Synthetic Studies Towards Multichromophore Arrays

Tahani Almutairi

This thesis is submitted in partial fulfilment of the requirements of the degree of Doctor of Philosophy at the University of East Anglia

2015

©This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognise that its copyright rests with the author and that no quotation from the thesis, nor any information derived therefrom, may be published without the author’s prior written consent.
DECLARATION

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

Tahani Almutairi
This thesis is dedicated

To my beloved

Parents, sister and brothers

Abdulrhman

Sultan
The overall aim of this project was to investigate strategies for linking macrocyclic chromophores to form arrays. Firstly the aim was to link a porphyrin to a triphenylene through phenyl alkynes. Interestingly, this study discovered a mesogenic dibromtetramethoxy triphenylene – the least heavily substituted triphenylene liquid crystal reported to date. The results of this investigation, however, show that, in general, it was challenging to force the reaction between porphyrin and triphenylene components to form acetylene links. Dimerization of the acetylene components was observed as the predominant reaction in all cases. However, it was possible to isolate a porphyrin-triphenylene dyad structure.

The second aim of this study was to investigate the synthesis of novel chromophore dyads and triads 102, 104 and 134 which are based on porphyrin and tetrabenzotriazaporphyrin (TBTAP) components. The first aim was to synthesise porphyrin–phenyl-TBTAP 102. A precursor porphyrin bearing aminoisooindoline functionality was successfully prepared. However, it could not be converted to either the porphyrin–phenyl-TBTAP 102 dyad or porphyrin-azaBODIPY-porphyrin triad 134. On the other hand, the suggested strategy towards the synthesis of porphyrin-TBTAP dyads linked through flexible chains (104) remains promising. Magnesium TBTAB-OH 135 was synthesised as one important reactant. However, the unfortunate choice of bromododecyloxyporphyrin 141, meant the synthesis of the desired dyad could not be achieved within this project because it could not be separated from excess dibromododecane. However, simple modification of the strategy (e.g using bromododecanol) will allow the compounds to be prepared in the future.
ACKNOWLEDGMENTS

First of all, I would like to express my deepest gratitude and appreciation to my supervisor Prof. Andrew Cammidge for the continuous help, support, patience and guidance. This thesis would not have been possible without his guidance and supporting during all the time of research and writing up of this thesis.

I would like to show my gratitude to Dr Maria Munoz-Herranz as a second supervisor and her group members for their cooperation and ease access for their facilities.

I would like to thank Dr Alejandro Díaz Moscoso, Dr Isabelle Chambrier and Dr Teresa Quirós for their valuable help. I would also like to thank all previous and current colleagues and friends from lab 3.17, in particularly, Dr Hemant Gopee, Dr Daniel, Dr Nuha, Dr Rebecca, Dr Sonia, Xiao, Rhoda, Nora and Ross. My special thanks are extended to all member in organic chemistry department.

I would like to acknowledge the help and advice provided by Dr Ateyatallah Aljuhani. I would like to thank Faizah for her support and valuable friendship.

I am very grateful for my parents, sister and brothers for their boundless love, engorgement and support. I would also to thank Abdulrhman and Sultan, my husband and son, who’s your supporting and understanding all the time give me the strength and the motivation to complete this journey.

Finally, I am grateful to the King Saud University for giving me a chance to study abroad.
# TABLE OF CONTENTS

Declaration .......................................................................................................................... I

Abstract ................................................................................................................................ III

Acknowledgments ................................................................................................................ IV

Table of figures ................................................................................................................... IX

Table of Schemes ............................................................................................................... XII

List of abbreviations ......................................................................................................... XV

1 Introduction ..................................................................................................................... 2

1.1 Early history of porphyrins ......................................................................................... 2

1.2 Structure of Porphyrin ............................................................................................... 2

1.3 Spectroscopic properties of porphyrin ................................................................. 4

1.3.1 NMR spectroscopy ............................................................................................... 4

1.3.2 UV-Vis spectroscopy ........................................................................................... 4

1.4 Synthesis of Porphyrins ........................................................................................ 5

1.4.1 Rothmund method ............................................................................................... 5

1.4.2 Adler-Longo method .......................................................................................... 6

1.4.3 Lindsey method ................................................................................................... 7

1.5 Applications of porphyrins .................................................................................... 7

1.6 Multiple porphyrin arrays .................................................................................... 13

1.6.1 Linear porphyrin arrays ..................................................................................... 13

1.6.1.1 Directly meso–meso linked linear porphyrin arrays ...................................... 13

1.6.1.2 Meso-meso ethyne linked linear porphyrin arrays ...................................... 16

1.6.1.3 Meso-meso ethene linked linear porphyrin arrays ..................................... 18

1.6.1.4 Hetero arrays of porphyrins ....................................................................... 19

1.6.2 Cyclic (ring) porphyrin arrays .......................................................................... 20
1.6.2.1 Structure of bacteria.................................................................20
1.6.2.2 Directly meso-meso linked porphyrin ring (cycle)..........................20
1.6.2.3 1, 3-Phenylene Linked Cyclic Porphyrin.....................................22
1.6.2.4 Meso-meso aromatic heterocycle bridged porphyrin ring (cycle).......22
1.6.2.5 Ethynyl and Butadiene linked porphyrin rings..............................25
1.6.2.6 Benzene-centred cyclic porphyrin..............................................31
1.7 Triphenylene and triphenylene-porphyrin conjugates...........................32
1.8 References ..........................................................................................34
2 Results and Discussion ...........................................................................38
2.1 Porphyrin and triphenylene Arrays .....................................................38
  2.1.1 Aims ...............................................................................................38
  2.1.2 Triphenylenes ...............................................................................40
  2.1.3 Using palladium catalysis in synthesis ...........................................42
    2.1.3.1 The Suzuki cross-coupling reaction .........................................42
    2.1.3.2 Sonogashira cross-coupling .....................................................43
  2.1.4 Synthesis of porphyrin-triphenylene-porphyrin triad 75 ..................45
    2.1.4.1 Synthesis of triphenylene component ......................................46
    2.1.4.2 Synthesis of porphyrin component ..........................................52
  2.1.5 Synthesis of triad 92 .....................................................................62
    2.1.5.1 Synthesis of porphyrin component ..........................................63
  2.1.6 Conclusion ....................................................................................71
2.2 Porphyrin and tetrabenzoazaporphyrin arrays .......................................72
  2.2.1 Background and aims ....................................................................72
  2.2.2 Tetrabenzoazaporphyrins (TBTAPs) ..............................................73
  2.2.3 Synthesis of TPP-phenyl-TBTAP dyad 102 ....................................78
    2.2.3.1 Synthesis of Aminoisoindoline porphyrin 103 ..........................79
    2.2.3.2 Attempted synthesis of TPP-phenyl-TBTAP 102 ......................81
2.2.4 Bis (porphyrin)-aza-dibenzo-BODIPY (TPP$_2$-aza-dibenzo-BODIPY) ....82
2.2.4.1 Background and aim ........................................82
2.2.4.2 Attempted synthesis of TPP$_2$-aza-dibenzo-DIPY 135 ....84
2.2.5 Synthesis Porphyrin-TBTAP Dyads linked through flexible chains ..........86
2.2.5.1 Synthesis of TBTAP component ................................87
2.2.5.2 Synthesis of porphyrin component ..........................92
2.2.6 Conclusion ................................................................93
2.2.7 References ................................................................94

3.1 Experimental Methods ..........................................................97
3.1 General information ..............................................................97
3.2 Synthesis of triphenylene components and their precursors .................98
3.2.1 Synthesis of 1, 2-dibromo-4, 5-dimethoxybenzene 79 ..................98
3.2.2 Synthesis of 4-methoxyphenylboronic acid 82 ..........................98
3.2.3 Synthesis of tetramethoxyterphenyl 83 ..................................99
3.2.4 Synthesis of tetramethoxytriphenylene 84 ...............................100
3.2.5 Synthesis of 2,7-Dibromo-3,6,10,11-Tetramethoxytriphenylene 76 ......101
3.3 Synthesis of porphyrin components and their precursors ......................102
3.3.1 Synthesis of 4-(3-methyl-3-hydroxy-1-butyn-1-yl) benzaldehyde 87 ....102
3.3.2 Synthesis of unsymmetrically substituted porphyrin 88 .................102
3.3.3 Synthesis of zinc porphyrin 89 ............................................103
3.3.4 Synthesis of zinc porphyrin 77 .............................................104
3.3.5 Synthesis of porphyrin 96 ..................................................104
3.3.6 Synthesis of zinc porphyrin 98 .............................................105
3.3.7 Synthesis of porphyrin triflate 97 .........................................105
3.3.8 Synthesis of zinc porphyrin triflate 93 .....................................106
3.3.9 Synthesis of porphyrin 141 ...............................................107
3.4 Synthesis of porphyrin triphenylene dyad 90 ..................................108
3.5 Synthesis of o-Bromobenzamidine hydrochloride 127 ........................................ 109

3.6 Synthesis of aminoisoindoline porphyrin 103 ................................................ 110

3.7 Synthesis of TBTAPs and their precursors ...................................................... 111

3.7.1 Synthesis of aminoisoindoline 138 .......................................................... 111

3.7.2 Synthesis of a magnesium TBTAP-OCH$_3$ 139 ........................................ 112

3.7.3 Synthesis of a magnesium TBTAP-OH 135 .............................................. 113

3.8 References .................................................................................................... 114
# Table of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Chlorophyll and haem structures</td>
</tr>
<tr>
<td>1.2</td>
<td>Macrocyclic structure of porphyrin</td>
</tr>
<tr>
<td>1.3</td>
<td>IUPAC system of porphyrins</td>
</tr>
<tr>
<td>1.4</td>
<td>$^1$H NMR spectrum of tetraphenylporphyrin 1</td>
</tr>
<tr>
<td>1.5</td>
<td>Typical UV-vis spectrum of tetraphenylporphyrin 1</td>
</tr>
<tr>
<td>1.6</td>
<td>Meso-substituted chlorin</td>
</tr>
<tr>
<td>1.7</td>
<td>Systematic illustration of components and operation of dye sensitized solar cell</td>
</tr>
<tr>
<td>1.8</td>
<td>Different binding modes of porphyrins 5 and 6 onto TiO$_2$ surface</td>
</tr>
<tr>
<td>1.9</td>
<td>Molecular structures of YD0, YD1 and YD2</td>
</tr>
<tr>
<td>1.10</td>
<td>Molecular structure of D-205</td>
</tr>
<tr>
<td>1.11</td>
<td>Molecular structures of SM315 and GY50</td>
</tr>
<tr>
<td>1.12</td>
<td>Examples of ruthenium sensitizers for DSSCs</td>
</tr>
<tr>
<td>1.13</td>
<td>Absorption spectrum of a- porphyrin, b- chlorin, c-phthalocyanine; d-Correlation between the absorption of light by the photosensitisers molecule and the penetration of the light through the tissue</td>
</tr>
<tr>
<td>1.14</td>
<td>Molecular structure of porphyrin isothiocyanates</td>
</tr>
<tr>
<td>1.15</td>
<td>Molecular structure of ATPP-EDTA</td>
</tr>
<tr>
<td>1.16</td>
<td>Directly meso–meso linked linear porphyrin arrays Z$_N$</td>
</tr>
<tr>
<td>1.17</td>
<td>Molecular structure of meso–meso linked porphyrin dimer 13</td>
</tr>
<tr>
<td>1.18</td>
<td>Meso–meso linked porphyrin dimer with mixed meso substituent pattern</td>
</tr>
<tr>
<td>1.19</td>
<td>Meso-meso ethyne linked linear porphyrin arrays</td>
</tr>
<tr>
<td>1.20</td>
<td>Other examples of unsymmetrical alkyne-linked dimers</td>
</tr>
<tr>
<td>1.21</td>
<td>Structure of perylene-bis (porphyrin)-phthalocyanine array</td>
</tr>
<tr>
<td>1.22</td>
<td>Crystal structure of the LH2 complex from Rps.acidophila</td>
</tr>
<tr>
<td>1.23</td>
<td>Structures of CZ4, CZ6, and CZ8 (Ar = 3,5-Di-tert-butylphenyl)</td>
</tr>
<tr>
<td>1.24</td>
<td>Molecular structure of CZ12A, CZ24B</td>
</tr>
<tr>
<td>1.25</td>
<td>Molecular structures of β-2, 6-pyridylene-bridged porphyrin nanorings</td>
</tr>
<tr>
<td>1.26</td>
<td>Molecular structure of cyclic porphyrin hexamer</td>
</tr>
<tr>
<td>1.27</td>
<td>Molecular structures of cylic hexa porphyrin with template</td>
</tr>
<tr>
<td>1.28</td>
<td>Molecular structure of ethynyl-phenyl linked porphyrin</td>
</tr>
</tbody>
</table>
Figure 1.29: Molecular structure of 55........................................................................................................28
Figure 1.30: Molecular structure of cyclic porphyrin octamer 56.................................................................28
Figure 1.31: Molecular structure of linear porphyrin 57 octamer and octadentate ligand 58.........................................................29
Figure 1.32: a-Templated directed synthesis of c-P12, b-Structure of c-p12.T12 ..............................................29
Figure 1.33: Calculated structure of the sandwich complex (c-P12)2·(DABCO)12..............................................30
Figure 1.34: a-Vernier-template synthesis of c-P 12, b- structure of T6 template..............................................30
Figure 1.35: a- Vernier-templated synthesis of the nanorings c-P24, b- 58 template..........................30
Figure 1.36: Columnar hexaalkoxytriphenylenes 68.........................................................................................32
Figure 1.37: Triphenylene core-centered porphyrin hexamers........................................................................32
Figure 1.38: A schematic illustration of organization process. The purple square, yellow wavy line and blue round shapes stand for porphyrin, alkyl chain, and triphenylene units, respectively. The molecular sizes were estimated by DFT calculation....................................................33
Figure 2.1: Cartoon representation of the target molecule.................................................................38
Figure 2.2: Molecular structure of triphenylene............................................................................................39
Figure 2.3: Proposed structures for the model target molecules..............................................................39
Figure 2.4: 1H NMR Spectrum of terphenyl 83 in acetone-d6......................................................................47
Figure 2.5: MALDI-TOF MS spectrum of 83.................................................................................................47
Figure 2.6: 1H NMR of triphenylene 84 in acetone-d6 (* = solvent).............................................................49
Figure 2.7: HRMS (ESI) of triphenylene 84.....................................................................................................49
Figure 2.8: 1H NMR spectrum of triphenylene 76 in acetone-d6 (* = solvent)..............................................50
Figure 2.9: HRMS (ESI) of triphenylene 76....................................................................................................51
Figure 2.10: DSC of triphenylene 76 (heating/cooling rate 20 °C min⁻¹)..............................................................51
Figure 2.11: 1H NMR spectrum of aldehyde 87 in CDCl3 (* = solvent)............................................................52
Figure 2.12: 1H NMR spectrum of porphyrin 88 in CD2Cl2 (* = solvent)....................................................54
Figure 2.13: 1H NMR spectrum of zinc-porphyrin 89 in CD2Cl2 (* = solvent)....................................................55
Figure 2.14: 1H NMR of ethynyl porphyrin 77 in CD2Cl2 (* = solvent).............................................................56
Figure 2.15: MALDI-TOF MS of reaction mixture after 2h 43 min...............................................................58
Figure 2.16: MALDI-TOF MS of reaction mixture after adding more porphyrin 77.....................58
Figure 2.17: Fractions show dyad 90 (top) and dyad 91 (bottom).................................................................59
Figure 2.18: 1H NMR spectrum of dyad 90 in acetone-d6 (* = solvent)....................................................60
Figure 2.19: 1H NMR of dyad 90 in different solvents..............................................................................60
Figure 2.20: MALDI-TOF-MS of dyad 90.......................................................................................................61
Figure 2.21: 1H NMR spectrum of porphyrin 96 in CDCl3 (* = solvent)......................................................64
Figure 2.22: $^1$H NMR spectrum of porphyrin triflate 97 in CDCl$_3$ (* = solvent) ..............65
Figure 2.23: HRMS (ESI) of porphyrin triflate 97. .................................................................65
Figure 2.24: $^1$H NMR spectrum of zinc porphyrin triflate 93 in CDCl$_3$ (* = solvent). .........66
Figure 2.25: HRMS (ESI) of zinc porphyrin triflate 93. .........................................................67
Figure 2.26: Formation of zinc porphyrin triflate 93 accompanied with porphyrin triflate 97. ........................................................................................................................................68
Figure 2.27: MALDI-TOF MS of reaction mixture after adding boronic acid .........................69
Figure 2.28: Molecular structures of potential side products ....................................................69
Figure 2.29: MALDI-TOF MS of reaction mixture after 6 days ..............................................70
Figure 2.30: $^1$H NMR of reaction mixture after slow addition of triphenylene 94 .............71
Figure 2.31: Molecular Structures of Pc, TBP and the hybrid macrocycles .............................72
Figure 2.32: Molecular structures of proposed targets 102-104 ............................................73
Figure 2.33: Molecular structures of diiminoisoindoline 111 and aminoisoiindoline 125 ..77
Figure 2.34: $^1$H NMR of aminoisoiindoline porphyrin 103 in acetone-$d_6$ (* = solvent) ......80
Figure 2.35: HRMS (ESI) of aminoisoiindoline porphyrin 103 .............................................80
Figure 2.36: UV-vis spectra of porphyrin 103 ............................................................................81
Figure 2.37: MALDI-TOF MS of the reaction mixture (showing Pc 131 as a major product). ........................................................................................................................................82
Figure 2.38: Molecular structure of proposed bis (porphyrin)-aza-dibenzo-BODIPY triad 134.................................................................................................................................83
Figure 2.39: MALDI-TOF MS of reaction mixture after 4 h. ......................................................85
Figure 2.40: MALDI-TOF MS of reaction mixture above-after 9 h (top), 15 h (bottom) ......85
Figure 2.41: MALDI-TOF MS of fractions containing starting material porphyrin 103 ....86
Figure 2.42: $^1$H NMR of aminoisoiindoline 138 in CDCl$_3$ (* = solvent). .........................88
Figure 2.43: $^1$H NMR of a magnesium TBTAP-OCH$_3$ 139 in THF-$d_8$. .............................89
Figure 2.44: MALDI-TOF MS of fractions shows the formation of a magnesium TBTAP-OH 135 (top) and metal-free TBTAP-OH 140 (bottom) ..................................................................90
Figure 2.45: $^1$H NMR of a magnesium TBTAP-OH 135 in THF-$d_8$. ..................................91
Figure 2.46: MALDI-TOF MS of porphyrin 141 .................................................................92
Figure 2.47: $^1$H NMR of porphyrin 141 in CDCl$_3$ showing contamination with dibromododecane ..........................................................................................................................93
TABLE OF SCHEMES

