



# **Synthesis of Staggered Triphenylene Twins Linked Through Ferrocene Bridges.**

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

**2016**

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## **PREFACE**

The research described within this thesis is, to the best of my knowledge, original and my own work, except where due reference has been made.

# DEDICATION

**This thesis is dedicated to my**

***Late parents***

**Late Sunday Kromkyes & late Rifkatu**

**Sunday Kromkyes (RIP)**

**&**

**My Children**

**Jacob Beskeni, Happy Beskeni**

**& Peace Beskeni**

## ACKNOWLEDGEMENTS

I am very grateful to my thesis supervisor Prof Andy Cammidge for his valuable and inspiring guidance throughout my research work. There are no adequate words to explain his interest, patience, kind advice, sustained encouragement, constant help and thought provoking discussions that I had with him during this time. It was a great experience to work with him and I learn so many things from him as a committed scientist and as a human being. His encouragement is to be a good researcher and I have learned from his humbleness. It has been a great pleasure and I really enjoyed working with him.

I would also like to express my gratitude to my second supervisor Dr Chris Richards for his commitment.

I also appreciate the kind gesture and financial assistance offered to me by the school of Chemistry, Dean of students, UEA development and student Union at the time of my hardship during this work. I most appreciate Dr Racheal Mcshane UEA medical doctor for her medical care and advice.

I take this opportunity to give special thanks to Dr Alejandro Díaz Moscoso, Dr Isabelle Chambrier, Dr Teresa Quirós, Dr Sonia Remiro, Dr Paulina Glowacka and Dr Tahani for their support at the period of this work.

I would like to specially appreciate my lab mates Shazia and Lucas for their valuable help, support and friendship at the time of this work. Also, Xiao, Ahad, Faezah, Aziz and Fakreah for their friendship at the period of this work. My other lab colleagues Dr Ateyat Allah, Dr Rebecca, Dr Daniel, Dr Nuha, Nora, Harry, Daniel, Jacob and other organic chemistry department colleagues Dr Maria Paz, Dr Sean Bew, Dr Stephenson Richard, Dr Yohan, Dr Ross, Dr Francesca, Dr Jose, Lisa and Nawaf for their help and encouragement. Sarah Delf you are not left behind, I appreciate your encouragement and smiles you put on my face daily (RIP).

I wish to express my gratefulness to Francis Oreyaju for his valuable commitment before and at the time of my course. Also, my friend Dr Duguryil Zipporah for her help and encouragement. Dr Ozoji Bennedita for her encouragement and lovely care to my children in my absence.

My deep gratitude to my beloved siblings, especially, Mr and Mrs Joseph Kromkyes, Friday Kromkyes, Esther Emmanuel and Alice Caleb and family, my aunties and Uncles. Also, my younger sister Nanbam who took care of my children in my absence.

My sincere thanks goes to Mr D. A. Beskeni for his enduring patience at the time of this studies and my beloved children Jacob Beskeni, Happy Beskeni and Peace Beskeni for their kind patience and support to each other in my absence.

My special thanks goes to Prophet and Mrs Isa Elbuba for their valuable spiritual support and encouragement at the period of this work.

Finally, I thank TETFUND Nigeria for their sponsorship and Federal College of Education Pankshin for giving me the opportunity for this study.

## ABBREVIATIONS

aq	Aqueous
ar	Aryl
Atm	Atmosphere
b.p	Boiling Point
Bu	Butyl
Col	Columnar
Conc.	Concentrated
d	Doublet
$\delta$	Chemical Shift In Parts Per Million (Ppm)
DDQ	2, 3-Dichloro-5, 6-Dicyano-1,4-Benzoquinone
DL	Discotic Lamellar
DLC	Discotic Liquid Crystal
DIPEA	N, N-Diisopropylethylamine
DMF	N, N-Dimethylformamide
DMSO	Dimethylsulphoxide
eq.	Equivalent
FET	Field Effect Transistor
h	Hour
HATs	Hexaalkoxy-triphenylenes
HOMO	Highest Occupied Molecular Orbital
I	Isotropic Liquid
IR	Infra-red
$\lambda$	Wavelength
LC	Liquid Crystal
LCD	Liquid Crystal Display
LUMO	Lowest Unoccupied Molecule Orbital
M	Multiplet
MALDI-TOF	Matrix-assisted laser desorption/ionisation-time-of-flight
MHT	Monohydroxytriphenylene
MOF	Metal-Organic Framework
mol	Mole



mmol	Millimole
m.p.	Melting Point
MS	Mass Spectrometry
<i>m/z</i>	Mass to Charge Ratio
N <sub>c</sub>	Nematic Columnar
N <sub>d</sub>	Nematic Discotic
N <sub>l</sub>	Nematic Lateral
NMR	Nuclear Magnetic Resonance
OFET	Organic Field Effect Transistor
OLED	Organic Light Emitting Diode
PAH	Polycyclic Aromatic Hydrocarbon
PE	Petroleum Ether
Ph	Phenyl
ppm	Parts Per Million
Psi	Pound Per Square Inch
rt	Room Temperature
s	Singlet
t	Triplet
TEA	Triethylamine
TFA	Trifluoroacetic Acid
TLC	Thin Layer Chromatography
TNP	Trinitrophenol
Tp	Triphenylene
UV/Vis	Ultraviolet/Visible Spectroscopy

## **Abstract**

The main target of this research was to investigate strategies for linking triphenylene discogens via staggered, ferrocene links. The thesis begins with a general introduction to liquid crystals and triphenylenes. The results of this research are then described. In the first part, a new and improved synthesis of dibromotriphenylene intermediates is described. The new procedure allows convenient access to the material without extensive chromatography. Attempts to couple dibromotriphenylenes with ferrocene derivatives is then discussed using ferrocene boronic acid and via acetylene links (Sonagashira couplings). Unfortunately, the required twinned structures were not observed, but a number of new monomeric derivatives (Ferrocenyl triphenylenes) were isolated. The reactions of ethynyl triphenylenes were complicated by efficient and competing homocoupling.

The remainder of the thesis describes a changed strategy whereby triphenylenes were linked via ester bridges. The molecular geometry was varied by linking monohydroxytriphenylene through 1,1'- ferrocene dicarboxylic acid plus three isomeric phthalic acids. The mesophase behaviour of the new materials is described.

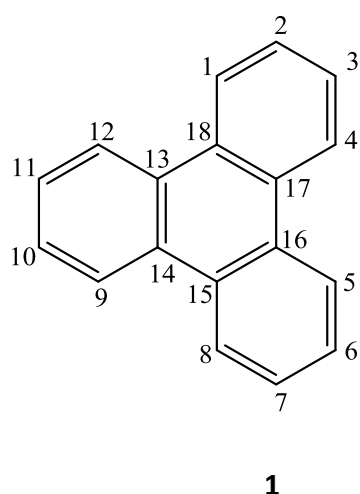
## CHAPTER 1 INTRODUCTION

### 1.1 Triphenylene

Triphenylene is a flat, polycyclic aromatic hydrocarbon (PAH) which consists of four fused benzene rings. Triphenylene can be isolated from coal tar. However, since it is a trimer of benzene, it may also be generated synthetically using benzene chemistry. Schultz was the first to discover the triphenylene (**1**) compound, which was initially isolated from pyrolytic benzene products.<sup>1</sup>

### 1.2 Structure of Triphenylenes 1

Triphenylene has the molecular formula of  $C_{18}H_{12}$ . One molecule of triphenylene has delocalized  $18-\pi$ -electron systems, based on a planar structure. The structure is composed only of full benzene rings, which are interconnected by single carbon-carbon bonds. It is possible to draw the three benzene as the three outer rings. The central ring is formed by one face of each and the three carbon-carbon single bonds. Triphenylene has much greater resonance stability than its isomers: chrysene, benz[*a*] anthracene, benzo [*c*] phenanthrene, and tetracene. It is therefore considerably more difficult to hydrogenate to the saturated hydrocarbons. Triphenylene has twelve possible sites for substitution. The peripheral sites 2, 3, 6, 7, 10 and 11 are most commonly derivatised.



**Figure 1.1:** Structure of Triphenylene **1** and numbering system.

### **1.3 Properties of Triphenylene**

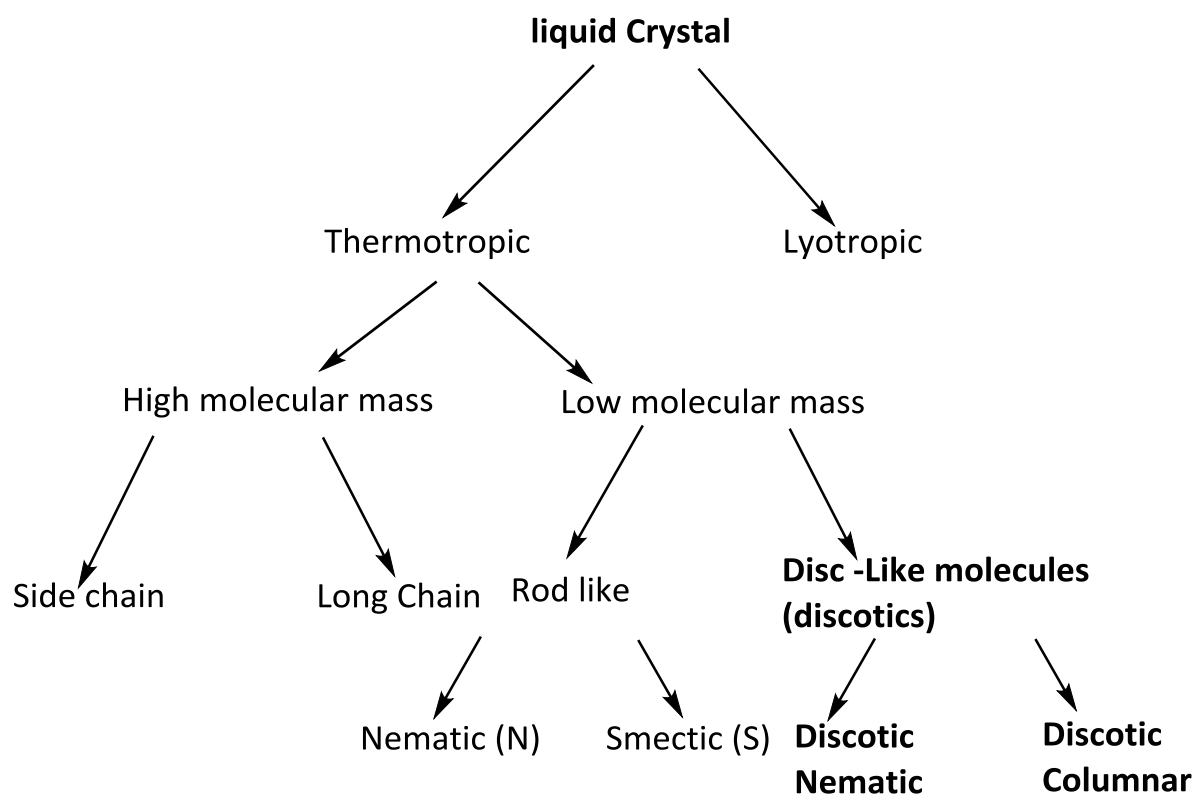
Triphenylene compounds have a variety of properties which make them interesting subjects for investigation. One of the main reasons that triphenylene compounds are so widely studied is their ability to form liquid crystalline mesophases. Triphenylene derivatives are also thermally and chemically stable. Their one-dimensional charge transfer is of particular interest, along with the energy migration, which makes them potentially useful in optics and electronics. Triphenylene crystals are colourless and needle-like and it gives off UV irradiation in the form of a bluish-purple fluorescence.

Triphenylene derivatives have been studied more widely than any other types of discotic liquid crystals.<sup>2,3</sup> Many derivatives form stable columnar mesophases which demonstrate anisotropic conduction. Triphenylenes have unique spectroscopic and geometric features and this frequently found structural motif is useful in a variety of contexts. There is considerable documentation in the literature for the use of triphenylenes as building blocks in discotic liquid crystals in both supramolecular and solid-state chemistry. In addition, triphenylenes have applications as fluorescent labels and as components of functional polymers.

### **1.4 Triphenylene as Liquid Crystals**

Various molecules form liquid crystal phases. A common characteristic they share is that they are anisotropic. They may have different shapes in their molecular axis and, in some instances, they have different solubility properties. The interaction between these anisotropic molecules facilitates orientation and sometimes, positional order in what is otherwise a fluid phase.

## Classification of Liquid Crystal



**Figure 1.2:** Classification of liquid crystals

Liquid crystals are classified as thermotropic (temperature dependent) and lyotropic (concentration dependent). Thermotropic liquid crystals are materials that can be both high molar masses (polymers) and low molar masses.

