)-O(32)	168.5(2)
C(3)-C(4)-C(5)-C(6)	2.1(3)	C(4)-C(5)-N(5)-O(52)	-7.7(3)
C(3)-C(4)-C(5)-N(5)	-174.7(2)	C(6)-C(5)-N(5)-O(52)	175.6(2)
C(2)-C(1)-C(6)-O(6)	177.3(2)	C(4)-C(5)-N(5)-O(51)	170.4(2)
C(2)-C(1)-C(6)-C(5)	1.3(3)	C(6)-C(5)-N(5)-O(51)	-6.4(3)
C(4)-C(5)-C(6)-C(1)	-3.3(3)	C(1)-C(6)-O(6)-C(61)	113.2(2)
N(5)-C(5)-C(6)-C(1)	173.3(2)	C(5)-C(6)-O(6)-C(61)	-71.0(3)
C(4)-C(5)-C(6)-O(6)	-179.0(2)	C(6)-O(6)-C(61)-C(62)	-14.2(3)
N(5)-C(5)-C(6)-O(6)	-2.4(3)	C(6)-O(6)-C(61)-C(66)	168.0(2)
C(1)-C(2)-O(2)-C(21)	-90.1(2)	O(6)-C(61)-C(62)-C(63)	-177.2(2)
C(3)-C(2)-O(2)-C(21)	93.9(3)	C(66)-C(61)-C(62)-C(63)	0.5(3)
C(2)-O(2)-C(21)-C(22)	1.3(3)	C(61)-C(62)-C(63)-C(64)	0.7(3)
C(2)-O(2)-C(21)-C(26)	180.0(2)	C(61)-C(62)-C(63)-C(631)	-179.5(2)
O(2)-C(21)-C(22)-C(23)		C(62)-C(63)-C(64)-C(65)	-1.6(3)
177.05(19)		C(631)-C(63)-C(64)-C(65)	178.6(2)
C(26)-C(21)-C(22)-C(23)	-1.5(3)	C(62)-C(63)-C(64)-C(641)	177.7(2)
C(21)-C(22)-C(23)-C(24)	0.7(3)	C(631)-C(63)-C(64)-C(641)	-2.1(3)
C(21)-C(22)-C(23)-C(231)	-175.1(2)	C(63)-C(64)-C(65)-C(66)	1.3(3)
C(22)-C(23)-C(24)-C(25)	0.8(3)	C(641)-C(64)-C(65)-C(66)	-177.9(2)
C(231)-C(23)-C(24)-C(25)	176.7(2)	C(64)-C(65)-C(66)-C(61)	-0.1(4)
C(22)-C(23)-C(24)-C(241)	-177.3(2)	C(62)-C(61)-C(66)-C(65)	-0.8(4)
C(231)-C(23)-C(24)-C(241)	-1.4(3)	O(6)-C(61)-C(66)-C(65)	177.0(2)
C(23)-C(24)-C(25)-C(26)	-1.6(3)	C(62)-C(63)-C(631)-N(631)	59(22)
C(241)-C(24)-C(25)-C(26)	176.4(2)	C(64)-C(63)-C(631)-N(631)	-121(22)
C(24)-C(25)-C(26)-C(21)	0.9(4)	C(65)-C(64)-C(641)-N(641)	168(3)
C(22)-C(21)-C(26)-C(25)	0.7(4)	C(63)-C(64)-C(641)-N(641)	-11(3)
O(2)-C(21)-C(26)-C(25)	-177.9(2)		

Crystal structure analysis of 1,5-(NO₂)₂,2,4-(OC₆H₃(CN)₂-3,4)₂-C₆H₂

Crystal data: C₂₂H₈N₆O₆, M = 452.34. Monoclinic, space group P21/n (equiv. to no. 14), a = 15.3939(6), b = 7.3053(3), c = 16.8282(6) Å, β = 91.567(3) °, V = 1891.74(13) Å³. Z = 4, D_c = 1.588 g cm⁻³, F(000) = 920, T = 140(1) K, μ(Mo-Kα) = 1.2 cm⁻¹, λ(Mo-Kα) = 0.71069 Å.

Crystals are clear, pale yellow plates. One, *ca* 0.010 x 0.03 x 0.08 mm, was mounted in oil on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to θ_{max} = 25°, was 23318 of which 3333 were unique (R_{int} = 0.085); 2315 were 'observed' with I > 2σ_I.

Data were processed using the CrysAlisPro-CCD and -RED (1) programs. The structure was determined by the direct methods routines in the SHELXS program (2A) and refined by full-matrix least-squares methods, on F²'s, in SHELXL (2B). The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were located in a difference map and were refined freely. At the conclusion of the refinement, wR₂ = 0.087 and R₁ = 0.088 (2B) for all 3333 reflections weighted w = [σ²(F_o²) + (0.0277P)²]⁻¹ with P = (F_o² + 2F_c²)/3; for the 'observed' data only, R₁ = 0.051.

In the final difference map, the highest peak (*ca* 0.2 eÅ⁻³) was near N(631).

Scattering factors for neutral atoms were taken from reference (3). Computer programs used in this analysis have been noted above, and were run through WinGX (4) on a Dell Optiplex GX620 PC at the University of East Anglia.

References

- (1) Programs CrysAlisPro, Oxford Diffraction Ltd., Abingdon, UK (2010).
- (2) G. M. Sheldrick, SHELX-97 – Programs for crystal structure determination (SHELXS) and refinement (SHELXL), *Acta Cryst.* (2008) **A64**, 112-122.
- (3) '*International Tables for X-ray Crystallography*', Kluwer Academic Publishers, Dordrecht (1992). Vol. C, pp. 500, 219 and 193.
- (4) L. J. Farrugia, *J. Appl. Cryst.*, (1999) **32**, 837-838 .

Legends for Figures

Figure 1. Views of a molecule of 1,5-(NO₂)₂,2,4-(OC₆H₃(CN)₂-3,4)₂-C₆H₂, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Notes on the structure

The two nitro group planes are rotated about the C-N bonds by 10.93(14) and 9.05(14) °, and the normals to the phenyl rings of C(21-26) and C(61-66) are 85.82(7) and 77.29(7) ° from that of the central C(1-6) ring.