Scheme 1.1: Synthesis of meso-substituted porphyrins by the Rothmund method. ..........5
Scheme 1.2: Synthesis of meso-substituted porphyrins by the Adler-Longo method. .........6
Scheme 1.3: Synthesis of meso-substituted porphyrins by Lindsey method. .................7
Scheme 1.4: Synthesis of meso–meso linked linear porphyrin dimer using PIFA or PIDA. .................................................................14
Scheme 1.5: Synthesis of meso–meso linked linear porphyrin arrays. .........................14
Scheme 1.6: Synthesis of meso–meso linked linear porphyrin arrays using Suzuki coupling. ................................................................................................................15
Scheme 1.7: Synthesis of asymmetrical alkyne-linked dimers........................................16
Scheme 1.8: Synthesis of linear trimers by copper-free Sonogashira coupling...............17
Scheme 1.9: Synthesis of meso-ethyne-bridged diporphyrin (Ar = 3, 5-di-tert-butylphenyl). .................................................................................................................................18
Scheme 1.10: Synthesis of meso-meso ethene linked linear porphyrin dimers. .............19
Scheme 1.11: Synthesis of meso-meso directly linked porphyrin rings (Ar =3,5-Di-tert- butylphenyl). .................................................................................................................................21
Scheme 1.12: Suzuki-Miyaura cross-coupling reaction for pyrrole-bridged cyclic porphyrin. .................................................................................................................................23
Scheme 1.13: Suzuki-Miyaura cross-coupling reaction for thiophenylene-bridged cyclic porphyrin. .................................................................................................................................24
Scheme 1.14: Synthesis of benzene-centered cyclic porphyrin hexamers.......................31
Scheme 1.15: Synthesis of hexakis porphyrinato benzenes 63......................................31
Scheme 2.1: Different routes to the triphenylene core. Black lines indicate the structures of the key intermediates and red lines represent the bonds or fragments that become part of the triphenylene in the final stage of the synthesis. .........................................................40
Scheme 2.2: Synthesis of disubstituted triphenylene 72 via oxidative cyclisation..........41
Scheme 2.3: Synthesis of tetrasubstituted triphenylene 74 via photocyclization ..........41
Scheme 2.4: General Suzuki Coupling. ........................................................................42
Scheme 2.5: Mechanism of Suzuki cross coupling reaction......................................43
Scheme 2.6: General Sonogashira coupling..................................................................43
Scheme 2.7: Mechanism of Sonogashira cross coupling reaction.............................44
Scheme 2.8: Mechanism of copper-free Sonogashira cross coupling reaction............45
Scheme 2.9: Retrosynthesis of porphyrin-triphenylene-porphyrin triad 75. ..........................46
Scheme 2.10: Synthesis of terphenyl 83. ..................................................................................46
Scheme 2.11: Synthesis of triphenylene 84. ..............................................................................48
Scheme 2.12: One possible mechanism of cyclisation of terphenyl 83 using ferric chloride. .........................................................................................................................48
Scheme 2.13: Synthesis of triphenylene 76. .............................................................................50
Scheme 2.14: Synthesis of aldehyde 87 ......................................................................................52
Scheme 2.15: Synthesis of porphyrin 88. .....................................................................................53
Scheme 2.16: Synthesis of zinc porphyrin 89. ............................................................................54
Scheme 2.17: Synthesis of ethynyl porphyrin 77. ......................................................................55
Scheme 2.18: Deprotection of the acetylene .............................................................................56
Scheme 2.19: Retrosynthesis of triad 75. ...................................................................................57
Scheme 2.20: The summary of the reaction between triphenylene 76 and porphyrin 77 ........................................62
Scheme 2.21: Retrosynthesis of triad 92. ...................................................................................63
Scheme 2.22: Synthesis of porphyrin 96. ...................................................................................63
Scheme 2.23: Synthesis of porphyrin triflate 97. ......................................................................64
Scheme 2.24: Synthesis of zinc porphyrin triflate 93. .................................................................66
Scheme 2.25: Formation of porphyrin triflate 97 as a side product ................................ .......67
Scheme 2.26: Retrosynthesis of triad 92. ...................................................................................68
Scheme 2.27: Attempted synthesis of triad 92. .........................................................................70
Scheme 2.28: The early synthesis of CuTBTAP 108 employing mixed cyclisations between a phthalonitrile and methylenephthalimidine or its precursor. ........................................74
Scheme 2.29: Linstead’s first syntheses of TBTAPs. ..................................................................74
Scheme 2.30: Synthesis of TBTAP 113. ....................................................................................75
Scheme 2.31: Synthesis of t-butyl-substituted hybrids using malonic acid .............................75
Scheme 2.32: Synthesis of TBTAP 119. .....................................................................................76
Scheme 2.33: Synthesis of The meso-phenyl-TBTAP 124 .........................................................76
Scheme 2.34: Synthesis of the aminoisoindoline 129 via Sonogashira coupling. ....................77
Scheme 2.35: Efficient synthesis of meso-substituted magnesium TBTAP 130. .......................78
Scheme 2.36: Synthesis of dyad 102. .......................................................................................79
Scheme 2.37: Retrosynthesis of dyad 102. ..............................................................................79
Scheme 2.38: Attempted synthesis of TPP-Phenyl-TBTAP dyad 102. .................................81
Scheme 2.39: Synthesis of Aza-(dibenzo)BODIPY Derivatives 133. .....................................83
Scheme 2.40: Retrosynthesis of proposed TPP2-aza-dibenzo-BODIPY 134. .........................84

XIII | Page
Scheme 2.41: Attempted synthesis of TPP$_2$-aza-dibenzo-DIPY 135.................................84
Scheme 2.42: Retrosynthesis of dyad 104. .................................................................87
Scheme 2.43: Synthesis of aminoisooindoline 138. .....................................................87
Scheme 2.44: Synthesis of a magnesium TBTAP-OCH$_3$ 139.....................................88
Scheme 2.45: Synthesis of a magnesium TBTAP-OH 135. .........................................89
Scheme 2.46: Metalation of TBTAP-OH 140. ..............................................................91
Scheme 2.47: Synthesis of bromoalkoxyporphyrin 141. .............................................92
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BINAP</td>
<td>(2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift in parts per million (ppm)</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-Dichloro-5,6-dicyanobenzoquinone</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>dil.</td>
<td>Dilute</td>
</tr>
<tr>
<td>Diglyme</td>
<td>Diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>DABCO</td>
<td>1,4-Diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-Diazabicyclo[5.4.0]undec-7-ene</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulphoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EET</td>
<td>Excitation energy transfer</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>EtOAc</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>Et3N</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>ε</td>
<td>Molar extinction coefficient</td>
</tr>
<tr>
<td>eq.</td>
<td>Equivalent</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>HRMS</td>
<td>High resolution mass spectrometry</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant in Hertz</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix associated laser desorption ionization- time-of-flight.</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>Mp</td>
<td>Melting point</td>
</tr>
<tr>
<td>M⁺</td>
<td>Molecular ion peak.</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>OTf</td>
<td>Triflate</td>
</tr>
<tr>
<td>Pc</td>
<td>Phthalocyanine</td>
</tr>
<tr>
<td>PE</td>
<td>Petroleum ether</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>Rᵣ</td>
<td>Retention factor</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TBTAP</td>
<td>Tetrabenzotriazaporphyrin</td>
</tr>
<tr>
<td>Tf</td>
<td>Triflate</td>
</tr>
<tr>
<td>TPP</td>
<td>Tetraphenylporphyrin</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction
1 INTRODUCTION

1.1 EARLY HISTORY OF PORPHYRINS

The name porphyrin is derived from the Greek word *porphura*, used to describe the colour purple. This immediately indicates an important property of porphyrins, their intense purple colour.\(^1\) Porphyrins can be found in nature, especially in their metalled form, as iron porphyrin (called haem) or as a magnesium porphyrin derivative (chlorophyll), for example (Figure 1.1).

![Chlorophyll and Haem Structures](image)

Figure 1.1: Chlorophyll and haem structures.

The macrocyclic structure of porphyrin was first proposed by Kuster in 1912, but was not accepted because such a large ring was thought to be essentially unstable. In 1929, Fischer and his co-workers succeeded in synthesising haem, the iron porphyrin found in haem proteins, using pyrrole as a starting material, earning him the Nobel Prize for Chemistry in 1930.\(^1\)

1.2 STRUCTURE OF PORPHYRIN

Porphyrins are macrocycles, consisting of four pyrrole units connected by single methine bridges (Figure 1.2). Porphyrins have 22 π-electrons but only 18 of them form aromatic system according to Hückel’s rule \((4n+2 = 18, n = 4)\). The system of nomenclature for porphyrins was developed by Fischer.\(^1\) Each β-carbon on the pyrrole units is numbered from
1 to 8, and α-carbons adjacent to each nitrogen atom are unnumbered. The bridging (*meso*) positions are named using Greek lower case letters α, β, γ and δ.

![Diagram of porphyrin structure](image)

Figure 1.2: Macro cyclic structure of porphyrin.

The Fischer system is straightforward for naming simple porphyrins, but if the porphyrin derivative has different substituents on the β and *meso* positions, the system becomes challenging to implement. The inability of Fischer to name the enormous number of synthetic porphyrins led to the development of a new, more systematic, IUPAC nomenclature in 1979. It was completed in 1987. All atoms are numbered, including the nitrogen atoms (Figure 1.3). Therefore, hydroporphyrins, ring contracted or expanded porphyrins, porphyrins fused with other rings, and even more porphyrin complexes could be named.

![Diagram of IUPAC porphyrin structure](image)

Figure 1.3: IUPAC system of porphyrins.
1.3 SPECTROSCOPIC PROPERTIES OF PORPHYRIN

1.3.1 NMR spectroscopy
NMR spectra of porphyrins confirm their aromatic character. The proton signal of $\beta$-pyrrole and meso-protons are deshielded as a result of the paramagnetic ring current deshielding effect. Additionally, the internal N-H protons are shifted up-field due to the shielding effect of the ring current, which shields the protons inside the macrocycle (Figure 1.4).

![Figure 1.4: $^1$H NMR spectrum of tetraphenylporphyrin 1.](image)

1.3.2 UV-Vis spectroscopy
Porphyrrins display characteristic absorption properties in the UV-vis spectra. Metal-free porphyrins and metalloporphyrins have an intense absorption between 390-425 nm, referred to as B band or Soret band, in addition to two to four less intense bands called Q bands, between 480 and 700 nm (Figure 1.5). The number of Q bands indicates if the porphyrins are metalated or metal-free. Metalloporphyrins are more symmetrical than metal-free porphyrins and therefore typically have only two Q bands.$^1$

![Figure 1.5: Typical UV-vis spectrum of tetraphenylporphyrin 1.](image)
1.4 SYNTHESIS OF PORPHYRINS

Porphyrins can be synthesised via different strategies which, in general, involve pyrroles and aldehydes. The final porphyrin depends on the structure of pyrrole and aldehyde, so β and meso substituted porphyrins can be synthesised. The inner protons of porphyrins can be substituted by several types of metals (e.g., Zn, Cu, Ni, and Sn) using various metal salts. Here, we will focus on the synthesis of meso-substituted porphyrins. Various general methods to synthesise meso-substituted porphyrin are documented, such as the Rothmund, Adler, and Lindsey methods.

1.4.1 Rothmund method

*Meso*-tetra substituted porphyrins were first synthesised by Rothmund in 1936. In summary, a solution of pyrrole and aldehyde in pyridine was placed in a sealed tube at 145-155°C under nitrogen (Scheme 1.1). This method was extended to include several aliphatic and aromatic aldehydes such as methyl, propyl, butyl, iso-butyl and 4-methoxy phenyl groups. The yields from the Rothmund method were generally low. Moreover, the corresponding chlorin (2, 3-dihydroporphyrin) (Figure 1.6) was also formed. The yield of meso-tetraphenylporphyrin was subsequently improved from 4-5% to 10-11% by the addition of zinc acetate to the reaction mixture by Ball and co-workers in 1946.

![Scheme 1.1: Synthesis of meso-substituted porphyrins by the Rothmund method.](image_url)

\[
\text{CHO} \quad \begin{array}{c}
\text{2} \\
\text{3}
\end{array} \quad \text{pyridine} \quad 145-155 \, ^\circ\text{C} \quad \begin{array}{c}
\text{1} \\
(4-5 \%) \end{array}
\]
1.4.2 Adler-Longo method

Adler, Longo, and co-workers prepared porphyrins by refluxing pyrrole and aldehyde at low concentrations in propionic acid for half an hour, open to air (Scheme 1.2). Following cooling of the reaction, the porphyrin crystallised from the reaction mixture. It was demonstrated that the yields of prepared porphyrin could be significantly improved under these acidic conditions.\(^6\) Furthermore, similar to the Rothmund method, the corresponding chlorin was also formed.\(^5\) Although chlorin could be separated from the product by chromatography, Rousseau and Dolphin attempted to reflux the porphyrin crude mixture with DDQ in pyridine in order to oxidise the chlorin to porphyrin.\(^7\) The yields using various \(p\)-substituted aryl aldehydes were approximately 20\%, while the yields from \(o\)-substituted aryl aldehydes were generally lower. Although the Adler method was shown to successfully increase the yield, its use was limited to certain types of aldehydes.\(^5\)

![Scheme 1.2: Synthesis of meso-substituted porphyrins by the Adler-Longo method.](image-url)
1.4.3 Lindsey method

The Lindsey method is a two-step, one flask reaction. Firstly, a mixture of pyrrole and aldehyde(s) in the presence of boron trifluoride etherate is stirred in chlorocarbon solvent to form the porphrinogen. After one hour, an oxidant such as DDQ or $p$-chloranil is added to oxidise porphrinogen to porphyrin (Scheme 1.3).  

\[
\text{Scheme 1.3: Synthesis of meso-substituted porphyrins by Lindsey method.}
\]

1.5 Applications of Porphyrins

Porphyrins have important functions in nature, such as energy or light transfer in chlorophyll and oxygen transfer in blood, in addition to applications in different fields of chemistry, physics, biology, and medicine, such as light harvesting and photo medicine (for cancer therapy).

Renewable energy, particularly solar energy, has attracted much attention since it directly converts clean solar energy from the sun into electrical power without an environmental impact. Various types of solar cells exist, however dye-sensitised solar cells (DSSCs) have gained particular interest due to their low cost and high power conversion efficiency $\eta$.  

The performance of these cells strongly depends on the sensitiser, one of the key elements for harvesting solar energy and transferring it into electrical power (Figure 1.7).
Figure 1.7: Systematic illustration of components and operation of dye sensitized solar cell.\textsuperscript{12}

Porphyrrins, as sensitisers, have drawn much attention due to their strong absorption band in the visible region and their molecular structure, which can be readily modified.\textsuperscript{10, 13} Numerous porphyrrins have been synthesised, bearing at least one anchoring group in their molecular structure in order to attach the dye to TiO\textsubscript{2} (metal oxide semiconductor) (Figure 1.8).\textsuperscript{12}

Figure 1.8: Different binding modes of porphyrrins 5 and 6 onto TiO\textsubscript{2} surface.\textsuperscript{12}
Examples of porphyrins designed for use in DSSCs have been reported. Different zinc porphyrin derivatives, with a carboxyphenyl-ethynyl group as the electron withdrawing anchoring substituent, and diarylamine group as the strong electron donating substituent at the meso position, were prepared in order to enhance the cell performance (Figure 1.9). When one t-butyl phenyl group of \( \text{YD0} \) was replaced with a diarylamine phenyl group, the cell performance increased from 2.4% to 6.4%. Furthermore, when the \( \text{YD1} \) was modified to \( \text{YD2} \), the \( \eta \) value increased to 6.8. The performance of \( \text{YD2} \) was subsequently improved to 11% when the cell was co-sensitised with \( \text{D-205} \) dye (Figure 1.10) on a thin TiO\(_2\) film (2.4 \( \mu \)m).
Porphyrrins SM315\textsuperscript{17} and GY50\textsuperscript{18} have been synthesised with cell performance values of 13 and 12.75\% respectively (Figure 1.11).