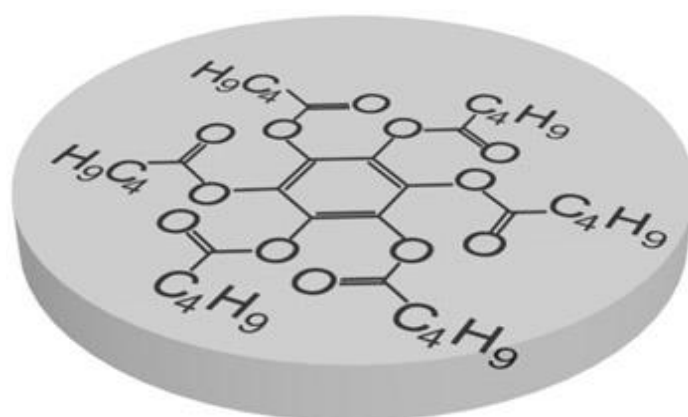
The high molar mass materials include main chain polymers. These chains align in one direction, or alternatively, they may have a comb-like structure with side chains hanging from the polymer. Materials with a low molar mass can be rod-like molecules (calamitic liquid crystals that typically show nematic and/or smectic phases), and disc-like molecules (with nematic and/or columnar phases).<sup>4</sup>

### 1.5 History of Liquid Crystals

The phenomena of liquid crystals was first discovered by Frederich Reinitzer, an Austrian botanist, in 1888.<sup>5</sup> The classification Scheme for liquid crystals (Figure 1.2) was produced in 1922 by G.Friedel, a French scientist.<sup>6</sup> The most significant liquid crystals so far, from a

technological and commercial viewpoint (4-alkyl and 4-alkoxy-4'-cyanobiphenyl) were discovered by Gray and coworkers in 1973.<sup>6</sup>

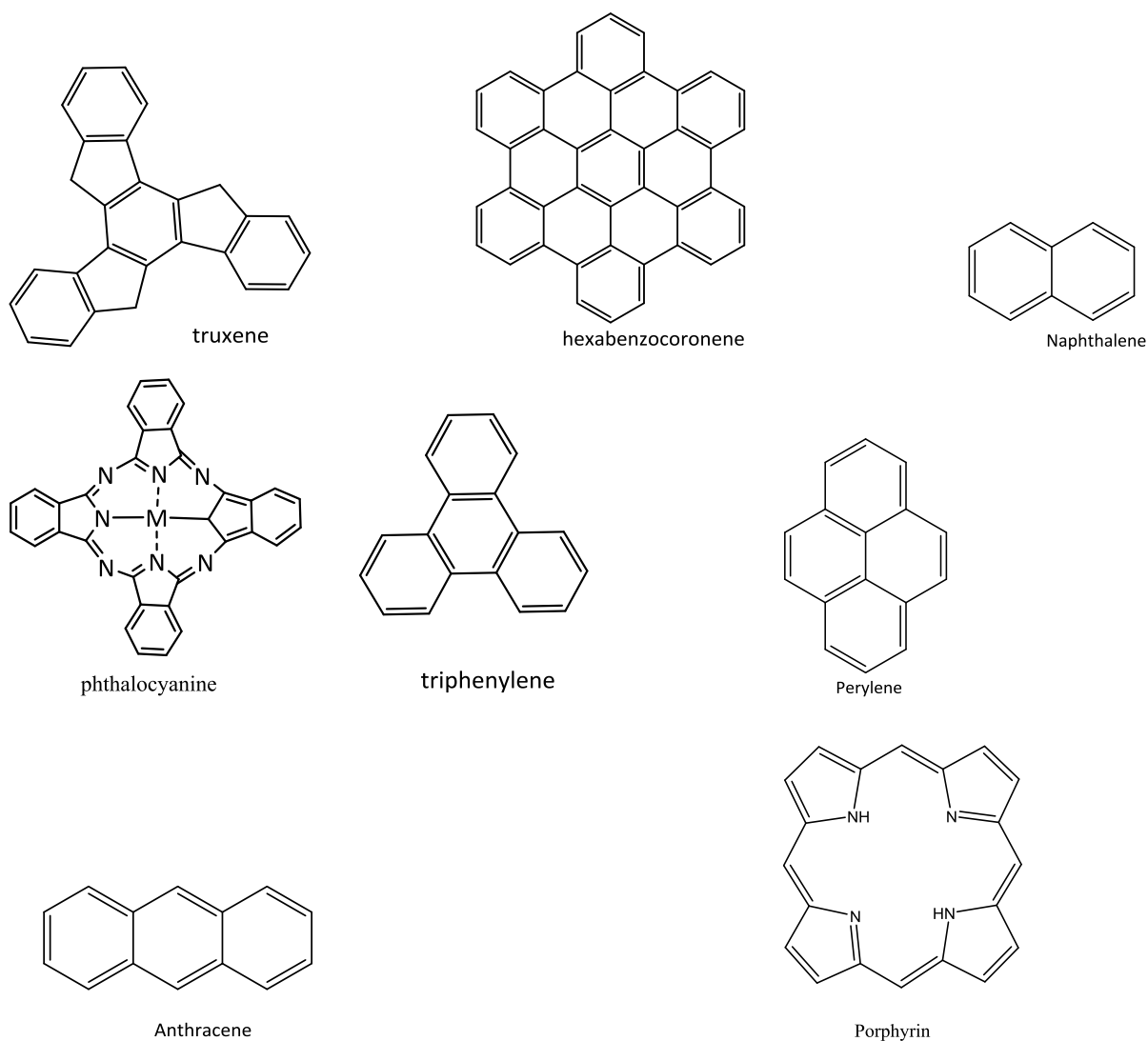
In 1978, it was first demonstrated that triphenylene derivatives could form mesophases,<sup>5</sup> immediately following Chandrasekhar's 1977 discovery that disc-shaped molecules could form liquid crystals.<sup>7</sup> Chandrasekhar synthesised a number of benzene-hexa-n-alkanoates (Figure 1.3). Their liquid crystalline properties could be observed, by optical, thermal and x-ray studies.



**Figure 1.3:** Structure of benzene-hexa-n-alkanoate, where R= n-C<sub>4</sub>H<sub>9</sub> to n-C<sub>9</sub>H<sub>19</sub>

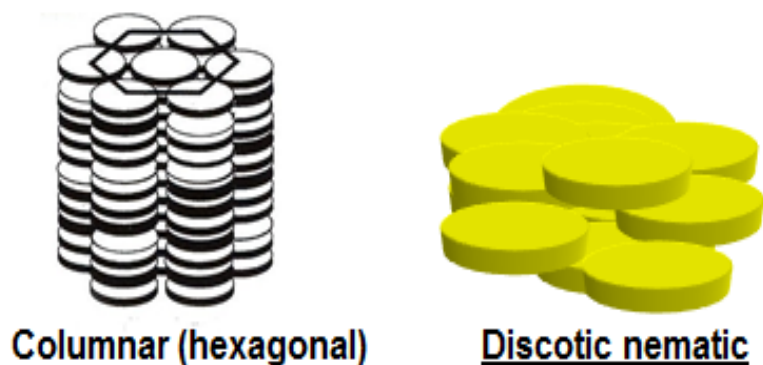
### 1.6 Discotic Liquid Crystal Phases.

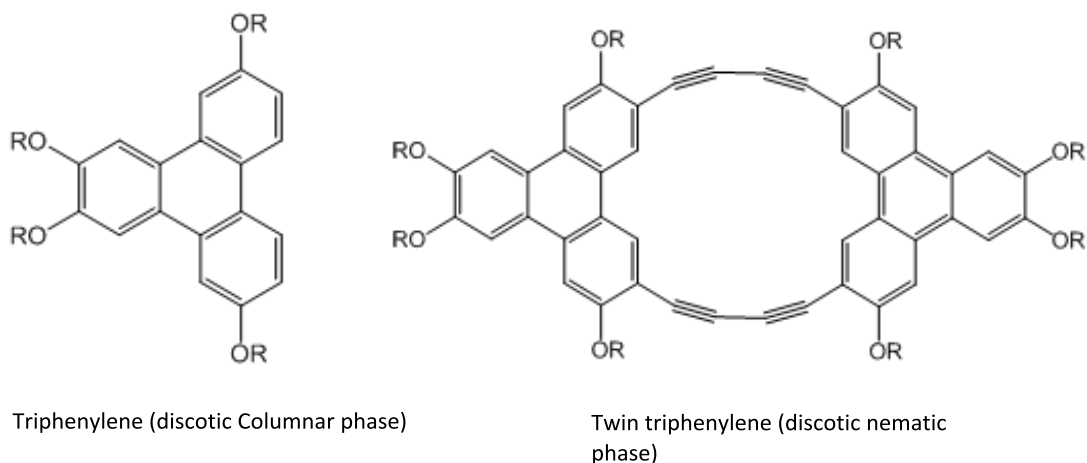
Discotic liquid crystals (DLCs) have attracted much research interest since they were discovered. Triphenylene **1** based discotic mesogens have been a particular focus of attention within this field.<sup>2</sup> DLCs are a unique type of matter, consisting of disc-shaped molecules which are capable of self-organization.<sup>3,9</sup> The essential feature is their supramolecular columnar architecture, which makes them models for charge migration in organized systems. A large number of different cores have been shown to form discotic mesophases. These include truxene, hexabenzocoronene, phthalocyanine, triphenylene, naphthalene, perylene anthracene and porphyrin, (Figure 1.4).



**Figure 1.4:** Cores that can exhibit DLC mesophases (when substituted).

Many liquid crystals (DLCs) formed by disc-shaped molecules are thermotropic. This means that the liquid crystals form as a function of temperature. Two basic types of discotic mesophases, columnar and nematic, are generally recognized.<sup>10</sup>



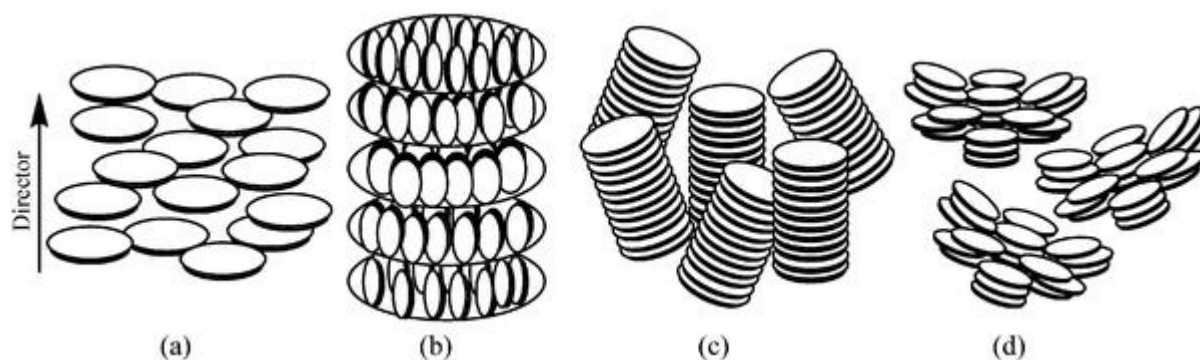


**Figure1.5:** Discotic liquid crystal showing columnar and nematic phases

As a result of observing many DLC mesophases, these have been further classified according to the arrangement of their molecules and the level of order they contain<sup>11</sup>. The types that have been noted are columnar, nematic, smectic and cubic. Further subcategorization have been made. Columnar mesophases are by far the most frequently seen of the discotic mesophases. The nematic mesophase is the second most common, while cubic and smectic mesophases are much rarer.

### 1.6.1 Nematic Phase

It is possible to subdivide discotic nematic phases into four types. These are **a.** discotic nematic ( $N_D$ ), **b.** chiral nematic ( $N_D^*$ ), **c.** Columnar nematic ( $N_{col}$ ), and **d.** nematic lateral ( $N_l$ ).<sup>6</sup>

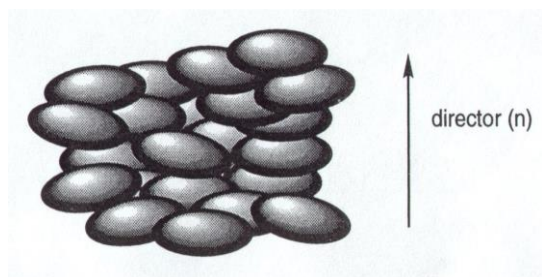


**Figure 1.6:** Types of nematic phase



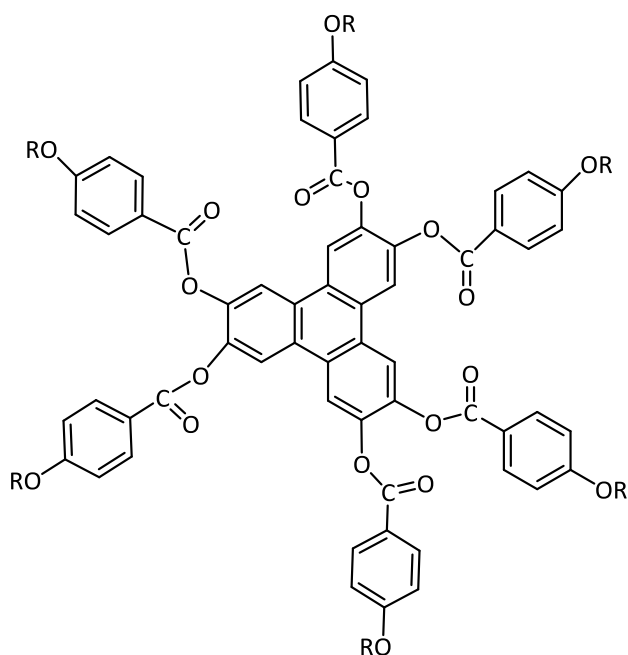
### 1.6.1.1 Nematic Discotic

Nematic discotic liquid crystals lack order. The mesogens are arranged in a parallel formation, which, although it has orientational order, has no long-range positional order. The short axis of the molecules defines the director, as shown in Figure 1.7.