In conclusion, porphyrin sensitisers have showed $\eta$ values that are similar to or even higher than those of the most effective ruthenium sensitisers such as N3\textsuperscript{19} and N719 (11.18\%)\textsuperscript{20} CY-B11\textsuperscript{21} (11.5\%) C101\textsuperscript{22} (11-11.3\%) (Figure 1.12).

Figure 1.11: Molecular structures of SM315 and GY50.

Figure 1.12: Examples of ruthenium sensitisers for DSSCs.
Porphyrids also have a role in a specific cancer treatment, photodynamic therapy (PDT). PDT treatment involves two key steps, the first of which is the use of a photosensitiser, which is activated by light in the presence of oxygen. A significant area of research has focused on developing a novel, effective photosensitisers. Photosensitisers applied in PDT can be divided into three generations. Haematoporphyrin and its derivatives were the first generation photosensitisers; the second were based on benzoporphyrin derivatives, chlorins, phthalocyanines, texaphyrins and natural compounds such as hypericin. The main difference between first and second generation photosensitisers is that the latter has an absorption spectrum extended to the red and near-infrared regions of the electromagnetic spectrum (600–800 nm) (Figure 1.13). Consequently, the red light can pass deeper into tissue in order to treat deep cancer cells.

Figure 1.13: Absorption spectrum of a- porphyrin, b- chlorin, c- phthalocyanine; d- Correlation between the absorption of light by the photosensitisers molecule and the penetration of the light through the tissue.
Furthermore, first and second generation photosensitisers were not selective to cancer cells and also killed adjacent healthy cells. The third generation of photosensitisers were produced by conjugating first and second generation photosensitisers to various biological modifiers such as antibodies and nanoparticles. For example, Staneloudi and his co-workers conjugated isothiocyanato porphyrins 7 and 8 (Figure 1.14) to antibodies (colorectal tumour-cell specific scFv). This generation is more selective than the previous versions.

A 2015 study suggested that ATPP-EDTA (Figure 1.15) was an ideal photosensitiser for PDT application to cancer cells since it displays an absorption peak at 650 nm, selectively targeted cancer cells, and thus caused tumour destruction.
1.6 MULTIPLE PORPHYRIN ARRAYS

1.6.1 Linear porphyrin arrays

1.6.1.1 Directly meso–meso linked linear porphyrin arrays

Directly meso–meso linked linear porphyrin arrays are of interest to researchers as they show promising applications in nanotechnology and optical electronic devices. Different methods have been used to generate directly meso–meso linked linear porphyrin arrays. For example, Zn have been synthesised by oxidative coupling using silver salts in order to ensure the porphyrin monomers are closer, enabling rapid energy transfer (Figure 1.16).

![Figure 1.16: Directly meso–meso linked linear porphyrin arrays Zn.](image)

Directly meso–meso linked linear porphyrin arrays can be synthesised using iodine(III) reagents. Chen et al. prepared 10, 12 in a good yield using PhI(OCOCF₃)₂ [PIFA, also named as bis(trifluoroacetoxy)iodo]benzene or PhI(OAc)₂(PIDA) as the iodine reagents (Schemes 1.4 and 1.5)].
Scheme 1.4: Synthesis of *meso–meso* linked linear porphyrin dimer using PIFA or PIDA.

Scheme 1.5: Synthesis of *meso–meso* linked linear porphyrin arrays.

In addition, porphyrin dimer 13 (Figure 1.17) has been prepared by Jiblau et al. in a good yield (75%) using PIFA as the iodine(III) reagent.\(^{32}\)

Figure 1.17: Molecular structure of *meso–meso* linked porphyrin dimer 13.
Directly *meso-meso* linked bisporphyrins with mixed *meso* substituent groups can be synthesised using organolithium reagents. Senge and Feng reacted 5,15-disubstituted free base porphyrins with organolithium reagents under anhydrous conditions in order to give 5,10,15-trisubstituted porphyrin anions. Oxidation with DDQ subsequently yielded 14 (Figure 1.18).30

![Diagram of meso-meso linked porphyrin dimer with mixed meso substituent pattern.](image)

**Figure 1.18:** *Meso–meso* linked porphyrin dimer with mixed *meso* substituent pattern.

In addition, porphyrin boronates 15 have been used to synthesise directly linked arrays 17 by Suzuki coupling. Bromoporphyrin 16 and porphyrin boronate 15 were reacted in the presence of Pd(PPh₃)₄ under Suzuki conditions (Scheme 1.6).33,34

![Scheme of Suzuki coupling reaction](image)

**Scheme 1.6:** Synthesis of *meso–meso* linked linear porphyrin arrays using Suzuki coupling.
1.6.1.2 *Meso-meso* ethyne linked linear porphyrin arrays

In 1994, Therien and co-workers generated a new class of porphyrin arrays. In these arrays, porphyrin chromophores are wired together via single ethynyl bridges at the *meso* position (Figure 1.19). Porphyrin dimers 18 with a single ethyne bridge, as well as a porphyrin trimer 19, have been synthesised by the coupling of 5-bromo-10,20-diphenylporphinatozinc and ethyne-elaborated porphyrin synthons under palladium-catalysed coupling. These acetylene-linked porphyrins produced excellent electronic interactions between the chromophores and display unique photophysical and electrochemical properties.\(^{35}\)

![Meso-meso ethyne linked linear porphyrin arrays](image)

Figure 1.19: *Meso-meso* ethyne linked linear porphyrin arrays.

A series of symmetrical and unsymmetrical porphyrin arrays, linked by conjugated linkers, namely alkyne and phenyl acetylene, were synthesised by palladium-catalysed C–C coupling (Schemes 1.7 and 1.8) (Figure 1.20).\(^{33}\)

![Synthesis of asymmetrical alkyne-linked dimers](image)

Scheme 1.7: Synthesis of asymmetrical alkyne-linked dimers.
Moreover, direct meso-alkynylation of β,β-dipyridylporphyrin with several alkynyllithium reagents has been achieved, since the reaction is supported by adjacent dipyridyl groups through double coordination to the lithium reagents. This method enabled the synthesis of a meso-ethyne-bridged diporphyrin 31 in 60% yield by direct mesoalkynylation, reacting Ni 2,18-di-(2-pyridyl)porphyrin 30 and ethynylporphyrin (Scheme 1.9). 36
Scheme 1.9: Synthesis of meso-ethyne-bridged diporphyrin (Ar = 3, 5-di-tert-butylphenyl).

1.6.1.3 *Meso-meso* ethene linked linear porphyrin arrays

The preparation of *meso-meso* ethene linked linear porphyrin arrays leads to the formation of *cis* and *trans* isomers. Ethane-linked porphyrin 32 was heated at 60-70 °C in acetic acid for 20 min to produce the *trans* isomer in 85%. Further heating of the *trans* isomer or refluxing of the ethane-linked porphyrin in acetic acid yields a mixture of *cis* (face-to-face orientation) and *trans* (1: 2 ratio), which can be separated by column chromatography on silica gel (Scheme 1.10).
1.6.1.4 Hetero arrays of porphyrins

Linked porphyrins with different components, such as phthalocyanine, led to the formation of hetero arrays. Lindsey and co-workers prepared a linear array of chromophores containing a perylene unit and phthalocyanine, which exhibits efficient light-harvesting properties (Figure 1.21).\(^{38}\)

![Diagram of meso-meso ethene linked linear porphyrin dimers](image)

**Scheme 1.10:** Synthesis of meso-meso ethene linked linear porphyrin dimers.

**Figure 1.21:** Structure of perylene-bis (porphyrin)-phthalocyanine array.
1.6.2 Cyclic (ring) porphyrin arrays

1.6.2.1 Light harvesting by bacteria
The structure of light harvesting (antenna) complexes (LHs) of purple bacteria encouraged scientists to synthesise similar structures (Figure 1.22). They are multiple chromophores organised as cyclic structures in order to absorb light and achieve rapid light energy migration.

![Crystal structure of the LH2 complex from *Rps. acidophila*.](image)

Covalently and non-covalently linked (ring) cyclic porphyrins have been synthesised. There are different units linking the cyclic porphyrins in order to modulate the molecular structure and adjust the electronic interaction between neighbouring porphyrins. There are directly *meso* linked porphyrin, 1,3-phenyl, aromatic heterocycle and butadiyne bridges.

1.6.2.2 Directly *meso-meso* linked porphyrin ring (cycle)
Osuka and his co-workers synthesised compounds *CZ4*, *CZ6* and *CZ8* (Figure 1.23), which are of interest due to their symmetrical structure. The electronic interaction is large and regular, which leads to efficient electronic interactions and excitation energy transfer (EET).

![Structures of *CZ4*, *CZ6*, and *CZ8*](image)

*Figure 1.22: Crystal structure of the LH2 complex from *Rps. acidophila*. *Figure 1.23: Structures of *CZ4*, *CZ6*, and *CZ8* (Ar = 3,5-Di-tert-butylphenyl).*
Osuka et al. prepared directly linked cyclic porphyrin arrays starting with the 5,10-diaryl zinc porphyrin monomer 38 under the Ag(I)-promoted coupling reaction (Scheme 1.11). Dimer 39 (24% yield) and trimers 40a and 40b (totally 7% yield) were then gained from 38, while tetramers 41a and 41b (total 40% yield) were synthesised from 39. The rotation in these oligomers around the meso-meso linkage was impossible, due to steric interference. 40a and 41a are suitable precursors for cyclic arrays since they contain unsubstituted meso-positions on the same side. Under dilute conditions (2 × 10^{-5} M), cyclic tetramer CZ4 was synthesised in 74% yield while cyclic octamer CZ8 was obtained at higher concentration (3.3 10^{-3} M). Cyclic hexamer CZ6 was isolated in 22% yield from the coupling reaction of 40a in CHCl₃ at 1.0 × 10^{-4} M for 2 hours. Silica-gel column chromatography was required to separate the target cyclic arrays, and their structures were characterised by NMR and mass spectrometry. Generally, these cyclic porphyrins have shown an efficient EET process along the cyclic structure. 43

Scheme 1.11: Synthesis of meso-meso directly linked porphyrin rings (Ar =3,5-Di-tert-butylphenyl). 43
1.6.2.3 1,3-Phenylene Linked Cyclic Porphyrin

CZ12A and CZ24B are examples of 1,3-phenyl-bridged porphyrin arrays, prepared by cyclisation of linear precursor 12-mer and linear precursor 24-mer (Figure 1.24).43

Figure 1.24: Molecular structure of CZ12A, CZ24B.43

1.6.2.4 Meso-meso aromatic heterocycle bridged porphyrin ring (cycle)

Cyclic porphyrin arrays with aromatic heterocycle-bridges, such as pyrrole,40 thiophene44 and pyridine, have been synthesised. Song et al. synthesised a cyclic porphyrin with a pyrrole bridge, as the pyrrole has electron-rich properties, effective conjugation, and the ability to hydrogen-bond.40 Meso-to-meso 2,5-pyrrolylene-bridged cyclic porphyrin arrays were also synthesised. 5,10-diaryl-15,20-dibromoporphyrin and 2,5-diborylpyrrole were reacted under one-pot Suzuki Miyaura cross-coupling conditions in order to obtain pyrrolylene-bridged cyclic porphyrins (44-46). Interestingly, this reaction is an unusual example of the application of one-pot synthesis in preparing large ring arrays from porphyrin monomers as the precursor, without a template (Scheme 1.12).40
Additionally, cyclic porphyrin arrays bridged by meso-to-meso 2,2-bithiophene spacers were synthesised, presenting an effective electronic delocalisation through thiophenyl linkages. Similarly the pyrrole-bridged large cyclic arrays, these were obtained in a one-pot reaction from a monomeric porphyrin precursor, without any template molecules, as a rare case (Scheme 1.13).
Scheme 1.13: Suzuki-Miyaura cross-coupling reaction for thiophenylene-bridged cyclic porphyrin.

Moreover, β-2,6-pyridylene-bridged porphyrin nanorings have been synthesised with good yields by Suzuki–Miyaura coupling of β,β-diborylated Ni porphyrin with 2,6-dibromopyridine. These porphyrin arrays show weak electronic coupling among porphyrins and longer singlet-excited state lifetimes. Therefore, they have an obvious advantage in the process of excitation energy transfer (Figure 1.25).\(^{45}\)
Ethynyl and Butadiene linked porphyrin rings

Ethynyl spacers are frequently used due to the ease with which they can be integrated into porphyrin arrays and facilitate the extension of the conjugation networks. In 1999, the macrocyclic tetraaryl porphyrin hexamer 51 (Figure 1.26) was prepared in low yield without a template via multiple steps and cyclisation of the linear hexaporphyrin intermediate in the presence of palladium.

Figure 1.25: Molecular structures of β-2,6-pyridylene-bridged porphyrin nanorings 50.

Figure 1.26: Molecular structure of cyclic porphyrin hexamer 51.
However, in 2006 the linear hexaporphyrin intermediate was cyclised in the presence of 52 as a template, in a one-step process with good yield (Figure 1.27). This demonstrated the role of the template (self-assembly) as an effective way to control the synthesis of the cyclic compounds, as will be discussed later in this chapter. Yield increase from 8 to 30% (variable yield) to 50% (reproducible yield).\(^{47}\)

![Figure 1.27: Molecular structures of cyclic hexa porphyrin 53 with template 52.](image)

Lindsey and co-workers have synthesised a series of ethynyl-phenyl linked porphyrins (Figure 1.28).\(^{48}\)
Figure 1.28: Molecular structure of ethynyl-phenyl linked porphyrin.

Square-shaped conjugated cyclic porphyrin linked by butadiynes have been synthesised (Figure 1.29).
In 2007, Hoffmann and co-workers synthesised a cylindrical belt-shaped structure, conjugated butadiyne-linked cyclic porphyrin octamer 56 (Figure 1.30). The main step in the synthesis of 56 was the octadentate ligand 58, prepared as a template. The template contained eight flexible butyloxy side chains to confer high solubility (Figures 1.31).\(^4^9\)
Chapter 1

Introduction

Figure 1.31: Molecular structure of linear porphyrin 57 octamer and octadentate ligand 58.

This strategy enables the synthesis of a larger belt-shaped structure such as a 12 porphyrin nanoring (c-P12) (Figure 1.32). Adding DABCO and 4,4'-bipyridine to the c-P12 form sandwich complex (c-P12)32(DABCO)12] (Figure 1.33).

Figure 1.32: a- Templated directed synthesis of c-P12, b- Structure of c-p12.T12.
However, the synthesis of larger targets requires larger templates, which can be challenging. Therefore, Anderson and colleagues have synthesised 12 and 24 porphyrin nano rings by Vernier complex synthesis (Figure 1.34) (Figure 1.35).

Moreover, \textit{c-P24} has been synthesised by two Vernier-templated methods: the linear porphyrin octamer \textit{l-P8} was coupled in the presence of hexapyridyl template \textit{T6}, or the linear porphyrin hexamer \textit{l-P6} was coupled in the presence of the template \textit{58} (Figure 1.35).

Figure 1.33: Calculated structure of the sandwich complex (\textit{c-P12})_2\cdot(\textit{DABCO})_{12}^{\text{51}}

Figure 1.34: a- Vernier-template synthesis of \textit{c-P12}, b- structure of \textit{T6} template.\textsuperscript{50}

Figure 1.35: a- Vernier-templated synthesis of the nanorings \textit{c-P24}, b- \textit{58} template.\textsuperscript{52}
1.6.2.6 Benzene-centred cyclic porphyrin

The synthesis of benzene-centred cyclic porphyrin hexamers was achieved by palladium and cobalt-catalysed trimerisation reactions of diphenylethynyl-bridged diporphyrins (Scheme 1.14).\textsuperscript{53}

![Scheme 1.14: Synthesis of benzene-centered cyclic porphyrin hexamers.](image)

Moreover, hexakis porphyrinato benzenes have been synthesised by the coupling of six porphyrin units to a central benzene core via an ether link. Hexakis-(bromomethyl) benzene was reacted with porphyrin 62 to yield the porphyrin arrays 63 (Scheme 1.15).\textsuperscript{54}

![Scheme 1.15: Synthesis of hexakis porphyrinato benzenes 63.](image)
1.7 TRIPHENYLENE AND TRIPHENYLENE-PORPHYRIN CONJUGATES

Triphenylene derivatives are disc-shaped molecules. When functionalised with flexible side chains they aggregate into supramolecular columnar structures that are arranged in a lattice (usually hexagonal) (Figures 1.36).

Figure 1.36: Columnar hexaalkoxytriphenylenes 68.55, 56

Triphenylene provides a rigid scaffold and synthetic chemistry has been developed allowing easy access to various derivatives. It is therefore a useful central unit for attachment of functional molecules. The stacking of the triphenylenes can also facilitate the synthesis of organised assemblies. Supramolecular structures that combine porphyrins and triphenylene have promising attributes, such as self-organisation and light-driven functionalities. However, this combination has not been widely investigated. Hosobe et al. synthesised a triphenylene core connected to six porphyrins via a different alkyl chain (Figure 1.37).

Figure 1.37: Triphenylene core-centered porphyrin hexamers.
The formation of aggregates and the resulting structure of these novel compounds has been demonstrated by X-ray diffraction (XRD). The XRD results were subsequently used to propose the molecular stacking formation in (H₂PAC15)₆TPh (Figure 1.38).^{57}

Figure 1.38: A schematic illustration of organization process. The purple square, yellow wavy line and blue round shapes stand for porphyrin, alkyl chain, and triphenylene units, respectively. The molecular sizes were estimated by DFT calculation.^{57}
1.8 REFERENCES


Chapter 1

Introduction

Chapter 2

Results and Discussion
2 RESULTS AND DISCUSSION

2.1 PORPHYRIN AND TRIPHENYLENE ARRAYS

2.1.1 Aims

The ultimate goal of this research is to synthesise an arrangement of (six) porphyrins rigidly attached to a central unit. We have chosen triphenylene as the central unit. Until recently, far too little attention has been paid to the combination of porphyrin and triphenylene. As mentioned earlier in Chapter 1, Hasobe and co-workers prepared the first example of this class, which combines porphyrin and triphenylene.¹ Therefore, this study aims to contribute to this area of research by synthesising six units of porphyrin attached to a central triphenylene core. The combination of triphenylene and porphyrins has promising potential for various applications including energy/electron transfer.² The difference between our aim and Hasobe and his co-workers’ compounds is the linkage between porphyrin and triphenylene. As described in the previous chapter in Figure 1.37, Hasobe et al. linked porphyrin units with a triphenylene core via different alkyl chains, while the linkage in this study aims to be more rigid “ethyne phenyl-conjugated”. Such an attachment via rigid linkers will provide a high local concentration of porphyrin chromophores but prevent intramolecular aggregation.

Figure 2.1: Cartoon representation of the target molecule.
Figure 2.1 shows the proposed design for the target molecule. Triphenylene is in the centre and is surrounded by six units of porphyrins. The connection between triphenylene and each porphyrin unit is rigid such as acetylene, which provides some spatial control. Although triphenylenes are disk-shaped molecules that are well known to self-assemble into supramolecular columnar structures that organise into hexagonal and nematic phases because of π–π stacking interactions, its function here is mainly as a simple representative core. In order to construct the target, hexa-substituted triphenylene units are needed and an unsymmetrical porphyrin bearing, for example, an ethynyl functional group.

Triphenylene will be the template for the target model and there are twelve positions on the triphenylene core (Figure 2.2) where functionalisation can be performed. However, the most common substitution sites are 2, 3, 6, 7, 10 and 11. These six possible positions could be substituted in order to link the triphenylene with the porphyrin.

![Figure 2.2: Molecular structure of triphenylene.](image)

It is apparent from the triphenylene’s structure that the gap between positions 2 and 3 is smaller than the gap between positions 3 and 6. In the final molecules this can be exploited to incorporate different (bidentate) ligands. For our study we began by considering triphenylenes substituted by two porphyrins. This approach would allow development of the synthetic chemistry and provide useful model compounds (Figure 2.3).

![Figure 2.3: Proposed structures for the model target molecules.](image)
2.1.2 Triphenylenes

Triphenylenes are flat polycyclic aromatic hydrocarbons with an 18 \( \pi \)-electron system based on a planar structure composed of four fused benzene rings. Triphenylene derivatives, especially those with medium-sized side chains, self-associate to form discotic liquid crystals in which they are arranged in columns due to the \( \pi \) stacking of the aromatic rings and Van der Waals interactions between their alkyl chains.\(^8\) Triphenylenes can be synthesised by different routes, as shown in Scheme 2.1.\(^9\)

![Scheme 2.1: Different routes to the triphenylene core. Black lines indicate the structures of the key intermediates and red lines represent the bonds or fragments that become part of the triphenylene in the final stage of the synthesis.](image)

In our work we will focus on type I routes, in which the main step is the cyclisation of a terphenyl by oxidative cyclisation or photocyclisation. Oxidative coupling was originally developed for the coupling of phenols using an excess of oxidising agents such as \( \text{K}_3\text{Fe(CN)}_6 \)
and FeCl₃. Palladium-catalysed couplings have been used to synthesise symmetrically and unsymmetrically substituted terphenyls.⁸ For example, to synthesise the disubstituted triphenylene 72, terphenyl 71 was prepared by Suzuki coupling of boronic acid 70 with o-dibromobenzene 69 (Scheme 2.2).³

![Scheme 2.2: Synthesis of disubstituted triphenylene 72 via oxidative cyclisation.](image)

The photocyclisation method was also applied to the synthesis of triphenylenes from terphenyls.⁹ For example, the treatment of terphenyl 73 with excess Iron(III) chloride results in a complex product mixture. Consequently, cyclisation was achieved photochemically to give 2,3,7,10-tetrakis (hexyloxy)triphenylene 74 (Scheme 2.3).⁸

![Scheme 2.3: Synthesis of tetrasubstituted triphenylene 74 via photocyclisation.](image)

Before turning to the synthesis of the triphenylenes and porphyrins, we need to look at a brief description of palladium catalysis reactions as they are an important tool to construct our targets.
2.1.3 Using palladium catalysis in synthesis

Transition metal-catalysed reactions are powerful tools in organic synthesis. Palladium-catalysed reactions, such as the Heck, Stille, Sonogashira and Suzuki reactions have numerous features that make them useful and versatile.\textsuperscript{10, 11} Palladium catalysis plays an important role in carbon–carbon bond formation. These palladium-catalysed reactions, especially, Suzuki and Sonogashira coupling, have been used extensively in this project to synthesise the target compounds or their precursors.

2.1.3.1 The Suzuki cross-coupling reaction

The Suzuki coupling is a palladium-catalysed cross-coupling between an aryl or alkenyl halide Ar-X (X mainly Br, I, OTf) and an organoboron compound, usually boronic acid, in order to form a C-C bond (Scheme 2.4). There are certain factors that make the Suzuki reaction a method of choice. Boronic acids are easy to handle, air and water stable, thermoresistant compounds, with low toxicity and high selectivity of cross-coupling.\textsuperscript{10}

\[
\text{Ar} - \text{X} + \text{R} - \text{B(OH)}_2 \xrightarrow{\text{Pd}^0 \text{ base}} \text{Ar} - \text{R} + \text{X} - \text{B(OH)}_2
\]

Scheme 2.4: General Suzuki Coupling.

The typical catalytic cycle of the Suzuki coupling is hypothesised to proceed via Pd\textsuperscript{0} complexes. Therefore, the mechanism of the reaction starts with an oxidative addition of the organohalide to the Pd\textsuperscript{0} to generate a Pd\textsuperscript{II} complex. Then, the base exchanges the halide on the palladium complex followed by transmetalation of the R group from the borate complex to the palladium complex. Reductive elimination eliminates the Pd\textsuperscript{0} to generate the coupling product (Ar–R) and regenerates the palladium catalyst, then the cycle can start again (Scheme 2.5).\textsuperscript{4, 10, 12}
2.1.3.2 Sonogashira cross-coupling

The palladium-catalysed cross-coupling between a terminal sp-hybridised carbon of an alkyne with an sp² carbon of an organohalide (or triflate) is commonly termed as a Sonogashira coupling (Scheme 2.6). 10, 13

![Scheme 2.5: Mechanism of Suzuki cross coupling reaction.](image)

**Scheme 2.5: Mechanism of Suzuki cross coupling reaction.**

Generally, the mechanism of reaction is similar to Suzuki coupling and takes place through two independent catalytic cycles (Scheme 2.7). The palladium cycle (cycle A) starts with the catalytically active species Pd⁰L₂. The first step in the catalytic cycle is initiated by oxidative addition of the organohalide to form a PdII complex. The complex is then transformed into a [PdIII(CArCR)] C complex after transmetalation with a copper acetylide that is generated in the copper cycle (cycle B). Complex C undergoes reductive elimination, after *cis/trans-
isomerisation, to the final alkyne, regenerating the catalyst [Pd⁰L₂]. The copper cycle (cycle B) is poorly understood. The base (organic or inorganic) is assumed to assist the copper acetylide F formation with the help of a π-alkyne copper complex E, which would make the alkyne terminal proton more acidic.¹⁰, ¹³, ¹⁴

![Scheme 2.7: Mechanism of Sonogashira cross coupling reaction.](image)

Although the addition of copper salt to the Sonogashira reaction is beneficial in terms of increasing the rate of the reaction, the presence of copper can result in undesirable formation of alkyne homocoupling. A solution to this problem was to perform the reaction in the absence of copper salt, this is known as copper-free Sonogashira coupling. The mechanism of copper-free Sonogashira reaction has been proposed (Scheme 2.8). The proposed mechanism suggested that, as usual, the catalytic cycle is initiated by the oxidative addition of the organohalide to the catalytic species [Pd⁰L₂]. The following step is a reversible π-
coordination of the alkyne, generating an alkyne–Pd\(^{II}\) complex (C) where the acetylenic proton is acidified facilitating its elimination by the base with coordination of the acetylene ligand to the metal. This [Pd\(^{II}\) (CArCR)L\(_2\)] complex releases the cross-coupled product by reductive elimination and reforms the catalytic species [Pd\(^{0}\)L\(_2\)].\(^{13}\)

Scheme 2.8: Mechanism of copper-free Sonogashira cross coupling reaction.

Having described the palladium-catalysed reactions, the following section will discuss progress towards the synthesis of the targets.

### 2.1.4 Synthesis of porphyrin-triphenylene-porphyrin triad 75

The first model system to be targeted was triad 75, where two porphyrin units are attached to the 2, 7 positions of a triphenylene core. Thus an unsymmetrical porphyrin bearing an ethynyl functional group and dibromo triphenylene unit are needed. The proposed strategy can be seen in Scheme 2.9. We recognised that solubilising groups would probably be needed on the triphenylene, and started with simplest core where the remaining β-positions had methoxy substituents. Use of alkoxy groups also allows specific isomers of triphenylene dibromides to be easily synthesised.
Scheme 2.9: Retrosynthesis of porphyrin-triphenylene-porphyrin triad 75.

2.1.4.1 Synthesis of triphenylene component

Synthesis of tetramethoxyterphenyl 83

Scheme 2.10: Synthesis of terphenyl 83.

Terphenyl 83 was synthesised via Suzuki coupling between 1,2-dibromo-3,4-dimethoxy benzene 79 and 4-methoxyphenylboronic acid 82. According to the procedure used by Cammidge and Gopee, the boronic acid 82 was easily prepared from 4-bromoanisole 80 via formation of the Grignard reagent 81 in THF, then transferring it slowly to a solution of trimethyl borate in THF to give 82. 1,2-Dimethoxybenzene 78 was easily brominated using bromine in DCM to yield 1,2-dibromo-3,4-dimethoxybenzene 79. Once the precursors 79 and boronic acid 82 were prepared, the Suzuki coupling between them was employed in the
presence of PdCl$_2$ as a catalyst, triphenylphosphine as the ligand and sodium carbonate as the base. A specific mixture of ethanol, toluene and water (3:3:1) was used as solvent and the mixture was heated and refluxed. The reaction was followed by TLC (Scheme 2.10). After work-up, the reaction mixture was purified by column chromatography and terphenyl 83 was obtained as a white solid. The $^1$H NMR spectrum (Figure 2.4) shows the symmetrical structure of terphenyl 83. Protons c and e both give doublets at 6.78 ppm and 7.04 ppm. A singlet peak at 6.91 ppm corresponds to protons at positions d. Moreover, two singlet peaks at 3.87 ppm and 3.76 ppm belong to the protons of methoxy groups. MALDI-TOF MS gives $m/z = 350$ [C$_{22}$H$_{22}$O$_4$] (Figure 2.5).

Figure 2.4: $^1$H NMR Spectrum of terphenyl 83 in acetone-$d_6$.

Figure 2.5: MALDI-TOF MS spectrum of 83.
Synthesis of tetramethoxytriphenylene 84

Cyclisation was achieved using Artal et al. procedure. Terphenyl 83 was dissolved in dichloromethane and nitromethane, then iron(III) chloride was added. The mixture was stirred for 2 h and monitored with TLC. When complete, the reaction mixture was poured onto cold methanol and the resulting solid filtered off. After purification, the novel triphenylene 84 was obtained (Scheme 2.11). The procedure is much more convenient than the photochemical cyclisation previously employed in our group to achieve related transformations.

Scheme 2.12: One possible mechanism of cyclisation of terphenyl 83 using iron(III) chloride.
The $^1$H NMR spectrum confirms the cyclisation of terphenyl 83 to triphenylene 84. There is a significant difference between the triphenylene and the terphenyl. As can be seen from Figure 2.6, there are four signals and each of them integrate for two aromatic protons in addition to protons of methoxy groups at 4.04 ppm, 4.06 ppm. Protons at position c present as dd ($2\,H, J = 9.1\,Hz, J = 2.6\,Hz$) at 7.29 ppm. Two doublet signals at 8.13 ppm ($J = 2.6\,Hz$) and 8.62 ppm ($J = 9.1\,Hz$) corresponded to protons e and f. A singlet peak at 8.08 ppm corresponded to protons at position d. Additionally, Figure 2.7 shows the MS spectrum of triphenylene 84 and confirms its formation.

Figure 2.6: $^1$H NMR of triphenylene 84 in acetone-$d_6$ (* = solvent).

Figure 2.7: HRMS (ESI) of triphenylene 84.
Synthesis of 2,7-Dibromo-3,6,10,11-Tetramethoxytriphenylene 76

The synthesis of triphenylene 76 was achieved according to the procedure of Cammidge and Gopee.\textsuperscript{3} Triphenylene 84 was dissolved in ice-cold dichloromethane and then bromine liquid was added dropwise and stirred for 24 h (Scheme 2.13). Following this, a solution of sodium metabisulfite was added and the mixture was extracted with DCM. The crude product was recrystallised from propan-2-ol as a white solid.

Figure 2.8 shows the $^1$H NMR spectrum of triphenylene 76. As can be seen there are only three resonances, each of them is a singlet corresponding to two aromatic protons. Moreover, as shown in Figure 2.9, since triphenylene 76 contains two bromines a distinctive isotopic pattern is seen in MS.

Figure 2.8: $^1$H NMR spectrum of triphenylene 76 in acetone-$d_6$ (* = solvent).

Scheme 2.13: Synthesis of triphenylene 76.
Triphenylenes bearing 4-6 long alkoxy chains are well known to form columnar liquid crystal phases. In general, for triphenylene discotics, a minimum chain length of 4 C-atoms is required (e.g. butyl chains). We were therefore very surprised to observe mesogenic behaviour in triphenylene 76. On heating, a mesophase is formed at 188°C. The mesophase has a moderate range, and forms the isotropic liquid at 267°C. On cooling, a texture characteristic of a columnar hexagonal mesophase is observed by microscopy. This remarkable observation means that triphenylene 76 is by far the least heavily substituted triphenylene to show mesophase behaviour (Figure 2.10).
2.1.4.2 Synthesis of porphyrin component

Synthesis of 4-(3-methyl-3-hydroxy-1-butyn-1-yl) benzaldehyde 87

Traditional preparation of porphyrins involves the acid-catalysed condensation of aldehydes with pyrrole. In order to prepare our required porphyrin starting material, a novel aldehyde-bearing 2-hydroxyisopropyl unit as the ethyne protecting group is needed. Thus, 4-bromobenzaldehyde 85 and 2-methylbut-3-yn-2-ol 86 were coupled under Sonogashira conditions (Scheme 2.14) by heating in triethylamine at 70 °C for 4 h in the presence of Pd(PPh₃)₂Cl₂ and CuI. After the reaction was completed, the resulting mixture was passed through a silica pad. Then, aldehyde 87 was purified by column chromatography. The ¹H NMR spectrum shown in Figure 2.11, confirms the formation of the required compound.

Figure 2.11: ¹H NMR spectrum of aldehyde 87 in CDCl₃ (* = solvent).
Synthesis of unsymmetrically substituted porphyrin 88\textsuperscript{16}

\begin{align*}
\text{OHC} & \text{CHO} \quad \text{2} \quad \text{3} \quad 1-\text{BF}_3\text{Et}_2\text{O}, \text{CHCl}_3 \quad 2-\text{Chloranil} \\
87 & \quad \text{OH} \quad \text{N} \quad \text{N} \quad \text{OH}
\end{align*}

Scheme 2.15: Synthesis of porphyrin 88.

Porphyrin 88 was synthesised using the Lindsey method.\textsuperscript{16} A solution of 1 eq. aldehyde 87, 3 eq. benzaldehyde 2 and 4 eq. pyrrole 3 in the presence of BF\textsubscript{3}.Et\textsubscript{2}O was stirred at room temperature under nitrogen for 1 h in chloroform. Following this, chloranil was added as a solid to the reaction and the mixture was stirred for a further 1.5 h (Scheme 2.15). Then, the reaction mixture was concentrated and passed through a silica pad to give a mixture of porphyrin products. Finally, a series of column chromatographic separations was needed to obtain the target in 15\% yield as a purple solid. Moreover, the reaction depends on the presence of 0.75\% ethanol in CHCl\textsubscript{3} as a stabiliser, since ethanol and BF\textsubscript{3} function as co-catalysts and provide a successful reaction. The reaction starts with the condensation of aldehyde 87 and benzaldehyde 2 with pyrrole 3 to give the tetrapyrromethane, which can cyclise to the porphyrinogen. Then, an oxidant was added in order to convert the porphyrinogen to the porphyrin.\textsuperscript{17}

The \textsuperscript{1}H NMR spectrum of porphyrin 88 is shown in Figure 2.12. It exhibits characteristics of porphyrin; for example, the inner protons of the macrocycle (NH) were observed at around -2.89 ppm. The \(\beta\) protons are identified by the peaks around 8.86 ppm. In addition, the single peak at 1.73 ppm corresponds to CH\textsubscript{3}. 
Figure 2.12: $^1$H NMR spectrum of porphyrin 88 in CD$_2$Cl$_2$ (* = solvent).