**Figure 1.7:** Arrangement of molecules in nematic discotic mesophase

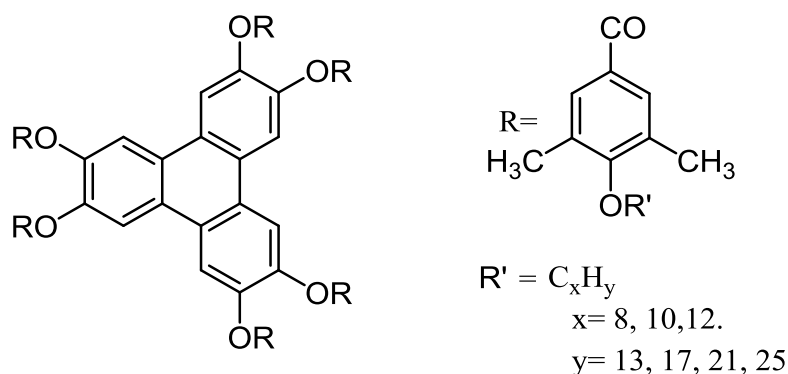
The ability of triphenylene-2, 3, 6, 7, 10, 11-hexyl hexakis (4-*n*-alkoxybenzoates) (Figure 1.8) to form nematic discotic mesophases was first described in 1981.<sup>12</sup>



**Figure 1.8:** Structure of triphenylene-2, 3, 6, 7, 10, 11-hexyl hexakis(4-*n*-alkoxybenzoate)

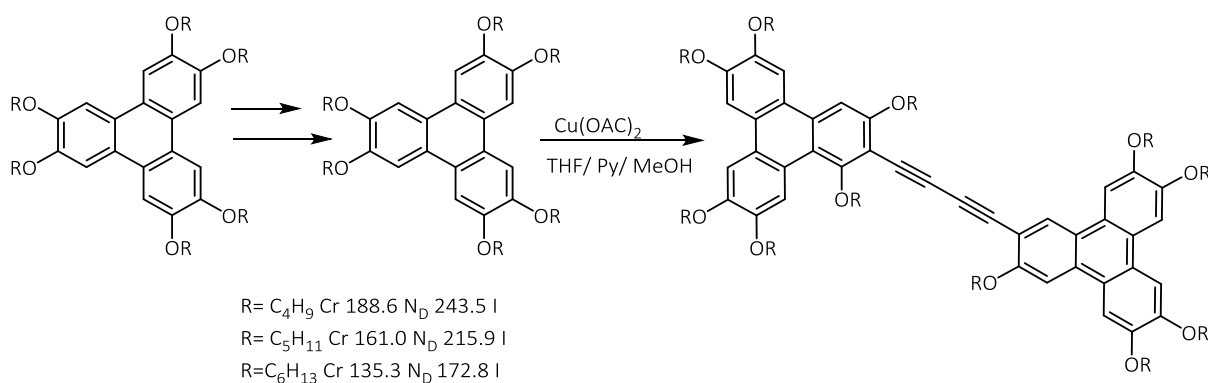
Work on the triphenylene-hexabenzoate series of compounds, which followed the 1981 discovery, has demonstrated that if ortho-methyl groups are introduced to the ester linkage, the columnar mesophase formation is suppressed. As a result, it is only  $N_D$  mesophases, which are observed (Figure 1.8).<sup>13</sup> Methyl groups meta to the ester link group also suppress the columnar mesophase. In addition, they show the hexagonal disordered columnar

mesophase. In those cases where the methyl groups point towards the triphenylene core, the phenyl rings are forced out of the triphenylene core's plane due to the steric interactions. As a result, those face to face interactions which encourage columnar phases are decreased. Thus, only nematic discotic phases are seen.



**Figure 1.9:** Effect of the methyl position on mesophase behaviour

Designing discotic mesogens to form nematic discotic phases is difficult. Few nematic discotic phases have therefore been reported. Following the work on the triphenylene-hexabenzoate series, attention has shifted to the synthesis of triphenylene dimers. In order to form nematic discotic phases, the  $\pi$ - $\pi$  interactions must be diminished. Kumar demonstrated, in 2002, that joining two triphenylene units using a rigid conjugated spacer produced nematic material (Scheme 1).<sup>6</sup>

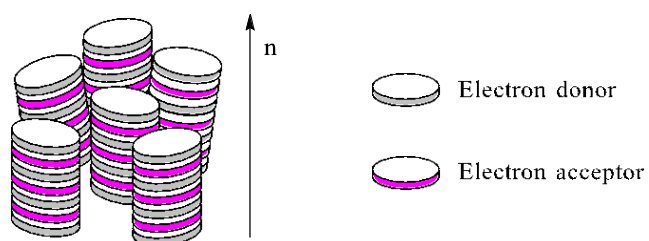


**Scheme 1:** Synthesis of triphenylene dimer showing nematic mesophases

The dimers were linked by a diacetylene bridge and exhibited nematic mesophases over a wide range of temperatures. It is noteworthy that in the monomers only ordered columnar mesophases were observed.

### 1.6.1.2 Nematic Columnar Mesophase

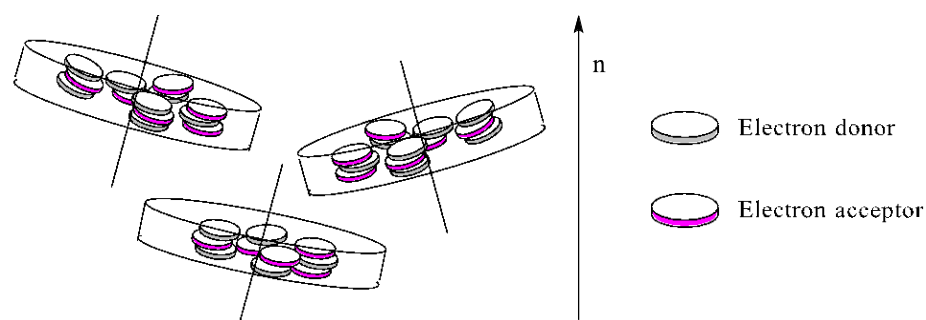
The nematic columnar mesophase ( $N_C$ ) is induced by the charge-transfer interactions. These occur between a donor molecule and an acceptor. The molecules are stacked in columns, which have short-range orientational order. However, these assembled columns do not form a 2D lattice because their side chains differ in length.



**Figure 1.10:** Arrangement of molecules in the  $N_C$  phase.

### 1.6.1.3 Nematic Lateral Mesophase

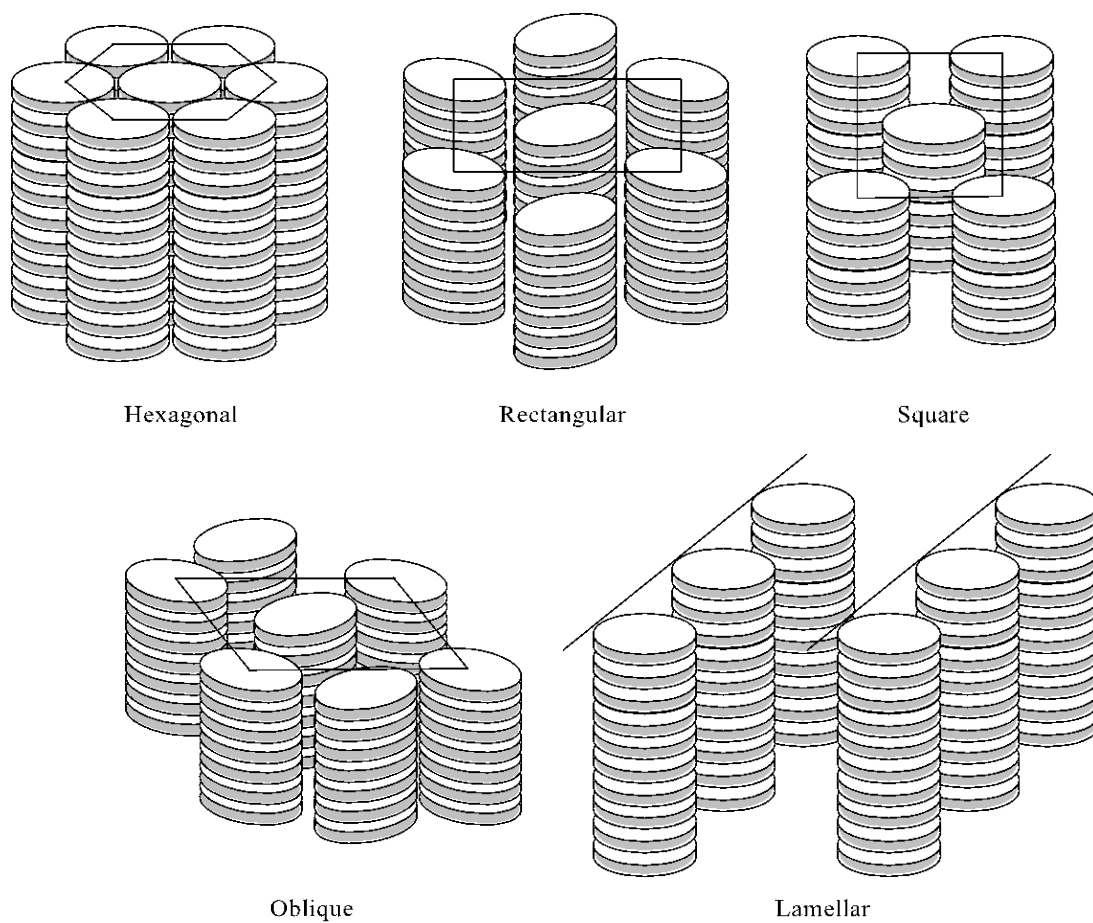
A new type of discotic mesophase was discovered in 2001. This was the nematic lateral ( $N_L$ ) phase.<sup>14</sup> It was demonstrated this  $N_L$  mesophase forms as a result of a charge-transfer complex between an electron acceptor and an electron donor. The molecules are arranged into disc-shaped superstructure with the nematic pattern (Figure 1.11).



**Figure 1.11:** Arrangement of molecules in the  $N_L$  phase.

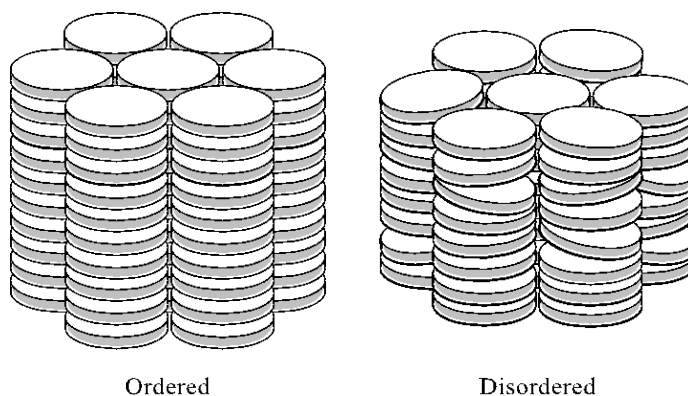
### 1.6.2 Columnar Phases

Researchers have been aware of columnar mesophases ever since 1977, when it was first demonstrated that disc-shape molecules could form liquid crystal phases.<sup>8</sup> The mesogens are stacked one on top of the other to form columns. This occurs because of the large  $\pi$ - $\pi$  interactions between the aromatic cores. It is for this reason that the majority of discotic liquid crystals are columnar. These columns form part of a larger 2D lattice. A number of symmetries are known, some of which are illustrated in Figure 1.12.



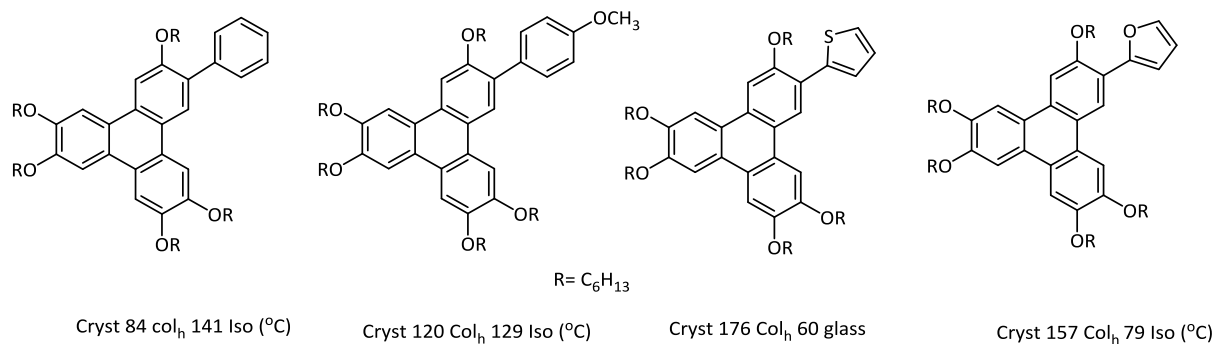
**Figure 1.12:** Symmetries of columnar DLC 2D lattices within the columns.

The mesogens can be in a regularly ordered pattern or disordered.



**Figure 1.13:** Ordering of mesogens within columnar phase various of triphenylene

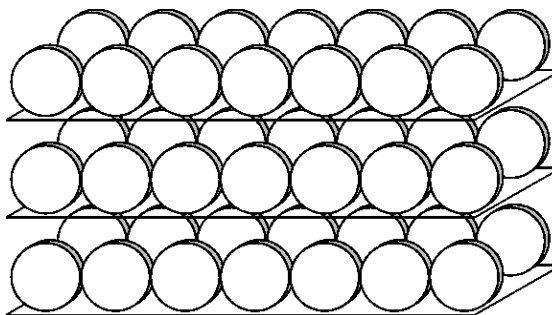
Triphenylene derivatives have been shown to form columnar mesophases. Some examples are illustrated in Figure 1.14.