**Synthesis of zinc porphyrin 89**

Zinc porphyrin 89 was prepared in high yield by adding a solution of zinc acetate in methanol to a solution of porphyrin 88 in DCM then refluxing for 1 h (Scheme 2.16). After that, the reaction mixture was filtered or passed through a small pad of dry silica using DCM as the eluent to give zinc porphyrin 89. The $^1$H NMR spectrum of zinc porphyrin 89 is similar to
that of porphyrin 88 with the exception of the absence of the signal at high field at -2.80 ppm (NH), which proves the metalation of the porphyrin 88 (Figure 2.13).

Figure 2.13: $^1$H NMR spectrum of zinc-porphyrin 89 in CD$_2$Cl$_2$ (* = solvent).

**Synthesis of zinc porphyrin 77**

![Scheme 2.17: Synthesis of ethynyl porphyrin 77.](image)

Deprotection of porphyrin 89 gave the desired ethynyl porphyrin 77. Thus, porphyrin 89 was deprotected by using sodium hydroxide in dry toluene and refluxing under nitrogen (Scheme 2.17). The mechanism of deprotection is shown in Scheme 2.18.
The $^1$H NMR spectrum shows the formation of porphyrin 77 (Figure 2.14) with the absence of the hydroxyl isopropyl protons in addition to the new peak at 3.37 ppm. This later peak is the resonance for the ethynyl proton.

Figure 2.14: $^1$H NMR of ethynyl porphyrin 77 in CD$_2$Cl$_2$ (* = solvent).

**Attempted synthesis of triad 75**

Once the syntheses of triphenylene 76 and porphyrin 77 were achieved successfully, we were in a position to consider the Sonogashira coupling to synthesise the triad 75, as illustrated in Scheme 2.19.
Several approaches were performed in order to achieve triad 75. The first approach to synthesise the proposed triad was done according to Hellal and Cuny. 1 eq. of triphenylene 76 and 2 eq. of porphyrin 77 were refluxed in DMF in the presence of PdCl$_2$ (MeCN)$_2$ as a catalyst, BINAP as ligand and DBU as base. The reaction was followed by TLC. After about 1 h, there was a new spot observed by TLC while triphenylene 76 was not all consumed (it still remained in the reaction mixture). After around 3 h the TLC was still showing the same outcome as the previous result. The reaction mixture was analysed by MALDI-TOF MS. The obtained results show peaks at $m/z = 1126$ and $m/z = 1402$. These peaks may be due to the formation of dyads 90 and 91 (Figure 2.15). However, there was no obvious result indicating the formation of the target compound 75, which is expected to be $m/z = 1744$ [C$_{114}$H$_{72}$N$_8$O$_4$Zn$_2$]. Meanwhile, the reaction was further refluxed and completed in about 5 h. However, increasing the time did not give a significantly improved result, as shown by TLC, except that the amount of porphyrin 77 had decreased. It seems possible that 77 was consumed to form dyads 90 and 91. Therefore, a further 1 eq. of porphyrin 77 was added to the reaction mixture in order to react with the remaining triphenylene 76 or dyad 90 to generate the target triad 75.

Scheme 2.19: Retrosynthesis of triad 75.

However, after the addition of more porphyrin 77 and reacting for 32 h, no change was observed. It was challenging to force the reaction to completion (Figure 2.16). Thus, the reaction was stopped, diluted in EtOAc and washed with water and brine. After the work-up, the crude mixture was purified by chromatography using PE:EtOAc (2:1) as an eluent. There were different fractions and they were analysed by MALDI-TOF MS to check what products were obtained. Some of them gave a peak at m/z = 1402 (Figure 2.17). Further analysis showed that it is associated with triphenylene 76 and it was subjected to several
purification techniques, such as column chromatography, washing and recrystallisation, yet it was difficult to separate them. In addition, an interesting fraction has a peak at \( m/z = 1126 \) (Figure 2.17). Therefore, this fraction was analysed by \(^1\)H NMR spectroscopy as shown in Figure 2.18. \(^1\)H NMR spectroscopy confirmed that the obtained compound is the new dyad 90. The triphenylene unit in dyad 90 is not symmetrical as in triphenylene 76. Therefore, each proton will give an individual resonance. The \(^1\)H NMR spectrum shows four signals for the methoxy groups. They show different peaks as well as aromatic protons, which are not equivalent anymore. It is worth mentioning that during characterisation of dyad 90 it was noticed that the positions of the aromatic proton peaks in the \(^1\)H NMR spectrum varied with change of the NMR solvent, as seen in Figure 2.19. Moreover, dyad 90 contains one bromine atom, therefore it has an M + 2 peak of almost equal in intensity to the molecular ion because of the presence of the molecular ion containing the \(^{81}\)Br isotope (Figure 2.20).

Figure 2.17: Fractions show dyad 90 (top) and dyad 91 (bottom).
Figure 2.18: $^1$H NMR spectrum of dyad 90 in acetone-$d_6$ (* = solvent).

Dichloromethane-$d_2$

Chloroform-$d$

Acetone-$d_6$

Figure 2.19: $^1$H NMR of dyad 90 in different solvents.
Overall, although dyad 90 has been obtained, there was no evidence for the proposed target. As a result, the reaction was repeated using modified conditions to those mentioned above. The only difference was the replacement of conventional reflux by microwave irradiation. The reaction mixture was irradiated for 1 h at 120 °C. However, this method did not give a significant improvement. Therefore, the copper-free Sonogashira reaction was abandoned and the Sonogashira coupling conditions by Cammidge were applied. A sealable tube was charged with 1 eq. of triphenylene 76, Pd(PPh₃)Cl₂, CuI and PPh₃, then evacuated and refilled with argon. After that, 14 eq. of porphyrin 77 was added and the reaction mixture heated in an oil bath at 100 °C for 24 h. After work-up, TLC showed the same results from the earlier attempts. In summary, these results show that a new dyad 90 was always obtained (Scheme 2.20). In addition, dyad 91 was always found accompanied with unreacted triphenylene 76. These results indicate that the homocoupling of the porphyrin acetylenes is far more favourable than cross-coupling.

Figure 2.20: MALDI-TOF-MS of dyad 90.
The failure of this reaction was unexpected and disappointing. Among the possible reasons, we noted that dibromide triphenylene 76 had low solubility. Therefore, in revising our strategy, we also decided to employ longer substituent chains (hexyl) on all triphenylene precursors.

2.1.5 Synthesis of triad 92

A modified route was chosen and applied to the attempted synthesis of triad 92. Scheme 2.21 shows the proposed strategy where we would react porphyrin triflate with ethynyl triphenylene, essentially reversing the strategy previously employed.
Porphyrim triflate 93 is needed to synthesise triad 92. Therefore, porphyrim triflate 93 was prepared through first preparing hydroxyl porphyrim then triflating it, then inserting the zinc.

2.1.5.1 Synthesis of porphyrin component

Synthesis of mono hydroxy phenyl porphyrin 96

\[
\text{CHO} + \text{CHO} + \text{H} \xrightarrow{\text{propionic acid, reflux, 30 min}} \text{porphyrin 96}
\]

Scheme 2.21: Retrosynthesis of triad 92.

Scheme 2.22: Synthesis of porphyrin 96.
Hydroxyphenylporphyrin 96 was synthesised using the Adler method.\textsuperscript{20} 4-Hydroxybenzaldehyde 95, benzaldehyde 2 and pyrrole 3 in a ratio 3:1:4 were refluxed in propionic acid for 30 minutes, open to the air (Scheme 2.22). Then, precipitation occurred after cooling and addition of ethanol to the reaction mixture. The isolated solid was filtered off and purified by column chromatography to yield hydroxy phenylporphyrin in a yield of 4%. Figure 2.21 presents the $^1$H NMR spectrum of porphyrin 96. It shows features of a porphyrin, for example, as porphyrin 96 is a metal-free porphyrin, there was a signal at –2.77 ppm.

![Figure 2.21: $^1$H NMR spectrum of porphyrin 96 in CDCl$_3$ (* = solvent).](image)

**Synthesis of porphyrin triflate 97**

![Scheme 2.23: Synthesis of porphyrin triflate 97.](image)

OTf = OSO$_2$CF$_3$
Hydroxyphenylporphyrin 96 was converted to porphyrin triflate 97 easily using trifluoromethanesulphonic acid anhydride.\textsuperscript{21} Hydroxyphenylporphyrin 96 was reacted with trifluoromethanesulphonic acid anhydride in dry DCM and pyridine at -78 °C under nitrogen (Scheme 23). After work up, porphyrin triflate 97 was isolated as a purple solid. Figure 2.22 shows the $^1$H NMR spectrum of porphyrin triflate 97. The aromatic protons of porphyrin triflate 97 appear more deshielded than those of porphyrin 96 since the hydroxyl group was replaced by triflate, which is an electron-withdrawing group. HRMS confirmed the formation of triflate 96 (Figure 2.23).

![Figure 2.22: $^1$H NMR spectrum of porphyrin triflate 97 in CDCl$_3$ (* = solvent).](image)

![Figure 2.23: HRMS (ESI) of porphyrin triflate 97.](image)
Synthesis of zinc porphyrin triflate 93

![Scheme 2.24: Synthesis of zinc porphyrin triflate 93.](image)

The synthesis of zinc porphyrin triflate 93 was achieved by refluxing porphyrin triflate 97 with zinc acetate in DCM (Scheme 2.24). After work up and evaporating the solvent, zinc porphyrin triflate 93 was obtained as a purple solid. The formation of zinc porphyrin triflate 93 was confirmed with $^1$H NMR spectroscopy (Figure 2.24) and HRMS (ESI) (Figure 2.25). It is worth mentioning that synthesis of zinc porphyrin triflate 93 was achieved through the strategy shown in Scheme 2.25. However, MALDI-TOF MS analysis shows the formation of mixture of porphyrins 93 and 97 as can be seen in Figure 2.26. The zinc partially was lost through triflate stage.

![Figure 2.24: $^1$H NMR spectrum of zinc porphyrin triflate 93 in CDCl$_3$ (* = solvent).](image)
Figure 2.25: HRMS (ESI) of zinc porphyrin triflate 93.

Scheme 2.25: Formation of porphyrin triflate 97 as a side product.
Figure 2.26: Formation of zinc porphyrin triflate 93 accompanied with porphyrin triflate 97.

**Attempted synthesis of triad 92**

Triphenylene 94 was obtained from a separate project. The procedure described by Hella and Cuny was adopted, a microwave vessel was charged with 1 eq. of triphenylene 94, PdCl₂(CH₃CN)₂, BINAP, and 4 eq. of zinc porphyrin triflate 93 then irradiated at 120 °C for 1 h. Following this, the reaction mixture was analysed by TLC and MALDI-TOF MS. However, no significant result was observed. It is possible that Pd⁰ was not generated, thus, boronic acid was added in order generate the Pd⁰. After that, the vial was irradiated for further 2 h. A yellow spot was observed by TLC. Therefore, the MALDI-TOF MS and
\(^1\)H NMR spectra were used to analyse the reaction mixture. However, both of them did not indicate the formation of triad 92. On the other hand, they were indicating that zinc porphyrin triflate 93 (\(m/z = 826\)) had not reacted (Figure 2.27). It seems possible that triphenylene 94 has generated triphenylene twin 99 or higher oligomers such as trimer 100 and 101 (Figure 2.28). However, none of them was observed in MALDI-TOF MS.

Figure 2.27: MALDI-TOF MS of reaction mixture after adding boronic acid.

![Figure 2.27: MALDI-TOF MS of reaction mixture after adding boronic acid.](image)

Figure 2.28: Molecular structures of potential side products.

![Figure 2.28: Molecular structures of potential side products.](image)
The procedure described by Cammidge and his co-workers was then investigated in order to synthesise triad 92 (Scheme 2.27).\(^6\)

Zinc porphyrin triflate 93 and Pd(PPh\(_3\))\(_2\)Cl\(_2\) in a mixture of freshly distilled triethyl amine and THF were stirred at room temperature for 15 min. CuI was then added, followed by a solution of triphenylene 94 in THF. The mixture was then heated at 50 °C. The reaction was examined by TLC and after 20 h the reaction mixture showed a yellow spot and zinc porphyrin triflate 93 still present. The reaction was left for 6 days. However, analysis using TLC, MALDI-TOF MS and \(^1\)H NMR, did not show significant improvements. In other words, the obtained results are quite similar to the previous method.

![Scheme 2.27: Attempted synthesis of triad 92.](image)

Therefore, excess of triphenylene 94 was added to the reaction mixture by slow addition in order to push the reaction toward the formation of triad 92. Although the reaction mixture
was left for 8 days after the addition, there was no obvious improvement and zinc porphyrin triflate 93 was recovered (Figure 2.30).

![Figure 2.30: 1H NMR of reaction mixture after slow addition of triphenylene 94.](image)

2.1.6 Conclusion

The purpose of this study was to link a porphyrin to a triphenylene through phenyl alkynes. The results of this investigation show that, in general, repeating the reactions several times, leaving it more time and raising the equivalents of the starting materials gave the same results. It was challenging to force the reaction to the formation of target triads 92 and 75. Therefore, strategies to synthesise a triphenylene core surrounded by six porphyrin units might involve massive equivalent of starting materials. Moreover, the reaction could generate a large number of products, which could lead to a long process of purification. To conclude, synthesis of linked porphyrin–triphenylenes through phenyl alkynes proved inefficient with dimerization being observed as the predominant reaction.
2.2 PORPHYRIN AND TETRABENZOTRIAzapORPHYRIN ARRAYS

2.2.1 Background and aims

Phthalocyanines (Pc) are man-made derivatives of porphyrin that incorporate nitrogen bridges and benzofusion. Hybrid structures that lie between porphyrins and phthalocyanines are interesting macrocycles since they offer the potential to bridge the properties of the two systems and provide new features within the field of macrocyclic chemistry. In this project we focus on tetrabenzotriazaporphyrin (TBTAP) which replaces one bridging nitrogen with an sp$^3$ carbon atom in meso-position of phthalocyanine (Figure 2.31). Therefore, functionalization of the meso-position could provide the ability to attach the macrocycle uniquely to surfaces or to synthesise more complex materials, such as multi macrocyclic systems.\textsuperscript{22}

![Molecular structures of Pc, TBP, TBTAP, TBDAP, and TBMAP](image.png)

Figure 2.31: Molecular structures of Pc, TBP and the hybrid macrocycles.
To the best of our knowledge, no previous study has attempted to combine porphyrin with TBTAP. Therefore, this project’s purpose was to synthesise unique chromophore dyads. These dyads combine porphyrin units to TBTAP (Figure 2.32). These new structures could have unique features making them useful in varied fields of materials chemistry, photochemistry, biology, and medicine.

Figure 2.32: Molecular structures of proposed targets 102-104.

The first unique dyad 102, is a porphyrin unit connected to TBTAP unit via phenyl at meso position. Therefore, this study aims to exploit newly developed synthetic chemistry by our group to construct this challenging dyad 102. To employ this new approach the unconventional precursor 103 is needed. The second new dyad 104 links porphyrin with TBTAP by a flexible alkyl chain. Therefore, unsymmetrical porphyrin is again needed. The synthesis of targets and their precursors will be discussed later.

2.2.2 Tetrabenzotriazaporphyrins (TBTAPs)

TBTAPs were first synthesised in 1938, but not much attention has been given to this system. The earliest attempt to synthesise TBTAPs was by Dent.\textsuperscript{22} CuTBTAP 108 was prepared by reacting phthalonitrile 105 with either methyleneephthalimidine 106 or phthalimidineacetic acid in the presence of a copper salt at 250 °C in chloronaphthalene to yield a green chromophore called CuTBTAP 108 (Scheme 2.28).\textsuperscript{22}
Later, Linstead synthesised TBTAP through treatment of phthalonitrile 105 with methyl magnesium iodide as a Grignard reagent or methyl lithium in cold ether and then the intermediate was further heated in a high boiling solvent such as quinoline, resulting in the formation of MgTBTAP 109 (Scheme 2.29). Magnesium can be removed via acid treatment, thus further metals such as copper, zinc, lithium and iron could be integrated. For example, Hoffman and co-workers later synthesised NiTBTAP by following the same route.

Scheme 2.29: Linstead’s first syntheses of TBTAPs.
The Linstead strategy was modified with alternative precursors to give TBTAPs in the late 1980s. A Bayer patent introduced nitrophthalimidine 112 as a meso-carbon provider to generate 113 (Scheme 2.30). Later, reactions of $t$-butyl substituted phthalimide 114 and iminoisoindoline 116 derivatives with malonic acid as precursors in the presence of zinc acetate were employed (Scheme 2.31).