**Figure 1.14:** Triphenylene derivatives showing columnar mesophases

### 1.6.3 Smectic Phase

As previously mentioned, the smectic mesophase is seldom seen in discotic mesogens. Nevertheless, a smectic mesophase may be observed when the number of peripheral side chains is reduced or if these side chains are unevenly distributed.<sup>15</sup> The smectic phase has also been called the discotic lamellar phase, denoted D<sub>L</sub>



**Figure 1.15:** Arrangement of molecules in the  $D_L$  phase.

#### **1.6.4 Cubic Phase**

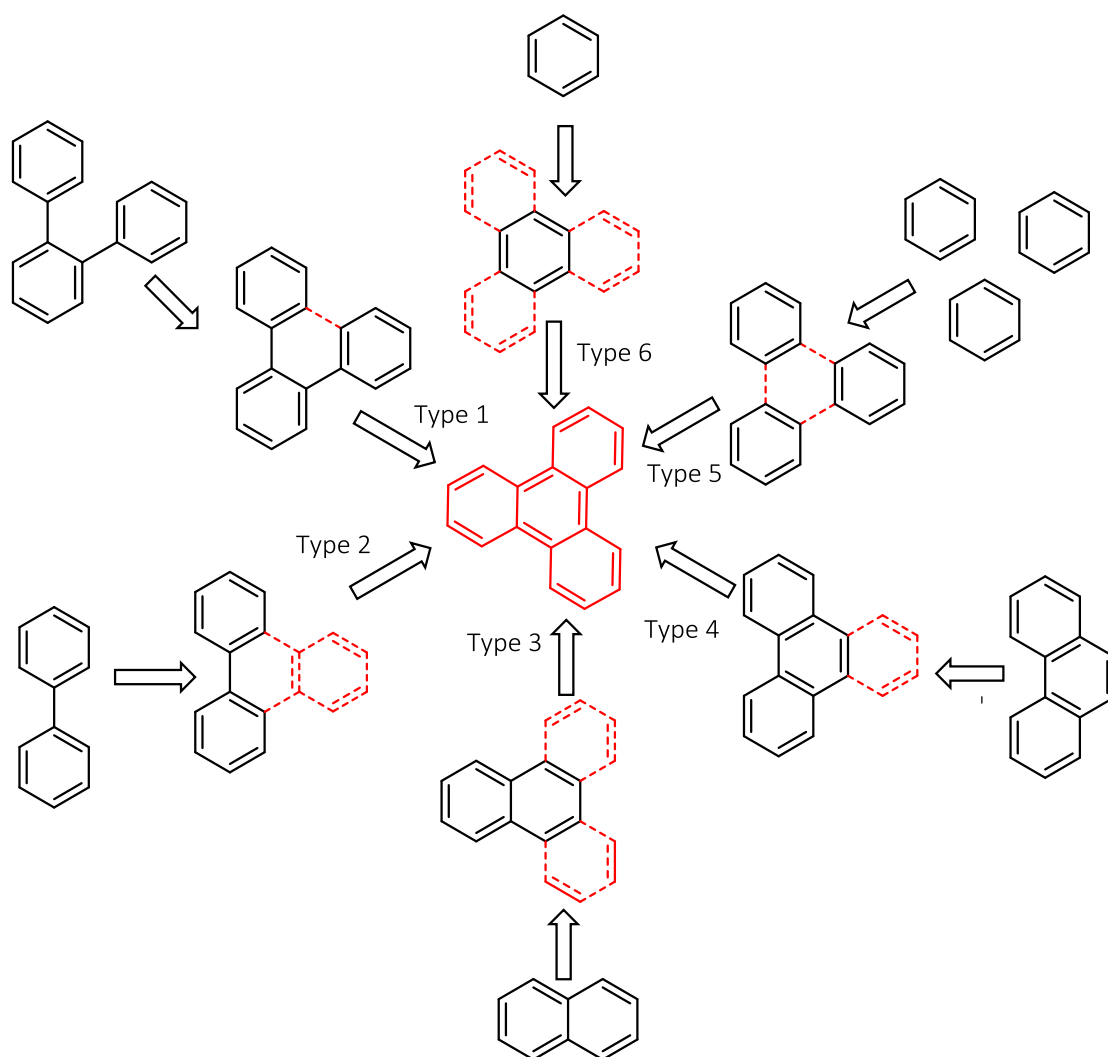
The cubic phase is seldom observed in discotic mesogens and has only been documented as forming from phthalocyanine derivatives. However, lyotropic liquid crystals, which form as a function solvent, often exhibit a cubic phase.<sup>16</sup> The structure is formed from linked, branched columns, which create the cubic lattice.

#### **1.6.5 General applications of discotic liquid crystals.**

Discotic liquid crystals have many applications and are among the materials used in organic electronics. Conjugated liquid crystals (LCs) are now forming the new generation of organic semiconductors because of their 'order and dynamics' characteristics. Their order, in particular, is an important parameter directing the performance of organic semiconductors in devices. The low, discrete molecular mass of liquid crystals allows chemical structures to be synthesised, which are not only free from defects, but can also have higher levels of purity than the majority of conjugated polymers. The unique features of DLCs include their molecular properties, their supramolecular order, their processing into thin films, and their device performance. In addition, the charge transport properties of discotic materials and their optical properties are also advantageous in view of their potential applications in photovoltaic cells or LEDs. This is because, in such applications, it is useful to have the absorption coefficients over a large range of wavelengths. This can be successfully achieved by enlargement of the aromatic core of PAH.

## 1.7 Synthesis of Triphenylene Core

The core of a liquid crystal is its most fundamental structural feature. This core is the rigid unit built from ring units, which are linked together. It is often defined as including any linking groups and any lateral substituents, which are joined to the rings. Perez and co-workers have summarized the practical synthesis of triphenylene so far, by categorizing it into six distinct kinds.<sup>17</sup> Triphenylene is synthesized by preparing and isolating it from terphenyl using oxidative cyclisation/ photocyclization (Type 1), from biphenyls using palladium catalyzed coupling/oxidative cyclisation (Type 2), from naphthyls using Diels-Alder cycloaddition (Type 3), from phenanthryls using the Diels-Alder reactions/photocyclization (Type 4), three benzene rings using oxidative trimerization (Type 5) and one (substituted) benzene ring using photochemical cyclisation (Type 6) (Figure 1.16).

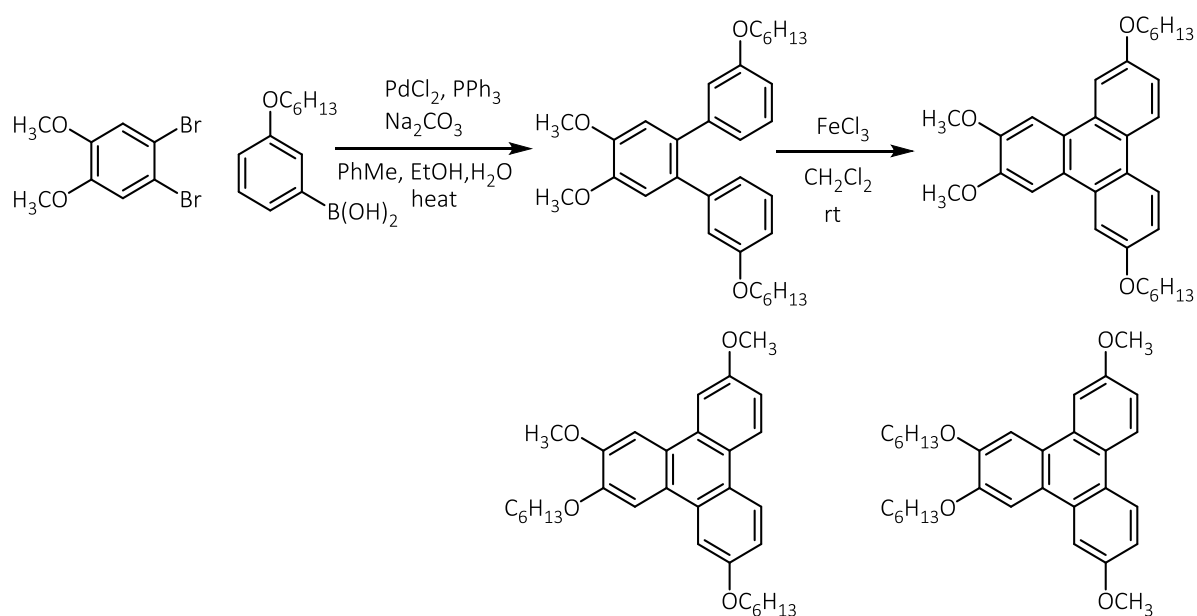


**Figure 1.16:** Different routes of triphenylene synthesis



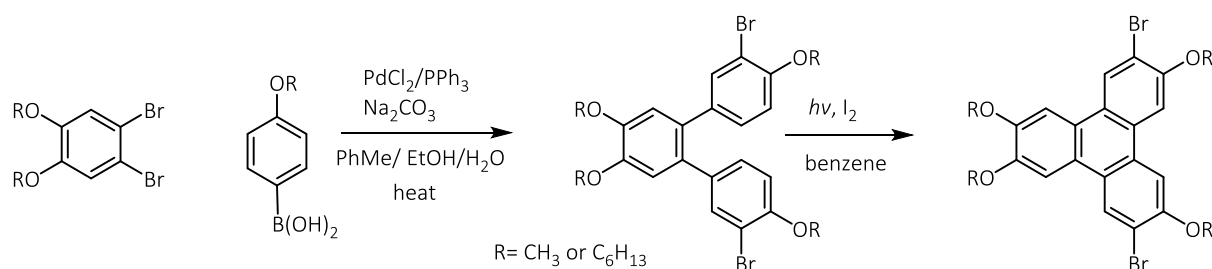
### 1.7.1 Oxidative Cyclisation/ Photocyclisation (Type 1 Synthesis)

The most important stage in type 1 syntheses is the cyclisation of an *ortho*-terphenyl. Examples of this being used in the synthesis of triphenylenes have been documented. Terphenyls are most often synthesised by the use of palladium-catalysed cross coupling reactions. Both symmetrically and unsymmetrically substituted triphenylenes can be produced using this form of synthesis. Oxidative cyclisation was originally developed for the synthesis of phenols. However, it is currently a classic step in the formation of biaryl bonds. Numerous different oxidizing agents have been used in this coupling reaction, for example  $K_3Fe(CN)_6$ ,  $VOCl_3$ ,  $Tl(OCOFCF_3)$ ,  $MoCl_5$ ,  $VOF_3$ , and  $FeCl_3$  (Scheme 2).



**Scheme 2:** Synthesis of unsymmetrical triphenylene.<sup>18</sup>

Photocyclisation is also used in type 1 syntheses. If the terphenyl is irradiated with UV light, using iodine as oxidant and propylene oxide (PO) as an acid scavenger, the yield from the cyclisation of terphenyl to triphenylene can be improved (Scheme 3).

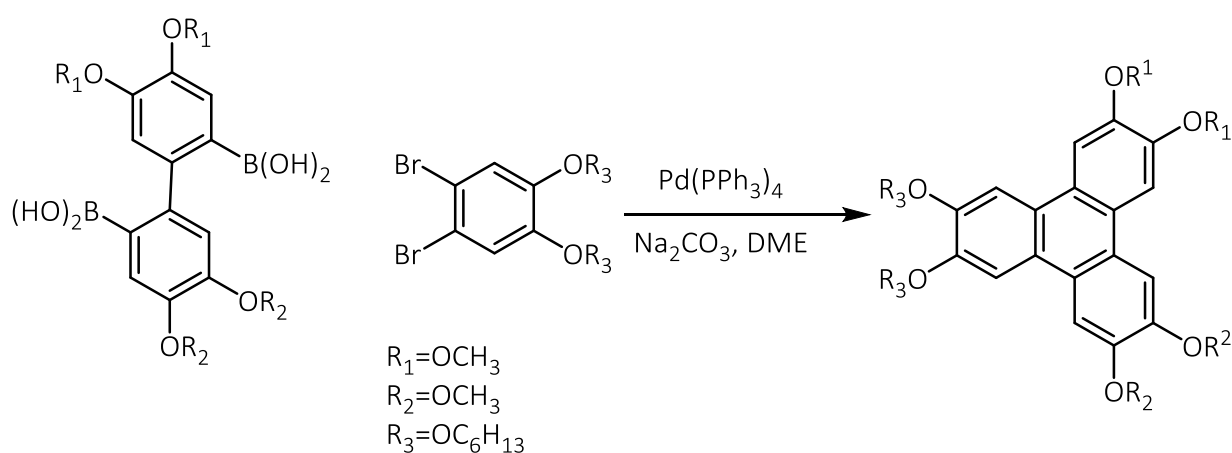


**Scheme 3:** Synthesis of symmetrical triphenylene.<sup>18</sup>

### 1.7.2.1 Palladium Catalysed Coupling (Type 2 Synthesis)

The step, which characterizes type 2 syntheses, is the formation of triphenylene from a biphenyl.

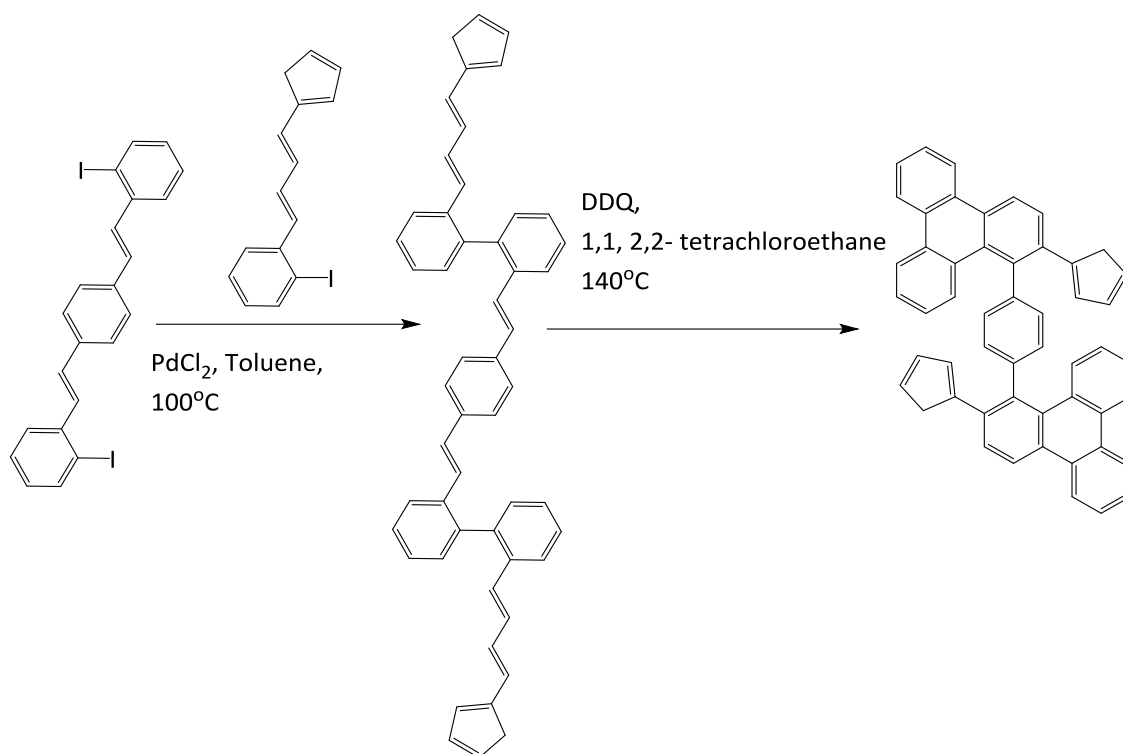
There are three possible ways in which this can be achieved: palladium-catalysed coupling, Diels-Alder cycloaddition and oxidative cyclisation. In Scheme 3 unsymmetrically substituted triphenylenes are synthesised by means of a double Suzuki coupling reaction between the diboronic acid and dibromide compound. This is an efficient method of generating unsymmetrically substituted triphenylenes. Numerous different alkyl/aryl-group have been found to work using this synthesis.



**Scheme 4:** Palladium-catalysed synthesis of unsymmetrical triphenylene from biphenyl.<sup>19</sup>

### 1.7.2.2 Diels- Alder Reactions

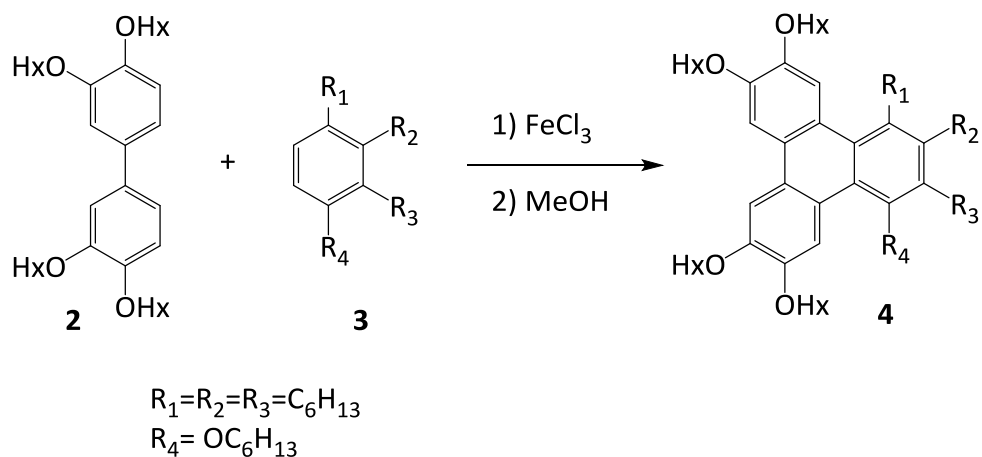
An interesting synthesis of triphenylene *via* intermolecular Diels-Alder reaction was published in 1996.<sup>20</sup> A double Diels-Alder reaction was used, after which re-aromatization with DDQ produced the required compound which contained two triphenylene units (Scheme 4).<sup>21</sup>



**Scheme 5:** Diels-Alder Synthesis of a triphenylene derivative.

### 1.7.2.3 Oxidative Cyclization

Oxidative cyclisation follows the same conditions as in type 1, many different oxidants can be utilised, and an example is shown in **Scheme 5**. The paper by Boden *et al.* shows that this route tolerates substituents in the sterically hindered  $\alpha$ -position, which were previously difficult to obtain.<sup>22</sup>

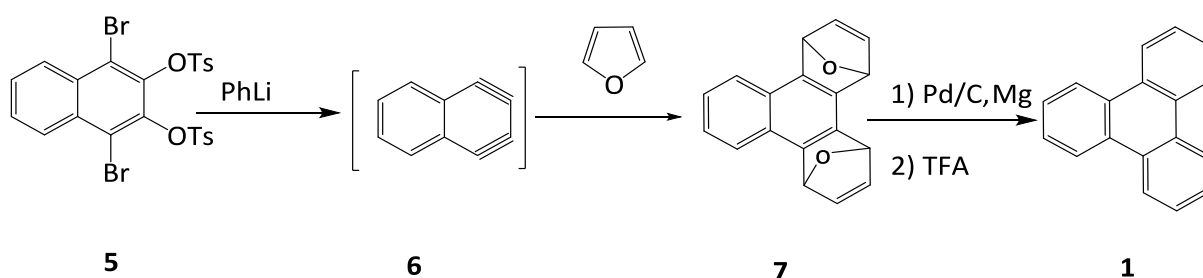


**Scheme 6:** Oxidative coupling of triphenylene from biphenyl.<sup>22</sup>

### 1.7.3 Diel-Alder Reaction (Type 3 Synthesis)

Type 3 methods focus on the synthesis of triphenylene from a naphthalene core. Most syntheses through this route go *via* a Diels-Alder reaction.

When Naphthalene 5 reacts with phenyllithium, an *in situ* tetradehyronaphthalene 6 is produced. When this reacts with furan, it generates biadduct triphenylene 7. This then undergoes deoxygenation by being treated with Pd/C and Mg. TFA is then added to produce triphenylene 1, (Scheme 6).



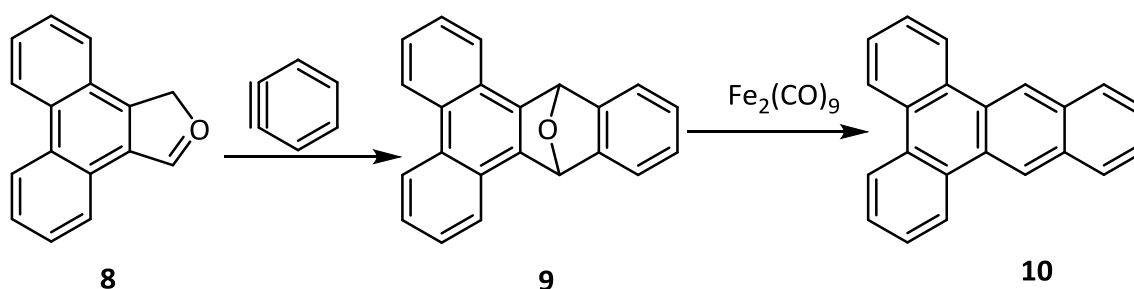
**Scheme 7:** Synthesis of triphenylene 1 *via* Diels-Alder.

### 1.7.4 Diels-Alder reactions/Photocyclization (Type 4 Synthesis)

In type 4 synthesis, the last ring on the triphenylene is produced by the Diels-Alder reaction and photocyclisation, using a phenanthrene derivative.

#### 1.7.4.1 Diels-Alder reaction.

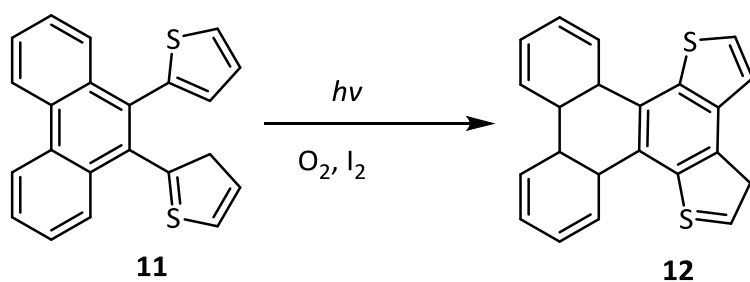
The phenanthrene diene has exocyclic double bond. This reacts with benzyne as dienophile to form endoxide **9**. Treating this with  $\text{Fe}_2(\text{CO})_9$  deoxygenates it to benzo triphenylene **10**, as shown in Scheme 7.<sup>23</sup>



**Scheme 8:** Synthesis of benzotriphenylene by Diels-Alder reaction.

#### 1.7.4.2 Photocyclisation reaction.

The required product **12**, can be produced by means of a photocyclisation reaction using phenanthrene derivative **11**. This then undergoes dehydroxylation, as shown in Scheme 8.



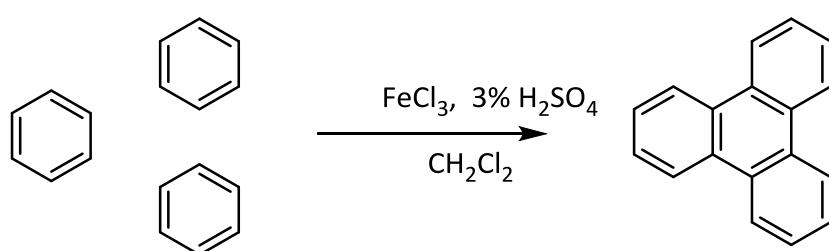
**Scheme 9:** Synthesis of triphenylene *via* photocyclisation of phenanthrene.<sup>24</sup>

### 1.7.5 Oxidative Trimerisation (Type 5 Synthesis)

Since the early work of Mannich, the most commonly used method of synthesizing triphenylene has been the oxidative trimerization of benzene.<sup>17</sup>

Following the discovery of triphenylene as liquid crystal, most of the focus has been on the

synthesis of hexaalkoxytriphenylenes. A widely used procedure, since 1960, has been the oxidative trimerisation of catechol derivatives and chloranil or  $\text{FeCl}_3$  in sulphuric acid. Bushby and co-workers<sup>19</sup> have optimised the experimental conditions for the trimerisation process using  $\text{FeCl}_3$ . Other oxidizing agents such as  $\text{MoCl}_5$  and  $\text{VOCl}_3$  can be used for this reaction, under the same conditions. This has been carried out by lowering the concentration of the  $\text{H}_2\text{SO}_4$  (Scheme 9). Methanol was added at the start of workup as a reducing agent. This produced a high yield of hexasubstituted alkoxy-triphenylenes. Other substituents ranged from hydroxyl, crown ether to chiral moieties.



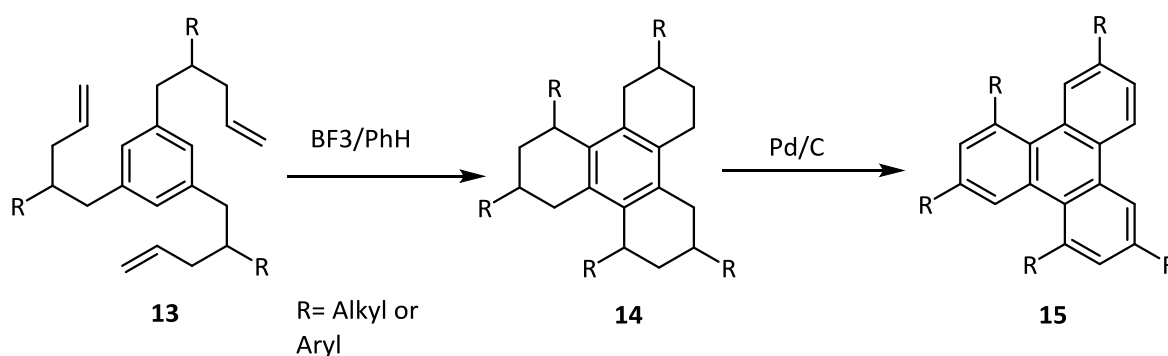
**Scheme 10:** Oxidative trimerization of benzene (substituents are needed)

## 1.7.6 Catalyzed and Photochemical Cyclisation (Type 6 Synthesis)

### 1.7.6.1 Catalyzed Cyclisation

Some examples of triphenylene synthesis using one pot formation of the peripheral rings has since been documented. This is a method, which is often used to synthesise compounds that are not easily synthesised using the standard methods.

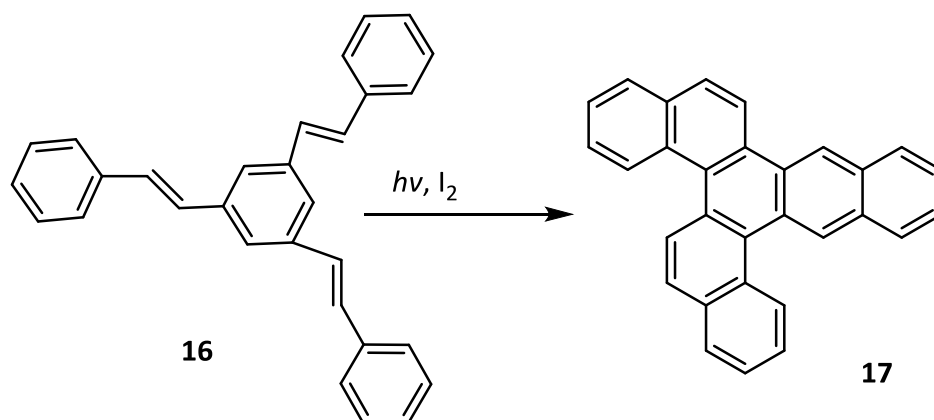
The starting material **13** underwent acid catalysed cyclisation. Dehydrogenation using palladium on carbon, generated product **15** (Scheme 11).<sup>25</sup>



**Scheme 11:** Synthesis of triphenylene by acid catalysed reaction.

### 1.7.6.2 Photocyclization Reaction

Photocyclisation has been used to synthesize tribenzotriphenylene **17** from stilbene **16** (Scheme 12).<sup>24</sup>

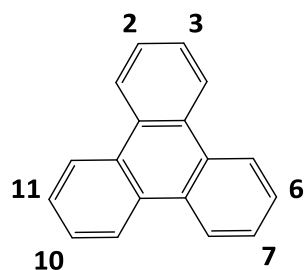


**Scheme 12:** Photocyclization of stilbene to triphenylene.

## 1.8 Triphenylene Substitution

### 1.8.1 Symmetrical and Unsymmetrical Triphenylene Core

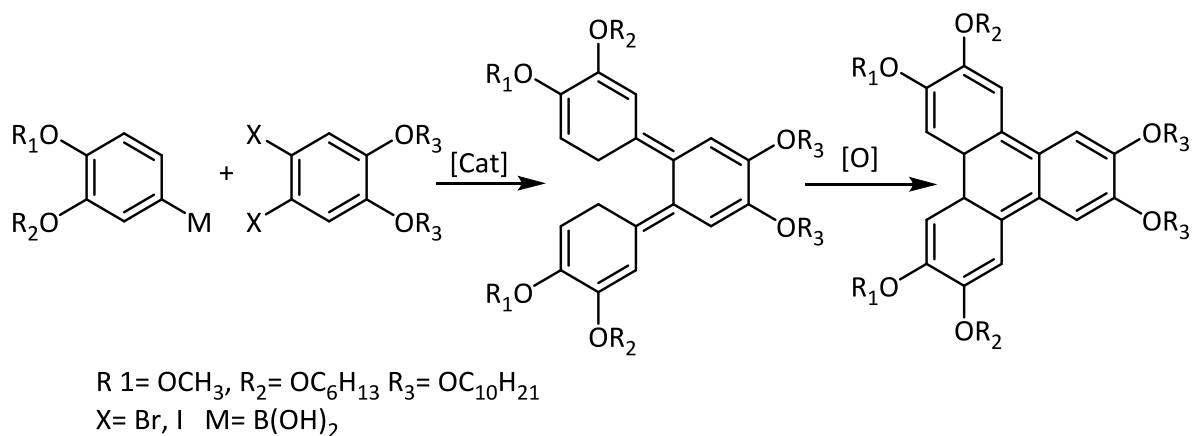
Research studies reveals that the sites for attachment of triphenylenes to give discotic liquid crystals are usually the 2, 3, 6, 7, 10 and 11 positions.