Nevertheless, these studies were limited to synthesis of TBTAPs without the incorporation of meso-substituents. This could be due to the lack of further investigation at that time. However, Leznoff and McKeown reinvestigated and modified the Linstead method. A key feature of their attempts was the use of a solubilising $t$-butyl- or neo-pentyloxy-group on the phthalonitrile precursor. They then treated these phthalonitriles with a range of alkyl Grignard reagents. For example, hexadecylmagnesium chloride was reacted with neo-pentyloxyphthalonitrile 118 to generate \((\text{neo-PeO})_4\text{H}_2\text{TBTAP-}n\text{-C}_{13}\text{H}_{31}\) 119 (after demetallation) in 13% yield, in addition to significant quantities of phthalocyanine 120 by-product and trace quantities of TBDAPs 121 and/or 122 (Scheme 2.32).
Moreover, TBTAPs bearing a functionalized phenyl group on the meso-carbon atom are attractive and challenging materials. The meso-phenyl-TBTAP has been synthesised via the reaction between benzyl Grignard reagents and phthalonitrile. However, the reaction is low yielding and unsatisfactory due to the formation of a mixture of products (Scheme 2.33).  

\[ \text{Scheme 2.32: Synthesis of TBTAP 119.} \]

\[ \text{Scheme 2.33: Synthesis of the meso-phenyl-TBTAP 124.} \]
Overall, these known strategies for the synthesis of meso-substituted TBTAPs, which involve treatment of phthalonitrile with an organometallic reagent and refluxing in high boiling solvents, are capricious and low yielding. Another drawback with these approaches is the formation of other hybrids combined with the TBTAP. Therefore, our group has recently developed a versatile new synthesis of TBTAPs that allows incorporation of a functionalised phenyl substituent at the new meso-site. A key feature of the new approach is employment of aminoisooindoline 125 as precursor to prepare meso-phenyl-TBTAP. Aminoisooindoline 125 is the Ar-C analogue of diiminoisooindolines 111 (Figure 2.33).

![Molecular structures of diiminoisooindoline 111 and aminoisooindoline 125.](image)

The main reason for choosing aminoisooindoline 125 was that it would be incorporated during macrocycle formation. Therefore, the formation of other hybrids and unwanted by-products will be avoided. A copper-free Sonogashira coupling was a practical approach to synthesise the key precursors like 129. The synthesis of aminoisooindoline 129 was done according to methodology reported by Hellal and Cuny from 2-bromobenzonitrile 126 as shown in Scheme 2.34.

![Synthesis of the aminoisooindoline 129 via Sonogashira coupling.](image)
Precursor 129 can be then reacted with phthalonitrile 105 in order to synthesise TBTAP 130 using a magnesium template. A second major product was identified as the self-condensation compound 132 (Scheme 2.35).28

![Scheme 2.35: Efficient synthesis of meso-substituted magnesium TBTAP 130.](image)

We recognised that the availability of new TBTAPs through this chemistry could allow new multichromophore arrays to be targeted.

### 2.2.3 Synthesis of TPP-phenyl-TBTAP dyad 102

Scheme 3.36 illustrates the proposed strategy to prepare the unique target 102. This strategy relies on the reported methodology from our group to prepare TBTAPs. The first stage was to prepare the HCl salt of the bromoamidine 127 and then react it with porphyrin 77 to yield the precursor 103. Finally, treatment of 103 with phthalonitrile 105 would synthesise 102 (Scheme 2.36).
2.2.3.1 Synthesis of Aminoisoindoline porphyrin 103

Scheme 2.37: Synthesis of aminoisoindoline 103.

The copper-free Sonogashira coupling was investigated to synthesise aminoisoindoline porphyrin 103. A flask was charged with PdCl₂(CH₂CN)₂, BINAP, 1eq. amidine 127 and 1.2 eq. porphyrin 77. Then, the flask was attached with condenser and argon. Once the flask had been evacuated and back filled with argon three times, DBU and DMF were added (Scheme 2.37). The reaction mixture was refluxed at 120°C under argon. The reaction was monitored by TLC and MALDI-TOF MS during 3 h. The analyses showed promising results.
indicating the formation of aminoisoidolone porphyrin 103. Thus, the reaction was stopped and purified. After work-up and purification by column chromatography using EtOAc:PE as eluent, the product was isolated with yields of around 10%. Figure 2.34 shows the $^1$H NMR spectrum of aminoisoidolone porphyrin 103. The peak at around 7.12 ppm proved the formation of the new porphyrin 103. Moreover, HRMS (ESI) and UV-vis analyses confirm the formation of porphyrin and these spectra are shown below (Figure 2.35) (Figure 2.36).

Figure 2.34: $^1$H NMR of aminoisoidolone porphyrin 103 in acetone-$d_6$ (* = solvent).

Figure 2.35: HRMS (ESI) of aminoisoidolone porphyrin 103.
The reaction was repeated, but this time the reaction was left to heat for 4 h and followed by TLC. It was expected that porphyrin 77 would remain in the reaction mixture as it was in excess. Therefore, 1 eq of amidine 127 was added in order to consume the excess of porphyrin 77. Then, the reaction mixture was refluxed for further 24 h. However, the reaction was not complete, thus excess of amidine 127 was added. The reaction had not completed, even after 39 h. Consequently, the temperature was raised from 120°C to 140°C and the reaction left for further 4 h. The reaction was stopped and analysed by MALDI-TOF MS. After work-up and purification by column chromatography the product was isolated as before.

2.2.3.2 Attempted synthesis of TPP-phenyl-TBTAP 102

Scheme 2.38: Attempted synthesis of TPP-Phenyl-TBTAP dyad 102.

With the successful synthesis of aminoisooindoline porphyrin 103 we were now ready to investigate the construction of the target 102. Following the newly reported procedure by our group, a suspension of phthalonitrile and MgBr₂ in dry diglyme was stirred for 10 min at 220°C, in a preheated mantle, under an argon atmosphere. A solution of aminoisooindoline porphyrin 103 and phthalonitrile 105 in dry diglyme was added dropwise over 1 h using a syringe pump. Finally, a third solution of DABCO and phthalonitrile in dry diglyme was
added dropwise over 1 h. The reaction was heated for 0.5 h at 220 °C under an argon atmosphere (Scheme 2.38). Then, the solvent was removed under an argon stream while cooling. A 1:1 mixture of DCM:MeOH (20 ml) was added and the mixture sonicated. The solvents were removed under vacuum and the crude was purified by column chromatography. The obtained fractions were analysed by MALDI-TOF MS, yet the results did not confirm the formation of 102. However, the results indicated that the major product was the formation of Pc 131 (Figure 2.37).

Figure 2.37: MALDI-TOF MS of the reaction mixture (showing Pc 131 as a major product).

2.2.4 Bis (porphyrin)-aza-dibenzo-BODIPY (TPP$_2$-aza-dibenzo-BODIPY)

2.2.4.1 Background and aim

As mentioned in the general synthesis of TBTAPs, self-condensation of aminoisoidolines like 129 could be achieved giving compound 132 as major product. They were then employed as precursors for a new class of conjugated aza-(dibenzo)-BODIPY 133 by the Cammidge group. Typically aminoisoidolines 129 were refluxed in toluene for 2 h, and the obtained product was isolated by crystallisation from dichloromethane to yield aza-(dibenzo)-DIPY 132. then, aza-(dibenzo)-DIPYs was converted into aza-(dibenzo)BODIPYs 133 by simply reacting with BF$_3$·OEt$_2$ (Scheme 2.39).
Scheme 2.39: Synthesis of Aza-(dibenzo)BODIPY Derivatives 133.

Consequently, our group contributed this smooth and efficient self-condensation of aminoisoiindolines to form the π-extended aza-dibenzo-DIPY derivatives.\textsuperscript{29} Therefore, we aimed to employ related conditions to prepare a unique bis (porphyrin)-aza-dibenzo-BODIPY triad 134 which combines aza-dibenzo-BODIPY unit with two porphyrin units (Figure 2.38). Thus, it is possible to generate new features leading to potential applications such as light energy harvesting.

Figure 2.38: Molecular structure of proposed bis (porphyrin)-aza-dibenzo-BODIPY triad 134.

To prepare the target TPP\textsubscript{2}-aza-dibenzo-BODIPY 134, TPP\textsubscript{2}-aza-dibenzo-DIPY 135 is needed as precursor (Scheme 2.40)
2.2.4.2 Attempted synthesis of TPP$_2$-aza-dibenzo-DIPY 135

With the aminoisindoline porphyrin 103 in hand we were now ready to investigate its self-condensation. Following the previously developed conditions, a solution of aminoisindoline 103 was heated under reflux in toluene under N$_2$ (Scheme 2.41).

The reaction was followed by TLC and MALDI-TOF MS. After 4h the TLC showed no change. However, the MALDI-TOF MS showed new peaks at m/z = 876 and m/z = 934; they are not the expected peaks for the target triad 135 (Figure 2.39).
Since the aminoisoindoline porphyrin 103 had not been fully consumed, the reaction was refluxed for longer. However, the result of the reaction after 9 h and after 15 h did not show any of the desired product (Figure 2.40).

Consequently, the reaction was stopped and the solvent was evaporated. The solid obtained was purified by column chromatography using EtOAc:MeOH:H₂O (45:5:3). The formation
of self-condensation of aminoisindolines 135 was not achieved and only the starting material (porphyrin 103) was obtained as an identifiable product (Figure 2.41).

Figure 2.41: MALDI-TOF MS of fractions containing starting material porphyrin 103.

2.2.5 Synthesis Porphyrin-TBTAP Dyads linked through flexible chains

We finally turned our attention to the synthesis of a porphyrin-TBTAP dyad linked through a flexible alkyl spacer. To this end, we aimed to synthesise novel dyad 104. Scheme 2.42 illustrates the proposed strategy to achieve TPP-TBTAP dyad 104. Therefore, a magnesium TBTAP 135 and a novel porphyrin 136 are needed.
2.2.5.1 Synthesis of TBTAP component

Synthesis of Aminoisoindoline 138\textsuperscript{28}

\[ \text{amide 127} + \text{H}_3\text{CO} - \text{Ph} \rightarrow \text{NH}_2\text{Ph} + \text{OCH}_3 \]

Scheme 2.43: Synthesis of aminoisoindoline 138.

Aminoisoindoline 138 was prepared according to the reported procedure by Hellal and Cuny; a mixture of amidine 127, BINAP and PdCl\(_2\)(MeCN) was sealed in a microwave vessel and then purged and refilled with N\(_2\) three times. Then, a solution of 4-ethynylanisole...
and DBU in dry DMF was added. The mixture was stirred under N₂ for 5 min to give a clear yellow solution with a white solid. Finally, the mixture was irradiated in a microwave reactor at 120°C for 1 h (Scheme 2.43). After the work-up, the crude was purified by column chromatography using AcOEt → AcOEt:EtOH:H₂O (90:5:3) → AcOEt:EtOH:H₂O (45:5:3) as solvent gradient to afford a yellow semisolid that was recrystallised from PE:DCM (1:1) to yield aminoisoindoline 138 as yellow needles. The ¹H NMR spectrum is shown in Figure 2.42.

![Figure 2.42: ¹H NMR of aminoisoindoline 138 in CDCl₃ (* = solvent).](image)

**Synthesis of a magnesium TBTAP-OCH₃ 139**

![Scheme 2.44: Synthesis of a magnesium TBTAP-OCH₃ 139.](image)
With aminoisindoline 138 in hand, magnesium TBTAP-OCH₃ 139 was prepared following the reported procedure.²⁸ A suspension of phthalonitrile and MgBr₂ in dry diglyme was stirred for 10 min at 220°C, in a preheated mantle, under an argon atmosphere. A solution of aminoisindoline 138 and phthalonitrile 105 in dry diglyme was added dropwise over 1 hour using a syringe pump. Finally, a third solution of DABCO and phthalonitrile in dry diglyme was added dropwise over 1 hour. The reaction was heated for 0.5 h at 220°C under an argon atmosphere (Scheme 2.44). Then, the solvent was removed under an argon stream while cooling. A 1:1 mixture of DCM:MeOH (20 ml) was added and the mixture sonicated. The solvents were removed under vacuum and the crude product purified by two consecutive flash chromatographies, the first one using DCM → DCM:Et₃N (20:1) → DCM:THF:Et₃N (10:4:1) as eluent gradient, and the second one using PE:THF:MeOH (10:3:1) as eluent. Recrystallisation from acetone and EtOH gave magnesium TBTAP-OCH₃ 139.

Figure 2.43: ¹H NMR of a magnesium TBTAP-OCH₃ 139 in THF-d₈.

Synthesis of a magnesium TBTAP-OH 135²⁸

Scheme 2.45: Synthesis of a magnesium TBTAP-OH 135.
The next steps in this synthetic strategy involved demethylation of the methoxy group into a phenolic group. The phenolic groups is needed in order to react TBTAP-OH 135 with bromo alkyl porphyrin. Therefore, a solution of TBTAP 139 and MgI₂ in toluene was placed in a sealed tube under N₂ and stirred at 170 °C for 19 h. After cooling, MeOH was added and the mixture stirred for 10 minutes. The solvents were removed under vacuum but the crude product could not be purified and it appeared to have decomposed. Consequently, 139 was hydrolysed using the following method. A solution of TBTAP 139 in distilled DCM was stirred at 0 °C for 5 min under an argon atmosphere. Then, a solution of BBr₃ was added dropwise over 1 h using a syringe pump. After finishing the addition, the reaction mixture was left to warm to room temperature and stirred for further 1 h (Scheme 2.45). MeOH was added and the mixture sonicated for 5 min. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel using PE:THF:MeOH (10:3:1) as eluent to give 135 in addition to the corresponding TBTAP that had lost its magnesium ion 140 (Figure 2.44).

Figure 2.44: MALDI-TOF MS of fractions shows the formation of a magnesium TBTAP-OH 135 (top) and metal-free TBTAP-OH 140 (bottom).
Therefore, a mixture of metal-free TBTAP-OH 140 and MgBr₂ were refluxed in DMF for 3 h (Scheme 2.46). EtOAc was added and the mixture was washed with water. The organic phases were mixed and concentrated. The crude was purified by column chromatography, using PE:THF:MeOH (10:3:1) as eluent to isolate magnesium TBTAP-OH 135. The ¹H NMR spectrum shows the absence of methoxy group at 4.20 ppm which confirm the formation of TBTAP-OH 135 (Figure 2.45).

Scheme 2.46: Metalation of TBTAP-OH 140.

Figure 2.45: ¹H NMR of a magnesium TBTAP-OH 135 in THF-"d₈".
2.2.5.2 Synthesis of porphyrin component

**Synthesis of bromoalkoxyporphyrin 141**

Hydroxyphenylporphyrin 96 was reacted with 1,12-dibromododecane in the presence of K$_2$CO$_3$ then refluxed in acetone for 24 h (Scheme 2.47). The crude mixture was then precipitated with distilled water and collected by filtration. The solids obtained were washed with MeOH to leave a purple solid which was purified by column chromatography over silica gel using PE: THF 3:1 as eluent and a recrystallisation from DCM/MeOH. The MALDI-TOF MS shows the expected peak of porphyrin 141 $m/z = 878.09$ (Figure 2.46). However, the $^1$H NMR shows that it still has excess of 1,12-dibromododecane (Figure 2.47). Unfortunately, further purification of porphyrin 141 was unsuccessful despite several attempts using chromatography and recrystallisation. All isolated fractions/products contained mixtures of the desired porphyrin and dibromododecane so the final synthesis of dyad could not be attempted.

**Scheme 2.47:** Synthesis of bromoalkoxyporphyrin 141.
Figure 2.47: $^1$H NMR of porphyrin 141 in CDCl$_3$ showing contamination with dibromododecane.