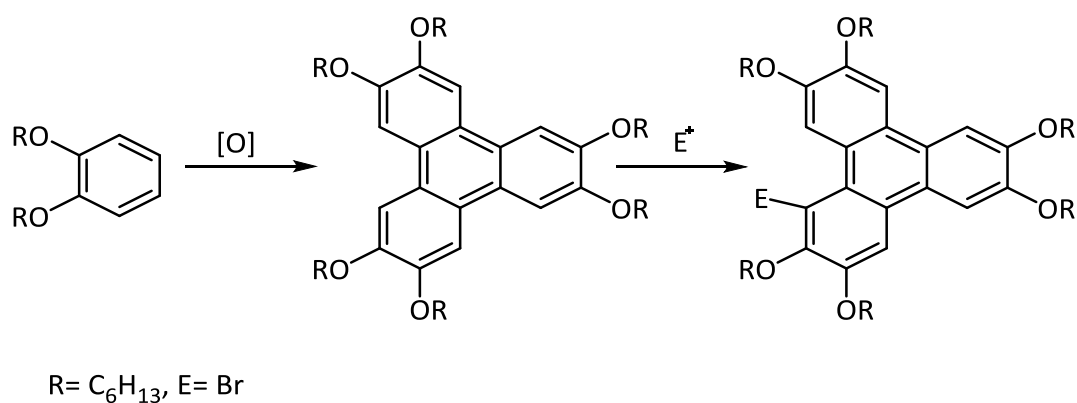
**Figure 1.17:** Peripheral attachments sites of triphenylene

Attached on these sites are most often flexible alkoxy chains (-OR), that reduce the melting points and allow liquid crystal phases formation.<sup>17</sup>

The alkoxy chains are also responsible for stabilising the molecular orientations needed for liquid crystals phase generation. The presence of polar groups do not necessarily reduce the melting points, but can stabilise the molecular orientation. Additionally, their physical properties are also strongly dependent upon the choice of terminal unit.



**Scheme 13:** Synthesis of Unsymmetrical Substituted Triphenylene



**Scheme 14:** Synthesis of unsymmetrical triphenylene with electrophilic Substitution

To maintain a disc like structure, the central core is usually symmetrical and the substituents are present in numbers that are appropriate for the central core; also having all the peripheral units as identical helps to maintain the overall discotic architecture of the structure.

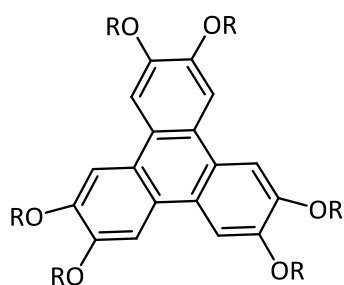
For unsymmetrical compounds with different peripheral chains, the reduction in symmetry causes a reduction in melting point as the unsymmetrical nature of the molecular structure means that the unsymmetrical compound is no longer truly disc like and this is the reason why the stability of the hexagonal mesophase is much reduced. In some cases, the less ordered columnar phase is exhibited.<sup>5</sup>

## 1.9 Synthesis of Alkoxytriphenylenes



### 1.9.1 Hexaalkoxy-triphenylenes (HATs);

Hexaalkoxy triphenylenes (HATs) are the most synthesised triphenylenes and their mesogenic properties are studied. HATs has the advantage of having been extensively studied and structurally characterised, which makes it an ideal model system for the study of the unification of polymer and self-assembly properties of the HATS.<sup>26</sup>

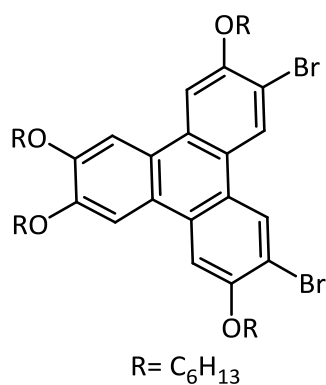


R = C<sub>10</sub>H<sub>21</sub>, C<sub>6</sub>H<sub>13</sub> or C<sub>5</sub>H<sub>11</sub>

**Figure 1.18:** Hexaalkoxy triphenylenes (HATs)

Several methods are being employed to synthesise hexaalkoxytriphenylenes. HATs can be substituted at  $\alpha$ -position, which support mesophase formation.

The tetrahexyloxytriphenylenes dibromide are often use as the intermediate for the synthesis of many triphenylenes discotics liquid crystals.<sup>27</sup>



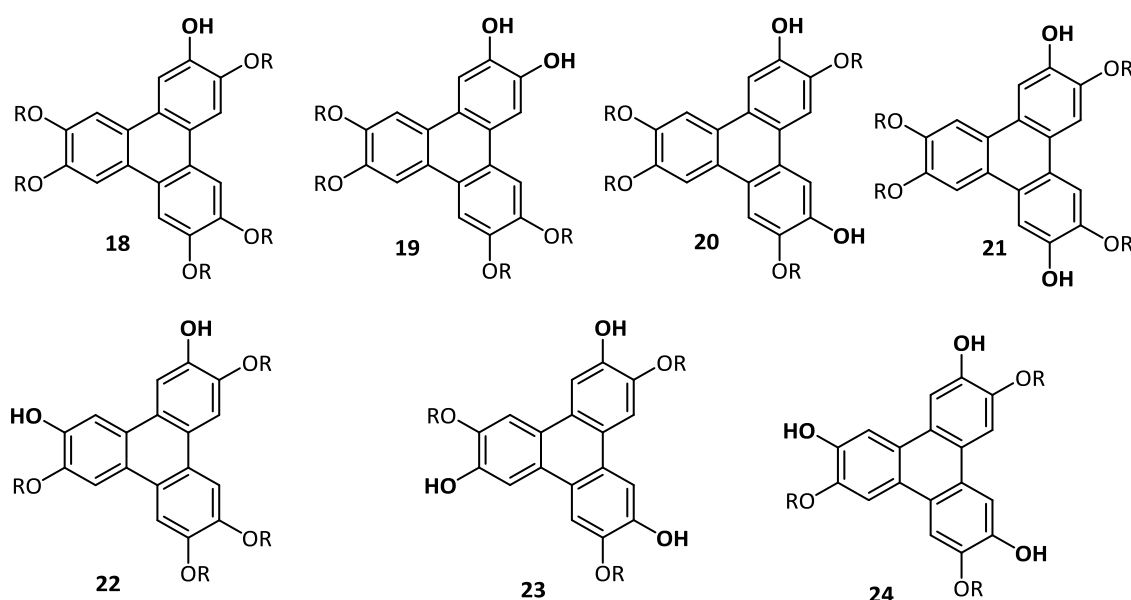
**Figure 1.19:** Tetra (hexyloxy) triphenylene dibromide

Most common method for synthesis of triphenylenes derivative is by trimerisation of di-alkoxy and biphenyl routes using electron rich precursors, yielding hexa-substituted derivatives (hexa-alkoxytriphenylenes). Triphenylene cores with low degree of substitution like trialkoxytriphenylenes cannot be synthesised using this method, but pentaalkoxy derivative could be prepared using the method but at a very low yield. Triphenylenes with less than six alkoxy groups are the most useful intermediates to prepare derivatives with new substituents; this is effectively done these days by 'Terphenyl route'.<sup>5</sup> (Scheme 1).

### 1.9.2 Hydroxyl (alkoxy) Triphenylenes.

The most common hydroxyl HATs synthesised are the monohydroxytriphenylenes (MHTs). The hydroxy-functionalised triphenylenes are very valuable precursors for the synthesis of dimers, oligomers, polymers, network, mixed tails, lower and higher degree substituted derivatives. There are other possibilities for the preparation of alkoxyhydroxytriphenylenes.

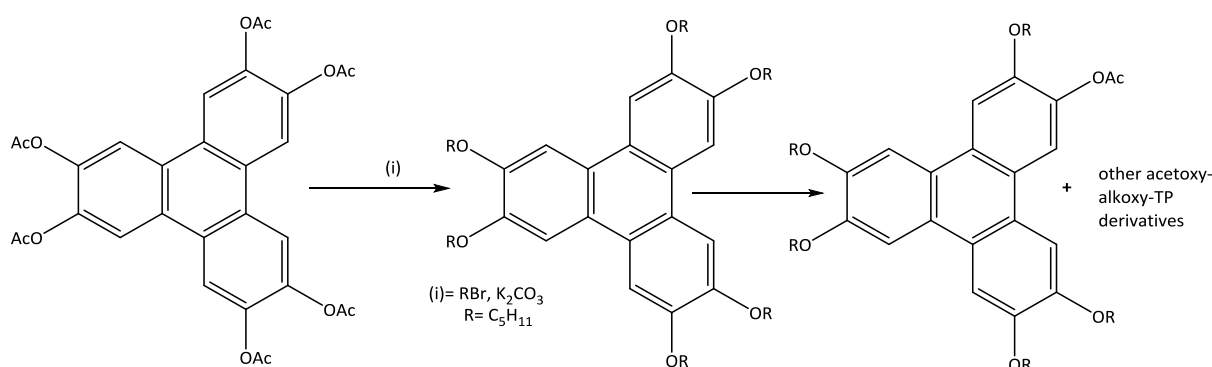
Seven different types have been prepared through selective and non-selective chemical method.<sup>6</sup>



**Figure 1.20:** Types of hydroxyl-alkoxy-triphenylene.<sup>6</sup>

The seven alkoxy-hydroxytriphenylenes that have been prepared using selective and non-selective chemical methods as represented with molecular structures above are monohydroxy-pentaalkoxy-TP **18**, 2,3-dihydroxy-6,7,10,11-tetraalkoxy-TP **19**, 2,6-dihydroxy-3,7,10,11-tetraalkoxy-TP **20**, 2,7-dihydroxy-3,6,10,11-tetraalkoxy-TP **21**, 2,11-dihydroxy-3,6,10,11-tetraalkoxy-TP **22**, 2,6,10-trihydroxy-3,7,11-tetraalkoxy-TP **23** and 2,7,10-trihydroxy-3,6,11-tetraalkoxy-TP **24**.

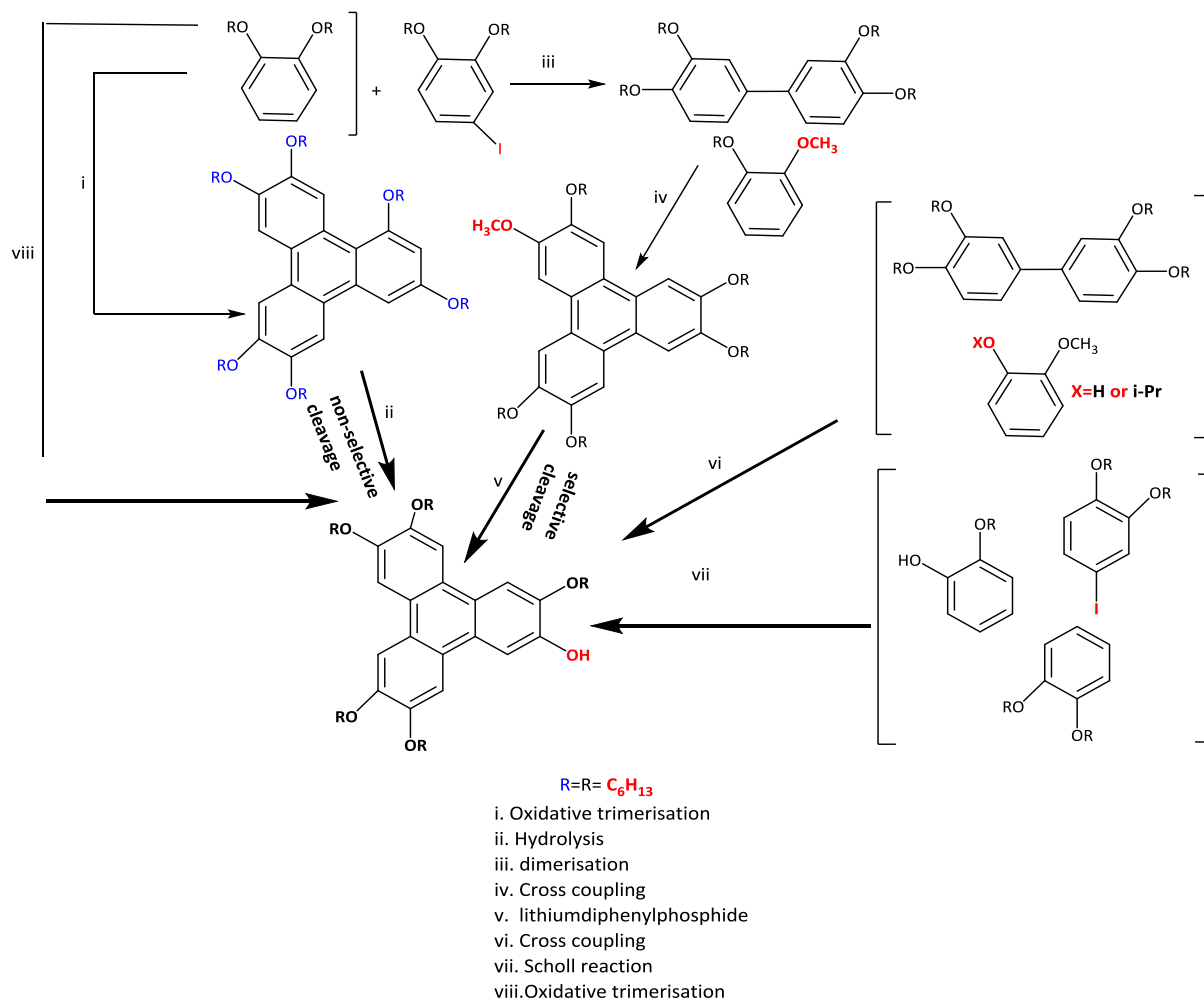
These hydroxy-functionalised triphenylenes can be achieved in different ways. The earliest one is the monohydroxypentaalkoxy-Tp synthesised by partial alkylation of hexaacetoxy-TP to monoacetyl-penta-alkoxy-TP in low yield, which can be hydrolysed to monohydroxy-pentaalkoxy-TP.



**Scheme 15:** Synthesis of unsymmetrical alkoxy-triphenylene by alkylation.<sup>6</sup>

Another important method is the non-selective cleavage of one of the alkoxy groups of the hexaalkoxytriphenylene. A selective cleavage of the methyl ether of monomethoxyalkoxy-TP prepared by biphenyl route with diphenylphosphide give the monohydroxytriphenylene at high yield; the disadvantage of this method is the low yield of biphenyl starting materials synthesised by Ullman coupling reaction. Synthesis of MHT by the direct coupling tetraalkoxybiphenyl and alkoxyphenols has also been reported.<sup>6</sup>

The summary of the different methods of synthesis of MHT reported by researchers is summarized as below in Scheme 16.



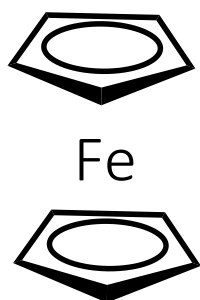
**Scheme 16:** Synthesis of Monohydroxytriphenylene (MHT).<sup>28</sup>

The synthesised monomethoxy-TP, Monohydroxy-TP and Pentaalkoxy-TP are not liquid crystalline. However, bromination of the pentaalkoxy-TP gives a liquid crystal derivative.<sup>28</sup>

### 1.10 Reaction of Ferrocene with Triphenylene

Ferrocene, which has the formula  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , is a kind of organometallic compound known as a prototypical metallocene. Structurally, ferrocene has a central metal atom with two cyclopentadienyl rings bound to it on opposite sides. It is therefore amongst those organometallic compounds, which are known as “sandwich compounds”. Ferrocene is unique in terms of structure, as well as its stability, both chemically and thermally. In addition, its sandwich structure, which is a three-dimensional aromatic system, gives it the potential for immediate use in a number of organic reactions.

Ferrocene was discovered in 1950 and, over the next 20-30 years, rapid progress was made in researching its chemistry. Research into ferrocene studied the many possible applications of this compound and its derivatives, such as in pharmaceuticals, and as additives for oils and motor fuels. It has also been used in fine organic synthesis, as a catalyst, as well as in and polymeric materials.<sup>29</sup>



**Figure 1.21:** Structure of ferrocene

The central metal atom in ferrocene is symmetrically bound to all five of the carbon atoms of each ring, and this is the compound's main, significant characteristic. However, the structure cannot accurately be described using the terminology of classical valency bonding because the metal is linked to each ring by means of just a single covalent bond. This type of bonding requires the availability of a d-orbital of the metal. Transition metals fulfil this condition, and it has now been demonstrated that all of them have the capacity to yield cyclopentadienyl derivatives.<sup>30</sup>

### **1. 10. 1 Monosubstitution of Ferrocenes**

If ferrocene is used as a terminal group, its large 3D structure produces a steric effect, which does not allow easy molecular packing. In the liquid crystalline phase, there is therefore a perceptible anisotropy of the intermolecular interactions.<sup>31</sup> This problem can be avoided in calamitic systems if extra benzene rings are added to enlarge the core (which is a rigid fragment) of the rod-shaped molecule. However, this results in a considerable rise in the transition temperature of the phase.

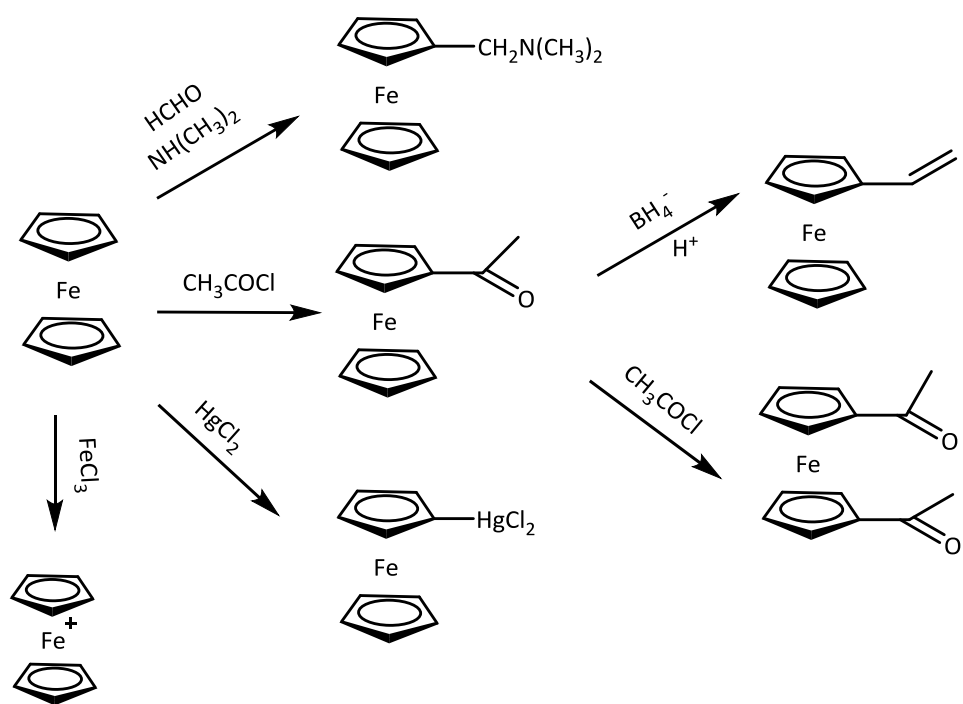
In calamitic systems, if mesomorphism is to occur when the ferrocene moiety is present, the molecular core must have a minimum of three aromatic rings. Where fewer benzene rings have been used, either no liquid-crystalline phase has been produced<sup>32, 33</sup> at all, or the result has been a smectic B phase with a high level of order, equivalent to plastic crystals.

Structures which have a trans-cyclohexane moiety, rather than benzene rings, are an exception, as are fused polycyclic moieties and some new compounds in which the two benzene rings, which form the rod-like fragment, are separated from the ferrocene moiety by a long hydrocarbon chain.<sup>34</sup> Another group of compounds is mostly made up of those ferrocene derivatives which have a cholesteryl group as their rigid core.

These cholesteryl group-containing mesomorphic compounds differ structurally from the majority of liquid crystals, which have characteristic traits in the molecule's rigid part. In liquid crystals made from monosubstituted ferrocenes, the properties they exhibit depend on a number of factors: the number of benzene rings, the length of the terminal group's hydrocarbon chain, the lateral substituents present in the aromatic system and the kind of linking groups found in the rigid molecular core.

### **1.10. 2. Electrophilic Reaction of Ferrocene**

Substituted derivatives can be produced from ferrocene because it goes through numerous reactions, which are typical of aromatic compounds.

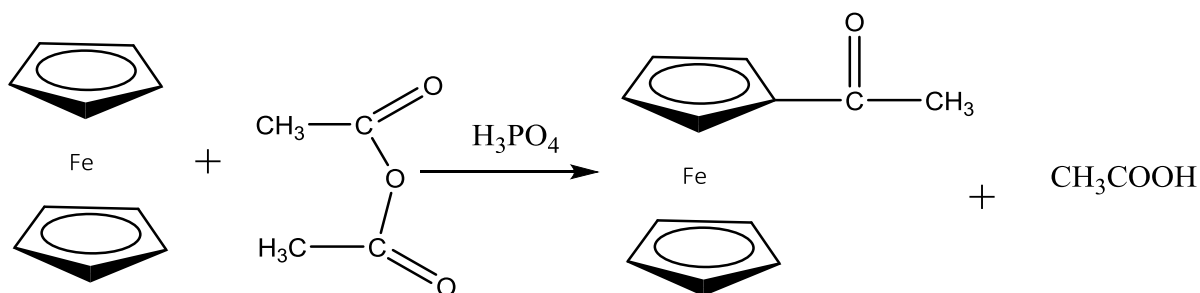


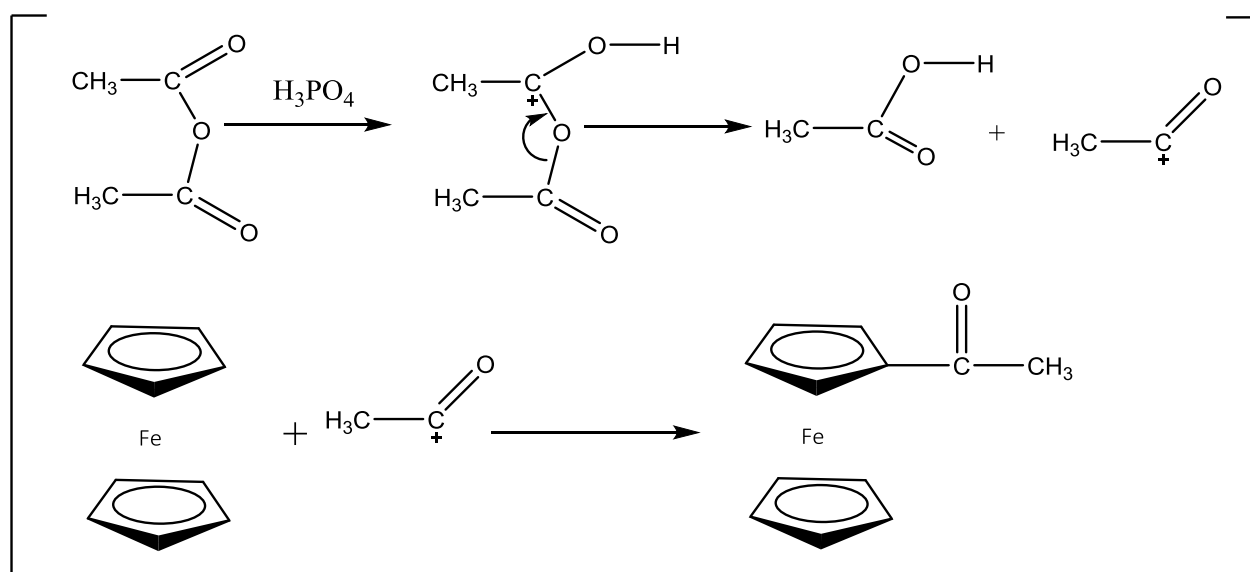
**Scheme 17:** Significant reactions of ferrocene with electrophiles as well as other reagents. <sup>35</sup>

A further example is the Friedel-Crafts acylation of ferrocene, an undergraduate experiment.

<sup>36</sup> This uses acetic anhydride with a catalytic quantity of phosphoric acid and yields acetylferrocene Scheme 18.