2.2.6 Conclusion

The aim of this study was to investigate the synthesis of novel chromophore dyads and triads 102, 104 and 134 which are based on porphyrin and TBTAP components. The first aim was to synthesise porphyrin–phenyl-TBTAP 102. A precursor porphyrin bearing aminoisooindoline functionality was successfully prepared 103. However, it could not be converted to either the porphyrin–phenyl-TBTAP 102 dyad or porphyrin-azaBODIPY-porphyrin triad 134. On the other hand, the targeted strategy toward the synthesis of Porphyrin-TBTAP dyads linked through flexible chains (104) remains promising. Magnesium TBTAB-OH 135 was synthesised as one important reactant. However, the unfortunate choice of bromododecyloxyporphyrin 141, meant the synthesis of the desired dyad could not be achieved within this project because it could not be separated from excess dibromododecane. However, simple modification of the strategy (e.g using bromododecanol) will allow the compounds to be prepared in the future.
2.2.7 References


Chapter 3

Experimental Methods
3.1 EXPERIMENTAL METHODS

3.1 GENERAL INFORMATION

Reagents and solvents were obtained from commercial sources and used without further purification, with the exception of: THF was freshly distilled from sodium and benzophenone when specified. Dichloromethane, pyrrole, trimethylamine and toluene were dried over CaH₂. CHCl₃ with 0.75% ethanol as preservative was purchased from Fisher chemical and dried over K₂CO₃. Phthalonitrile was recrystallised from hot xylene. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with Alugram® Sil G/UV254 (Macherey-Nagel) and was visualised with UV light and by staring with 0.1% ninhydrin in EtOH when necessary. Column chromatography: was carried out on silica gel Davisil ® LC60A 40-63 micron (Grace GmbH & Co). Brine is a saturated aqueous solution of sodium chloride and water refers to distilled water. Evaporation of solvent was carried out on a Büchi rotary evaporator at reduced pressure. NMR spectra were recorded on a Bruker 500 (500 MHz for ¹H NMR and 125.7 MHz for ¹³C NMR) and at room temperature. The residual solvent peaks were used as references. ¹H and ¹³C NMR signals are reported in ppm. The coupling constants J are given in Hertz. IR spectra were recorded using a Perkin-Elmer Spectrum BX FT-IR spectrometer. Absorption bands are given in cm⁻¹. MALDI-TOF mass spectra were obtained by using a Shimadzu Biotech Axima instrument. HRMS analyses were performed by the EPSRC National Mass Spectrometry Service Centre at Swansea University. Melting points were measured using a Reichert Thermovar microscope with a thermopar based temperature control. UV-vis spectra were recorded on Perkin Elmer Lamda 35 UV/VIS. Differential scanning calorimetry was performed on a TA DSC instrument with a heating/cooling rate of 20°C min⁻¹.
3.2 SYNTHESIS OF TRIPHENYLENE COMPONENTS AND THEIR PRECURSORS

3.2.1 Synthesis of 1,2-dibromo-4,5-dimethoxybenzene 79

A solution of 1, 2-dimethoxybenzene 78 (5 g, 36.2 mmol) in DCM (100 mL) was cooled to 0 °C. Bromine (12.7 g, 79.5 mmol) was added dropwise and the solution stirred for 2 h at 0 °C. Then, a solution of sodium metabisulfite was added and the organic layer separated. The aqueous layer was extracted with DCM (3 x 100). The combined organic phases were washed with water (50 mL) and brine (50 mL), and dried over Na₂SO₄. The solvents were evaporated and the solid obtained was then recrystallised from isopropanol to give compound 79 (8.32 g, 78%). Mp: 91 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.46 (s, 2H), 4.06 (s, 6H). ¹³C-NMR (126 MHz, CDCl₃): δ 149.1, 116.1, 114.9, 56.4. These data are consistent with literature values.¹

3.2.2 Synthesis of 4-methoxyphenyl boronic acid 82

Magnesium turnings (1.92 g, 80 mmol) and a crystal of iodine were stirred as a solid for 10 min under nitrogen atmosphere. Then, dry THF (100 mL) and 1,2-dibromomethane (0.5 mL) were added and the mixture was stirred for further 10 min. Next, a solution of 4-bromoanisole 80 (10.0 g, 53.5 mmol) in dry THF (5 mL) was added dropwise to the mixture. After addition was completed, the reaction mixture was refluxed for 1 h to the give the Grignard reagent 81. The prepared Grignard reagent 81 was cooled down to room
temperature and then slowly transferred to a solution of trimethyl borate (10.9 g, 105 mmol) in dry THF (100 mL) at -78 °C by syringe. The reaction mixture was stirred and allowed to warm up to room temperature overnight. A solution of 2 M HCl (100 mL) was added slowly and the mixture was extracted with diethyl ether (3 x 100 mL). The organic extracts were dried over MgSO₄. The solvent was evaporated and the solid obtained was washed with petroleum ether. The crude product was then recrystallised from water to give the title compound as a white solid (5.10 g, 63%). ¹H NMR (500 MHz, DMSO-d₆): δ 7.82 (s, 2H), 7.73 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H). ¹³C NMR (126 MHz, DMSO-d₆): δ 160.9, 135.8, 112.9, 54.8. These data are consistent with literature values.

3.2.3 Synthesis of tetramethoxyterphenyl 83

According to the procedure used by Cammidge and Gopee, a mixture of boronic acid 82 (4.10 g, 27.0 mmol), 1,2-dibromo-3,4-dimethoxybenzene 79 (2 g, 6.75 mmol), Na₂CO₃ (2.14 g, 0.02 mmol), PdCl₂ (0.19 g, 1.08 mmol) and PPh₃ (1.13 g, 4.32 mmol) was refluxed in a mixture of toluene, ethanol and water (3:3:1, 70 mL). The solvent was evaporated and water 200 ml was added. The mixture was extracted with DCM (3 x 150 mL) the solvent was evaporated to obtain a dark brown oil. This crude product was purified by column chromatography using PE:DCM as eluent to give terphenyl 83 as a white solid. (2.11 g, 89%). Rₚ: 0.32 PE:DCM (4:1). Mp: 144 °C. ¹H NMR (500 MHz, acetone-d₆): δ (ppm) 7.04 (d, 2 H, J = 10 Hz), 6.91 (s, 2 H), 6.78 (d, 2 H, J = 10 Hz), 3.87 (s, 3 H), 3.76 (s, 3 H). ¹³C NMR (126 MHz, acetone-d₆): δ (ppm) 159.2, 149.4, 135.0, 133.3, 131.8, 115.1, 114.2, 56.2, 55.4. UV-vis (DCM): λ max (nm) (ε (L mol⁻¹ cm⁻¹)) 227 (5.1 X 10⁴), 290 (1.6 X 10⁴). IR (NaCl), ν (cm⁻¹): 3367, 2922, 2851, 1608, 1499, 1463, 1291, 1236, 1203, 1177, 1037, 832, 809. MALDI-TOF MS: m/z = 350.32 [M]+ (100%) [C₂₂H₂₂O₄].
3.2.4 Synthesis of tetramethoxytriphenylene 84

Cyclisation was achieved using Artal et al. procedure.\textsuperscript{5} Terphenyl 83 (1.40 g, 4 mmol) was stirred in a mixture of DCM (70 mL) and CH\textsubscript{3}NO\textsubscript{2} (3.5 mL) at room temperature. Then, FeCl\textsubscript{3} (1.93 g, 12 mmol) was added and the mixture stirred for a further 2 h. The reaction mixture was poured onto cold methanol (100 mL) and left over night. The precipitate was collected by filtration as a white solid (0.50 g, 36%). R\textsubscript{f}: 0.19 PE:DCM (4:1). Mp: 175\textdegree C. 

\textsuperscript{1}H NMR (500 MHz, acetone-\textit{d}_6): \(\delta\) (ppm) 8.62 (d, \(J = 9.1\) Hz, 2H), 8.13 (d, \(J = 2.6\) Hz, 2H), 8.08 (s, 2H), 7.29 (dd, \(J = 9.1, 2.6\) Hz, 2H), 4.06 (s, 6H), 4.04 (s, 6H). \textsuperscript{13}C NMR (126 MHz, acetone-\textit{d}_6): 159.5, 150.6, 131.1, 126.0, 125.1, 124.2, 117.2, 106.9, 105.8, 56.4, 56.0. UV-vis (DCM): \(\lambda_{\text{max}}\) (\(\varepsilon\) (L mol\textsuperscript{-1} cm\textsuperscript{-1})) 229 (5.7 X 10\textsuperscript{4}), 265 (1.1 X 10\textsuperscript{5}), 272 (1.5 X 10\textsuperscript{5}), 306 (3.0 X 10\textsuperscript{4}), 354 (3.8 X 10\textsuperscript{5}), 374 (2.9 X 10\textsuperscript{5}). IR (NaCl), \(\nu\) (cm\textsuperscript{-1}): 2921, 2855, 1659, 1615, 1507, 1513, 1214, 1164, 763. MALDI-TOF MS: 348 [M]\textsuperscript{+} (100%) [C\textsubscript{22}H\textsubscript{20}O\textsubscript{4}]. HRMS (ESI) [C\textsubscript{22}H\textsubscript{21}O\textsubscript{4}] [M+H]\textsuperscript{+}: Calc: 349.1434; Found: 349.1431.
3.2.5 Synthesis of 2,7-Dibromo-3,6,10,11-Tetramethoxytriphenylene 76

According to the procedure of Cammidge and Gopee, triphenylene 84 (0.5 g, 1.44 mmol) was stirred in DCM (10 mL) at 0°C. Bromine (0.454 g, 2.87 mmol) was added dropwise and the solution stirred for a further 2 h. A solution of sodium metabisulfite was added and the organic layer separated. The aqueous layer was extracted with DCM (3 x 100 mL). The combined organic extracts were washed with brine and dried over Na₂SO₄. The solvents were evaporated to give the title compound which was recrystallised from isopropanol (0.40, 54%). Rf: 0.57 (PE:EtOAc) (2:1). ¹H NMR (500 MHz, CDCl₃): δ 8.43 (s, 2H), 7.72 (s, 2H), 7.53 (s, 2H), 4.13 (s, 6H), 4.09 (s, 6H). ¹³C NMR (126 MHz, CDCl₃): δ 154.2, 149.4, 128.7, 128.0, 125.1, 122.2, 113.3, 104.6, 103.8, 56.5, 56.2. UV-vis (DCM): λ max (nm) (ε (L mol⁻¹ cm⁻¹)) 236 (1.8 X 10⁴), 259 (4.0X 10⁴), 267 (6.0 X 10⁴), 277 (1.0 X 10⁵), 310 (2.1 X 10⁴), 331 (9.8 X 10³). IR (NaCl), ν (cm⁻¹): 2923, 2860, 1602, 1495, 1459, 1408, 1240, 1203, 1028, 1047, 827, 860, 695. MALDI-TOF MS: 503.52 [M]+ (24%) [C₂₂H₁₉Br₂O₄]. HRMS (ESI) [C₂₂H₁₉Br₂O₄][M+H]+: Calc.: 504.9645; Found: 504.9638 (isotope pattern see page 51).
3.3 SYNTHESIS OF PORPHYRIN COMPONENTS AND THEIR PRECURSORS

3.3.1 Synthesis of 4-(3-methyl-3-hydroxy-1-butyn-1-yl) benzaldehyde 87

\[ \text{OHC} - \text{C} - \text{OH} \]

A mixture of 4-bromobenzaldehyde 85 (6.02 g, 32.54 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.222 g, 0.34 mmol), CuI (0.051 g, 0.27 mmol), 2-methyl-3-butyne-2-ol 86 (3.8 mL, 38.8 mmol) and dry Et\(_3\)N (65 mL) was refluxed under N\(_2\) for 4 h at 70 °C. After the reaction was completed, the reaction mixture was passed through a silica pad using hexane: EtOAc (9:1) as eluent. The solvent was evaporated to give aldehyde 87 as a yellow oil (5.99 g, 98%). Rf: 0.43 hexane: EtOAc (9:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 10.00 (s, 1H), 7.82 (d, 2H, \(J\) = 10 Hz), 7.56 (d, 2H, \(J\) = 10 Hz), 2.09 (s, 1H), 1.63 (s, 6H). \(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) (ppm) 135.6, 132.3, 129.64, 129.20, 97.92, 81.50, 65.81, 31.46.

3.3.2 Synthesis of unsymmetrically substituted porphyrin 88

A solution of aldehyde 87 (4.89 g, 26.0 mmol), benzaldehyde 2 (8.29 g, 78 mmol) and pyrrole 3 (7.01 g, 104 mmol) in CHCl\(_3\) (1500 mL) was treated with BF\(_3\).OEt\(_2\) (2.8 mL, 22 mmol). The mixture was stirred at room temperature for 1 h, followed by addition of chloranil (19.4 g, 78 mmol) and stirring for 1.5 h. The solvent was evaporated in vacuo and reaction mixture was passed through silica pad (CHCl\(_3\)) and purified by column chromatography using toluene as eluent to obtain porphyrin 88 as a purple solid 2.70 g.
Chapter 3 Experimental Methods

15%). Rf: 0.2 (DCM). Mp: 229 °C. 1H NMR (500 MHz, CD2Cl2): δ 8.88 – 8.84 (m, 8H), 8.24 – 8.21 (m, 7H), 8.20 – 8.17 (m, 2H), 7.85 – 7.75 (m, 13H), 2.21 (s, 1H), 1.73 (s, 7H), -2.84 (s, 2H). 13C NMR (126 MHz, CDCl3): δ 158.1, 143.9, 143.1, 142.2, 137.2, 134.7, 134.6, 130.2, 127.9, 126.9, 126.8, 124.6, 123.6, 121.9, 120.7, 113.8, 112.1, 97.4, 81.8, 65.9, 31.6. MALDI-TOF MS: m/z = 696.85 [M]+ (100%) [C49H36N4O].

3.3.3 Synthesis of zinc porphyrin 89

A solution of porphyrin 88 (1.27 g, 1.8 mmol) in DCM (140 mL) was heated then treated with a solution of Zn(OAc)2 (10.7 g, 55 mmol) in MeOH (48 mL). The mixture was refluxed for 1h. After evaporation, the reaction mixture was passed through a small pad of dry silica using DCM as eluent to give the porphyrin 89 as a purple solid (1.36 g, 97%). Rf: 0.16 (DCM). Mp: > 300 °C. 1H NMR (500 MHz, CD2Cl2) δ 8.97 – 8.93 (m, 8H), 8.23 – 8.20 (m, 6H), 8.18 (d, J = 8.0 Hz, 2H), 7.84 – 7.74 (m, 11H), 2.22 (s, 1H), 1.72 (s, 6H). 13C NMR (126 MHz, CDCl3): δ 158.1, 143.9, 143.0, 142.2, 137.2, 134.7, 134.6, 130.2, 127.9, 126.9, 126.7, 124.6, 123.6, 121.8, 120.5, 113.8, 112.1, 97.4, 81.8, 65.9, 31.6. MALDI-TOF MS: m/z = 758.01 [M]+ (100%) [C49H34N4OZn].
3.3.4 Synthesis of zinc porphyrin \(77^6\)

A mixture of porphyrin \(89\) (1.40 g, 1.83 mmol) and \(\text{NaOH}\) (2.21 g, 55 mmol) in dry toluene (75 mL) was refluxed under nitrogen. The reaction was followed using TLC. After the completion, the reaction mixture was cooled and directly poured onto a dry silica pad using DCM as eluent to afford porphyrin \(77\) as a purple solid (1.71 g, 91%). \(R_f: 0.85\) (DCM). Mp: >300°C. \(^1\)H NMR (500 MHz, acetone-\(d_6\)): \(\delta 8.91 – 8.84\) (m, 8H), 8.26 – 8.19 (m, 8H), 7.93 (d, \(J = 8.1\) Hz, 2H), 7.85 – 7.77 (m, 9H), 3.90 (s, 1H). \(^13\)C NMR (126 MHz, acetone- \(d_6\)): \(\delta 150.09, 150.03, 150.01, 149.6, 143.3, 134.5, 134.3, 2x 131.8, 131.61, 131.58, 131.3, 2x 130.1, 128.6, 127.5, 126.5, 120.9, 120.8, 81.0, 79.2\). MALDI-TOF MS: \(m/z = 702.12\) [M]\(^+\) (54%) [\(C_{46}H_{28}N_{4}Zn\)].

3.3.5 Synthesis of porphyrin \(96^7\)

4-Hydroxybenzaldehyde \(95\) (3.05 g, 25.00 mmol) and benzaldehyde \(2\) (7.94 g, 75.00 mmol) were dissolved in propionic acid (250 mL) and to this was added pyrrole \(3\) (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 was left to precipitate overnight. The precipitation was filtered off and purified by column chromatography on silica eluting with
PE:DCM (7:3) followed by 100% DCM to yield the porphyrin 96 as a purple solid (0.62 g, 4%). Rf: 0.32 (PE:EtOAc) (2:1). Mp: > 300 °C. 1H NMR (400 MHz, CDCl3): δ 8.90 – 8.81 (m, 8H), 8.24 – 8.19 (m, 6H), 8.08 (d, J = 8.5 Hz, 2H), 7.80 – 7.71 (m, 9H), 7.22 (d, J = 8.5 Hz, 2H), 5.30 (s, 1H), -2.77 (s, 2H). MALDI-TOF MS: 631.52 [M]+ (100%) [C44H30N4O].

3.3.6 Synthesis of zinc porphyrin 98

A solution of porphyrin 96 (0.42 g, 0.67 mmol) in DCM (35 mL) was heated then treated with solution of Zn(OAc)2 (1.1 g, 6 mmol) in MeOH (6 mL). The mixture was refluxed for 30 min. After evaporation, the reaction mixture was purified by column chromatography on silica using DCM as eluent to give the porphyrin 98 (0.39 g, 86%). Rf: 0.83 (PE:acetone) (2:1). Mp: > 300 °C. 1H NMR (500 MHz, DMSO-d6): δ 9.86 (s, 1H), 8.86 (d, J = 4.6 Hz, 2H), 8.79 – 8.76 (m, 6H), 8.21 – 8.17 (m, 6H), 7.98 (d, J = 10.0 Hz, 2H), 7.83 – 7.78 (m, 9H), 7.19 (d, J = 10.0 Hz, 2H). MALDI-TOF MS: m/z = 692.06 [M]+ (100%) [C44H28N4OZn].

3.3.7 Synthesis of porphyrin triflate 97
Following the reported procedure,\(^8\) hydroxyphenylporphyrin \(96\) (0.5 g, 0.79 mmol) was dissolved with in dry DCM (50 mL) and lutidine (0.14 mL, 0.12 mmol) at -78 °C under nitrogen. Trifluoromethanesulphonic acid anhydride (0.3 mL, 1.98 mmol) was added dropwise and the reaction allowed to warm to room temperature and left to stir overnight. Water was added and the mixture was extracted with DCM (3 x 100 mL). The combined organic phase was washed with brine and dil. HCl and dried over MgSO\(_4\). The solvent was evaporated and the obtained crude was purified by column chromatography on silica eluting with PE:DCM (2:1) followed by PE:DCM (2:3) to gain porphyrin \(97\) as a purple solid (0.41 g, 67\%). \(R_f\): 0.32 (PE:DCM) (3:2). \(\text{Mp:} \ 180^\circ\text{C}\).

\(1^H\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.90 – 8.83 (m, 6H), 8.76 (d, \(J = 4.6\) Hz, 2H), 8.31 (d, \(J = 8.5\) Hz, 2H), 8.24 – 8.20 (m, 6H), 7.81 – 7.73 (m, 9H), 7.69 (d, \(J = 8.5\) Hz, 2H), -2.79 (s, 2H). \(1^C\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 156.0, 153.2, 149.7, 144.6, 144.2, 144.1, 143.9, 143.7, 136.0, 134.7, 133.0, 131.6, 129.6, 128.6, 128, 126.9, 120.6, 119.8. UV-vis (DCM): \(\lambda\) max (nm) (\(\varepsilon\) (L mol\(^{-1}\) cm\(^{-1}\))) 417 (4.09 X 10\(^5\)), 515 (2.2 X 10\(^5\)), 551 (8.4 X 10\(^3\)), 590 (6.6 X 10\(^3\)), 646 (4.1 X 10\(^3\)), 719 (2.2 X 10\(^3\)), 730 (2.1 X 10\(^3\)). IR (NaCl), \(\nu\) (cm\(^{-1}\)): 3318, 3056, 3031, 1597, 1559, 1496, 1474, 1426, 1213, 1140, 966, 887, 800, 731, 701. MALDI-TOF MS: \(m/z\) = 762.94 [M]\(^+\) (100\%) [C\(_{45}\)H\(_{29}\)F\(_3\)N\(_4\)O\(_3\)S].

HRMS (ESI) [C\(_{45}\)H\(_{29}\)F\(_3\)N\(_4\)O\(_3\)S] [M]\(^+\) Calc: 762.1912; Found: 762.1920.

3.3.8 Synthesis of zinc porphyrin triflate \(93\)

A solution of porphyrin \(97\) (0.12 g, 0.16 mmol) in DCM (25 mL) was heated then treated with solution of Zn(OAc)\(_2\) (0.14 g, 0.79 mmol) in MeOH (5 mL). The mixture was refluxed for 30 min. After evaporation, the reaction mixture was passed through a small pad of dry silica using DCM as eluent to give the porphyrin \(93\) (0.1 g, 77\%). \(R_f\): 0.16 (PE:DCM) (3:2). \(\text{Mp:} > 300^\circ\text{C}\). \(1^H\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 9.00 – 8.93 (m, 6H), 8.86 (d, \(J = 4.6\) Hz, 2H), 8.31 (d, \(J = 8.4\) Hz, 2H), 7.82 – 7.71 (m, 9H), 7.68 (d, \(J = 8.4\) Hz, 2H), 8.24 – 8.18 (m, 6H).
3.3.9 Synthesis of porphyrin 141

Following to the method in literature,9 a solution of porphyrin 96 (0.1 g, 0.16 mmol) and 1,12-dibromododecane (1.04 g, 3.17 mmol) were dissolved in acetone (20 mL). Then, K2CO3 (0.07 g, 0.51 mmol) was added and the reaction mixture was refluxed for 24 h. The crude mixture was then precipitated with distilled water (50 mL) and filtered. The solids obtained were washed with MeOH to leave a purple solid. After column chromatography of the obtained solid over silica gel using PE:THF (3:1) as eluent to give the porphyrin 141 and recrystallisation (DCM:PE). Rf: 0.62 (PE:THF) (3:1) contaminated with dibromoundecane. (For 1H NMR see page 93).
3.4 SYNTHESIS OF PORPHYRIN TRIPHENYLENE DYAD 90

Porphyran triphenylene dyad 90 was isolated as a side product from following methods:

**Method A:** according to Hellal and Cuny, a mixture of triphenylene bromide 76 (0.034 g, 0.06 mmol), porphyrin 77 (0.11 g, 0.16 mmol), BINAP (0.002 g, 0.003 mmol) and PdCl\(_2\)(MeCN)\(_2\) (0.001 g, 0.003 mmol) were placed in a flask with a magnetic bar and then attached to a condenser and refilled with argon three times. Then, DBU (0.02 g, 0.16 mmol) and dry DMF (0.3 mL) were added. The mixture was refluxed under argon for at 120°C for 2.30 h. After that, the porphyrin 77 (0.05 g, 0.07 mmol) was added and the reaction mixture was refluxed for 2 days. After cooling, EtOAc (20 mL) was added and the mixture was washed with water (10 mL) and brine (10 mL). The organic layer was dried over MgSO\(_4\), filtered and concentrated. The crude was purified by column chromatography using PE:EtOAc as eluent (2:1) → (1:1) → (1:2) to give dyad 90 (0.02 g, 25%).

**Method B:** a mixture of triphenylene bromide 76 (0.029 g, 0.05 mmol), porphyrin 77 (0.05 g, 0.06 mmol), BINAP (0.002 g, 0.003 mmol) and PdCl\(_2\)(MeCN)\(_2\) (0.001 g, 0.003 mmol) was sealed in a microwave vessel with a magnetic bar and then purged and refilled with argon three times. Then, DBU (0.02 g, 0.14 mmol) and dry DMF (0.2 mL) were added. The mixture was stirred under argon for 10 min. Finally, the mixture was irradiated in a microwave reactor at 120°C for 1 h. After cooling, EtOAc (20 mL) was added and the mixture was washed with water (10 mL) and brine (10 mL). The organic layer was dried (MgSO\(_4\)), filtered and concentrated. The crude was purified by column chromatography using PE:EtOAc as eluent (2:1) → (1:1) → (1:2) to obtain dyad 90 (0.01, 17%).

**Method C:** Cammidge’s procedure was applied. The triphenylene bromide 76 (0.027 g, 0.05 mmol), CuI (0.001 g, 0.006 mmol), Pd(PPh\(_3\))Cl\(_2\) (0.012 g, 0.018 mmol) and PPh\(_3\) (0.03 g, 0.11 mmol) were dissolved in dry Et\(_3\)N (30 mL) in sealable tube which was then purged and refilled with argon three times and heated to 100°C for 5 min. After that the porphyrin (0.5 g, 0.7 mmol) was then added. The mixture was
heated at 100°C for 24 h. The mixture was cooled, MeOH (20 mL) was added and the precipitate obtained was filtered off. The solid was dissolved in DCM (50 mL) and water was added and the organic layer extracted with DCM (3 x 20 mL). The organic extracts were dried (MgSO₄) and the solvent was removed in vacuo. The crude product was purified by column chromatography eluting with PE:EtOAc. The obtained solid was recrystallised from PE: EtOAc as a purple solid. Rf: 0.38 (PE:EtOAc) (2:1). Mp: > 300°C. ¹H NMR (500 MHz, acetone-d₆): δ (ppm) 8.99 (s, 1H), 8.95 (d, 2H, J = 5 Hz), 8.93 (s, 1H), 8.90 (d, 2H, J = 5 Hz), 8.86 (s, 4H), 8.32 (d, 2H, J = 10 Hz), 8.30 (s, 2 H), 8.24-8.22 (m, 7 H), 8.14 (s, 1H), 8.05 (d, 2H, J = 10 Hz), 7.82-7.79 (m, 9 H), 4.27 (s, 3 H), 4.20 (s, 3 H), 4.15 (s, 3 H), 4.12 (s, 3 H).

UV-vis (DCM): λmax (nm) (ε (L mol⁻¹ cm⁻¹)) 228 (2.1 X 10⁵), 278 (2.0 X 10⁴), 310 (1.8 X 10⁴), 355 (1.1 X 10⁵), 421 (3.7 X 10⁵), 547 (1.7 X 10⁵), 588 (2.5 X 10³). IR (NaCl), ν (cm⁻¹): 2920, 2850, 2331, 1702, 1599, 1601, 1464, 1440, 1415, 1205, 1002, 994, 832, 796, 718, 701. MALDI-TOF MS: m/z = 1126.67 [M]⁺ (12%) [C₆₈H₄₅BrN₄O₄Zn].

### 3.5 SYNTHESIS OF o-BROMOBENZAMIDINE HYDROCHLORIDE 127

![Diagram](image)

A 250 mL flask was charged with 1 M LiN(SiMe₃)₂ in anhydrous THF (25 mL). Then, a solution of o-bromobenzonitrile 126 in dry THF (2 mL) was added and the reaction mixture was stirring at ice bath for 4 h. After that, 6N HCl (in iPrOH, 15 mL) was added dropwise.
The crude reaction mixture was stirred at room temperature overnight. The precipitated product was filtered, washed with diethyl ether (2 x 10 mL) to yield amidine 127 (5.3 g, 98%). $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 8.32 (s, 1H), 7.85 – 7.81 (m, 1H), 7.66 – 7.52 (m, 3H). $^{13}$C NMR (126 MHz, DMSO-d$_6$): $\delta$ 133.2, 133.0, 129.8, 128.0, 123.00, 121.2, 119.5.

### 3.6 SYNTHESIS OF AMINOISOINDOLINE PORPHYRIN 103

The synthesis of the proposed dyad was performed according to the procedure of Hellal and Cuny.$^{10}$ A mixture of amidine 127 (0.012 g, 0.05 mmol), porphyrin 77 (0.04 g, 0.06 mmol), BINAP (0.002 g, 0.003 mmol) and PdCl$_2$(MeCN)$_2$ (0.001 g, 0.003 mmol) was placed in a flask with a magnetic bar and then attached to condenser and refilled with argon three times. Then, DBU (0.02 g, 0.13 mmol) and dry DMF (0.3 mL) were added. The mixture was refluxed under argon at 120°C for 3 h. After cooling, EtOAc (20 mL) was added and the mixture washed with water (10 mL) and brine (10 mL) three times. The organic layer was dried (MgSO$_4$), filtered and concentrated. The crude was purified by column chromatography using PE:EtOAc (1:2) as eluent to yield porphyrin 103 as a purple solid (0.004 g, 10%). $R_f$: 0.33 (PE:EtOAc) (2:1). M.p: > 300°C. $^1$H NMR (500 MHz, acetone-d$_6$): $\delta$ (ppm) 9.01 (d, 2H, $J = 5$ Hz, 8.89 (d, 2H), 8.86 (s, 2H), 8.72 (d, 2H, $J = 5$ Hz), 8.24-8.21 (m, 6 H), 8.20 (d, 2H, $J = 10$ Hz), 8.05 (d, 1H, $J = 5$ Hz), 7.88 (d, 1H, $J = 10$ Hz), 7.83-7.78 (m, 9H), 7.56 (td, 1H, $J = 10$ Hz, $J = 5$ Hz), 7.47 (td, 1H, $J = 10$ Hz, $J = 5$ Hz), 7.12 (s, 1H). $^{13}$C NMR (126 MHz, acetone-d$_6$): $\delta$ (ppm) 151.1, 150.97, 150.95, 144.4, 135.4, 135.3, 132.6, 132.5, 132.44, 132.43, 129.6, 128.3, 128.2, 127.4, 121.6, 121.5, 121.5, 120.6. UV-vis (DCM): $\lambda$ max (nm) (ε (L mol$^{-1}$ cm$^{-1}$)) 230 (7.0 X 10$^5$), 277 (1.1 X 10$^5$), 421 (5.5 X 10$^5$), 508 (5.9 X 10$^5$), 588 (8.4 X 10$^5$), 591(8.2 X 10$^5$). IR (NaCl), $\nu$ (cm$^{-1}$): 3357, 3060, 1683, 1598, 1525, 1486, 1441, 1378, 1339, 1245, 1205, 102, 994, 797, 718, 701. MALDI-TOF
MS: $m/z = 818.61 [M]^+ (100\%) \quad [C_{53}H_{34}N_6Zn]$. HRMS (ESI) $[C_{53}H_{36}N_6Zn] [M+H]^+ \text{Calc: } 819.2207; \text{Found: } 819.2209$.

### 3.7 SYNTHESIS OF TBTAPs AND THEIR PRECURSORS

#### 3.7.1 Synthesis of aminoisooindoline 138

A mixture of amidine 127 (0.71 g, 3 mmol), BINAP (0.102 g, 0.165 mmol) and PdCl$_2$(MeCN)$_2$ (0.039 g, 0.15 mmol) was sealed in a microwave vessel with a magnetic bar and then purged and refilled with N$_2$ three times. Then, a solution of 4-ethynylanisole 137 (0.48 g, 3.6 mmol) and DBU (1.14 g, 7.5 mmol) in dry DMF (12 ml) was added. The mixture was stirred under N$_2$ for 5 min to give a clear yellow solution with a white solid. Finally, the mixture was irradiated in a microwave reactor at 120°C for 1 h. After cooling, EtOAc (50 mL) was added and the mixture washed with a saturated solution of NaHCO$_3$ (75 mL) thrice. The organic layer was dried over MgSO$_4$, filtered and concentrated. The crude was finally purified by column chromatography using EtOAc $\rightarrow$ EtOAc:EtOH:H$_2$O (90:5:3) $\rightarrow$ EtOAc:EtOH:H$_2$O (45:5:3) as solvent gradient to afford a yellow semisolid that was recrystallised from a PE:DCM (1:1) to yield the aminoisooindoline 138 as yellow needles (0.50 g, 63%).

$R_f: 0.48 \quad \text{EtOAc:EtOH:H}_2\text{O} (45:5:3)$. Mp: 177°C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 7.7$ Hz, 1H), 7.49 (td, $J = 7.7$, 0.8 Hz, 1H), 7.36 (td, $J = 7.7$, 0.8 Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.74 (s, 1H), 3.78 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 164.4, 159.4, 143.0, 132.2, 130.4, 130.4, 129.4, 129.4, 127.1, 119.8, 119.2, 115.9, 114.2, 55.5. MALDI-TOF MS: $m/z = 250.95 [M]^+ (100\%) \quad [C_{16}H_{14}N_2O]$.
3.7.2 Synthesis of a magnesium TBTAP-OCH$_3$ 139$^{13}$

A suspension of phthalonitrile 105 (0.154 g, 1.2 mmol) and MgBr$_2$ (0.110 g, 0.6 mmol) in dry diglyme (0.5 mL) was stirred for 10 min at 220°C, in a preheated mantle, under an argon atmosphere. Then, a solution of aminoisoindoline 138 (0.100 g, 0.4 mmol) and phthalonitrile 105 (0.051 g, 0.4 mmol) in dry diglyme (1 mL) was added dropwise over 1 hour using a syringe pump. Finally, a third solution of DABCO (0.068 g, 0.6 mmol) and phthalonitrile 105 (0.051 g, 0.4 mmol) in dry diglyme (0.5 mL) was added dropwise over 1 hour. After that, the reaction mixture was heated for 30 min at 220°C under an argon atmosphere. Then, the solvent was removed under an argon stream while cooling. Following that, a 1:1 mixture of DCM:MeOH (20 mL) was added and the mixture was sonicated. The solvents were evaporated under vacuum and the crude purified by two consecutive flash chromatographies, the first one using DCM → DCM:Et$_3$N (20:1) → DCM:THF:Et$_3$N (10:4:1) as eluent gradient, and the second one using PE:THF:MeOH (10:3:1) as eluent. The obtained product was recrystallised from acetone and EtOH to give a magnesium TBTAP-OCH$_3$ 139 as purple crystals (0.102 g, 40%). Rf: 0.51 PE:THF:MeOH (10:3:1). $^1$H NMR (500 MHz, THF-d$_8$): $\delta$ 9.59 (d, $J = 7.6$ Hz, 2H), 9.53 – 9.49 (m, 4H), 8.19 – 8.17 (m, 4H), 8.04 (d, $J = 8.5$ Hz, 2H), 7.93 – 7.89 (m, 2H), 7.61 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 3H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 4.20 (s, 3H). MADLI-TOF MS: $m/z$ = 641.72 [M]$^+$ (100%) [C$_{40}$H$_{23}$MgN$_7$O].
3.7.3 Synthesis of a magnesium TBTAP-OH 135

Method A: a solution of a magnesium TBTAP-OCH₃ 139 (0.042 g, 0.062 mmol) in dry DCM (5 mL) was stirred at 0°C for 5 min under an argon atmosphere. Next, a solution of BBr₃ (1.25 mL, 1.25 mmol, 1 M in DCM) was added dropwise over 1 h using a syringe pump. After the completion of the addition, the reaction mixture was left to warm to room temperature and stirred for further 1 h. Then, MeOH (5 ml) was added and the mixture sonicated for 5 min. The solvents were evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel using PE:THF:MeOH (10:3:1) to give a magnesium TBTAP-OH 135 (0.02 g, 50%). Method B: a solution of a magnesium TBTAP-OCH₃ 139 (0.03 g, 0.046 mmol) and MgI₂ (0.06 g, 0.23 mmol, 5 eq) in toluene (2 mL) was placed in a sealed tube under N₂ and stirred at 170°C for 19 h. After cooling, MeOH (10 ml) was added and the mixture stirred for 10 minutes. Method C: a solution of a metal-free TBTAP-OH 140 (0.02 g, 0.03 mmol) and MgBr₂ (0.06 g, 0.33 mmol) in DMF (5 mL) was refluxed for 3 h. after that, EtOAc was added and the mixture washed with water. The solvents were evaporated under vacuum and the crude was purified by column chromatography using PE:THF:MeOH (10:3:1) as eluent to obtain magnesium TBTAP-OH 135 (0.012 g, 57%). Rf: 0.25 Pet.Et.:THF:MeOH (10:3:1). ¹H NMR (500 MHz, THF- d8): δ 9.60 – 9.57 (m, 2H), 9.54 – 9.49 (m, 4H), 8.96 (s, 1H), 8.20 – 8.17 (m, 4H), 7.91 (m, 4H), 7.66 – 7.60 (m, 2H), 7.39 – 7.33 (m, 4H). MADLI-TOF MS: m/z = 627.38 [M]+ (100%) [C₃₀H₂₁MgN₇O].
3.8 REFERENCES