Aluminium trichloride is often used as a catalyst for acylations. However, in this case it generates the disubstituted: 1,1'-diacetylferrocene. Phosphoric acid, which is milder, is therefore preferable as a catalyst, producing the acylium ion electrophile by means of protonation. Acetic acid is then lost. <sup>36</sup>





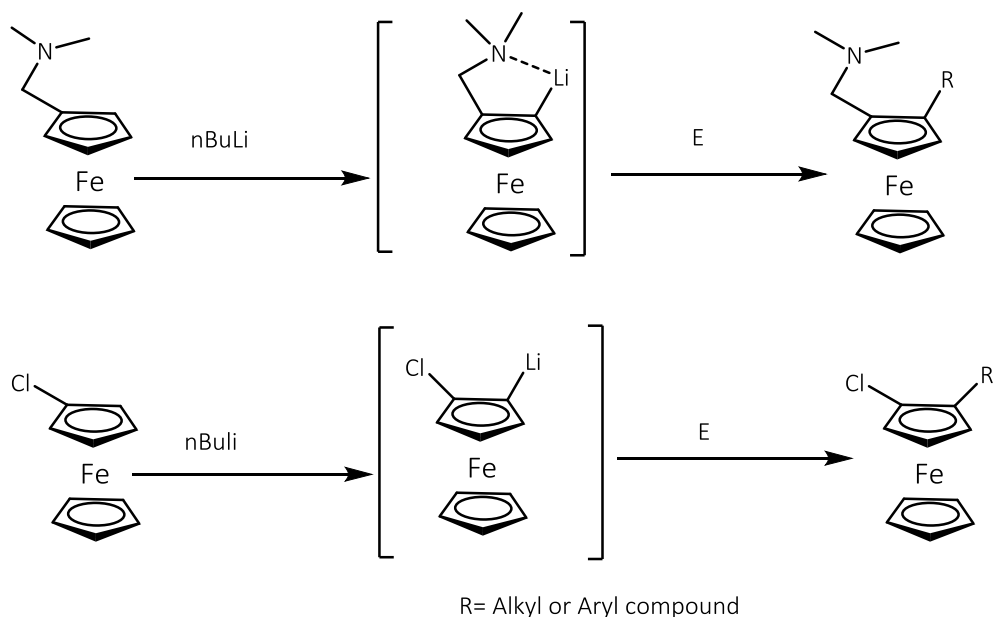
**Scheme 18:** Reaction and mechanism of acylation of ferrocene with acetic anhydride.

### 1.10.3 Disubstituted Ferrocenes

In order to compensate for the unwanted effects of the large ferrocene moiety, it is possible to use 1,3-disubstituted ferrocene substitutions, since the substituents, being in the same plane, make a rigid rod.<sup>37</sup>

These compounds exhibit other structural characteristics, such as planar symmetry. In addition, they have the potential to generate mesophases with chiralities as a result of the ferrocene moiety. However, in these cases, the enantiomers have to be separated, which is not easy. Thus new synthetic routes are being developed to achieve ferrocene derivatives of chiral smectic phases, which are planar, unsymmetrical substituted and have ferroelectric characteristics. 1,2-substituted derivatives are therefore most commonly used. Numerous methodologies for the synthesis of 1,2-disubstituted ferrocenes have been developed. Ortho-directing groups are used in most of these methods. For instance, *N,N*-dimethylaminomethylferrocene and chloroferrocene can both be ortho-deprotonated using *n*-butyllithium. It is then possible to react these lithiated intermediates with electrophiles to yield 1, 2-disubstituted products.



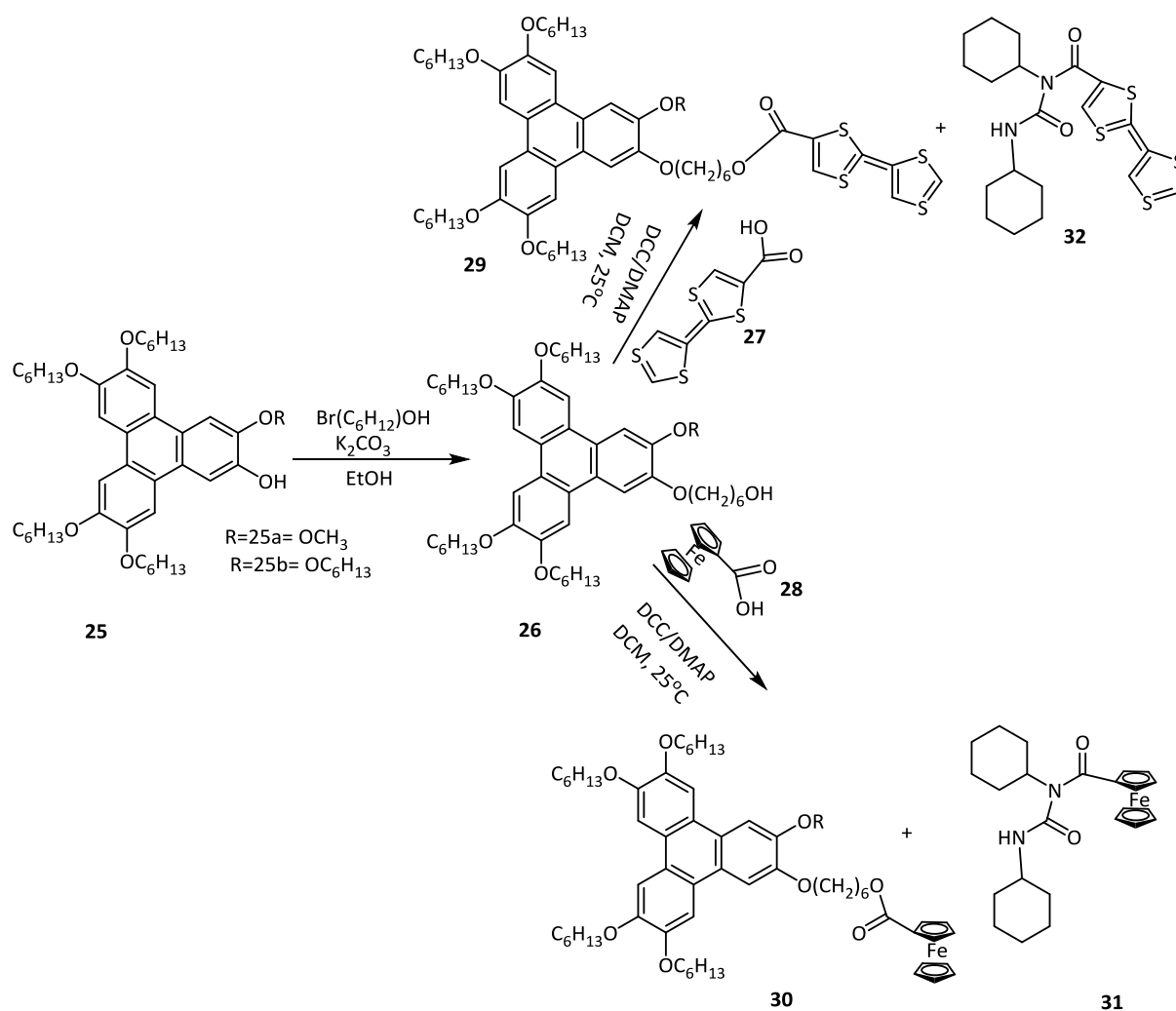


**Scheme 19:** Electrophiles of 1, 2 disubstituted ferrocene product

#### 1.10.4 Synthesis of Ferrocenyl Triphenylene

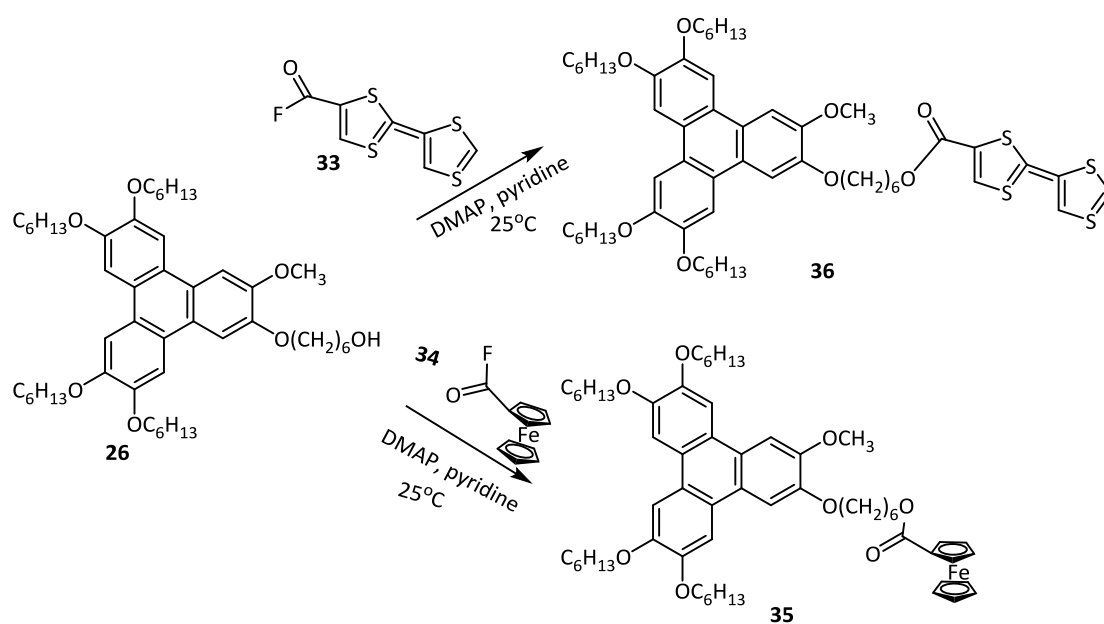
The chemistry of both ferrocene and triphenylene derivatives are a fascinating area for study, because these kinds of compounds have supramolecular formulations whose functionalised derivatives have the potential to generate a thermotropic discotic liquid crystal phase with high 1D conducting properties.

Work on producing Ferrocenyl triphenylene from monohydroxytriphenylene has been published by Cooke et al.<sup>38</sup> The triphenylene building blocks **26** were prepared from monohydroxy-triphenylene derivative **25**. This involved a  $K_2CO_3$  induced reaction using 6-bromohexan-1-ol. A good yield of triphenylenes **29** and **30** was produced using a DCC/DMAP esterification of compound with DCM at a temperature of 25 °C (Scheme 17). Replacing the methoxy ( $OCH_3$ ) on **25a** with a hexyl ( $OC_6H_{13}$ ) chain **25b** gave a higher yield of hexahydroxy-triphenylene derivative **26**.



**Scheme 20:** Synthesis of Ferrocenylcarboxy-triphenylene **29** and Tetrathiafulvalenylcarboxy-triphenylene **30**

Similar reactions were undertaken using **25a** with either **27** or **28** in DCM or THF. Only N-acyl ureas **31** and **32** were produced from these reactions. N-Acyl ureas are side products, which are known to form when carboxyl groups are activated with DCC.<sup>41</sup> The alcohol **26** in both of the DCM or THF solvents has low solubility. It would appear that this encourages the the O-acyl urea, which is produced in the initial reaction of the carboxy- derivatives with DCC, to reform as the N-acyl urea derivative.<sup>38</sup>



**Scheme 21:** Synthesis TTF-fluorocarboxyl-TP and Ferrocenyl-TP using Fluoro derivatives.

The use of fluorocarbonyl-TTF **33** and fluorocarbonyl-ferrocene **34** was investigated as an alternative to the DCC/DMAP esterification procedures, in order to avoid the high yields of by-products. These had already been demonstrated to be useful, effective reagents for the preparation of carboxylic esters. Derivatives **33** and **34** were found to be particularly effective reagents when preparing **35** and **36**. This concurred with the researchers' earlier work.

High yields of the required esters can be produced by adding DMAP to the reaction mixture.<sup>38</sup> The results achieved by Cooke et al demonstrate that using just DMAP as a catalyst and pyridine as a base can encourage the formation of the desired compound. However, rather than producing carboxylics, the derivatives formed are fluoro acyl compounds.

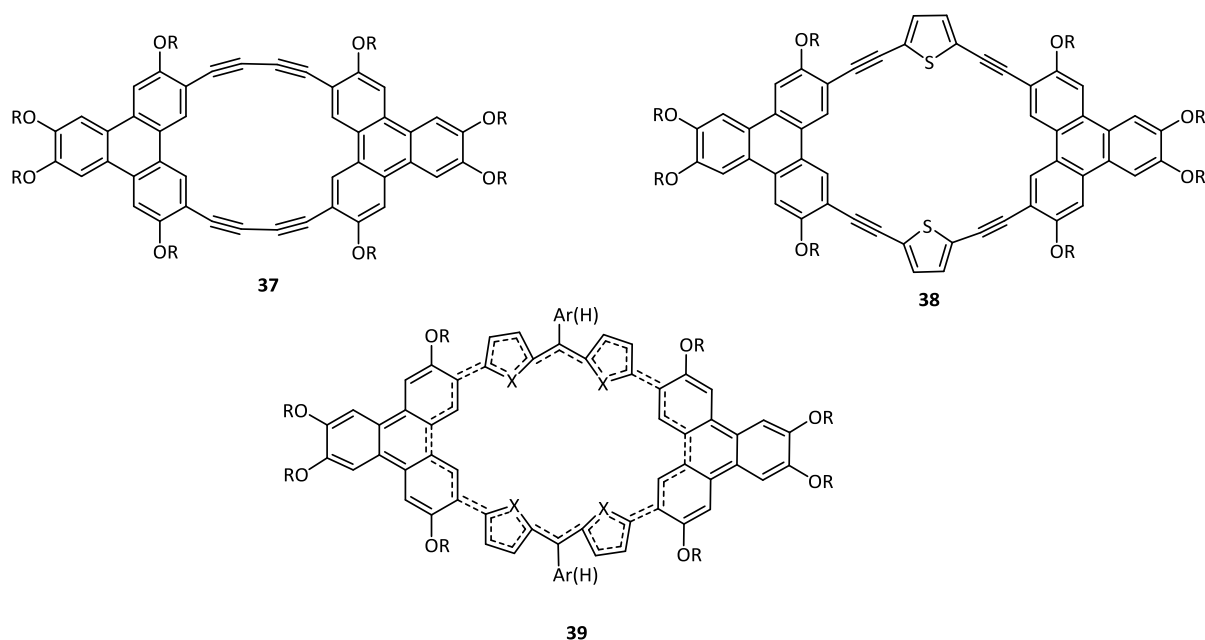
### 1.11 Synthesis and Properties of Twinned Triphenylenes (Dimers)

If two identical mesogen units with appropriate spacers are bound together, dimers can be produced. While the linking units can be either rigid or flexible, the flexible types are most frequently used. Dimers are the smallest oligomers and, due to their restricted molecular movement, exhibit physical characteristics which differ from those of conventional monomeric liquid crystals with low molar masses.<sup>39,40</sup>

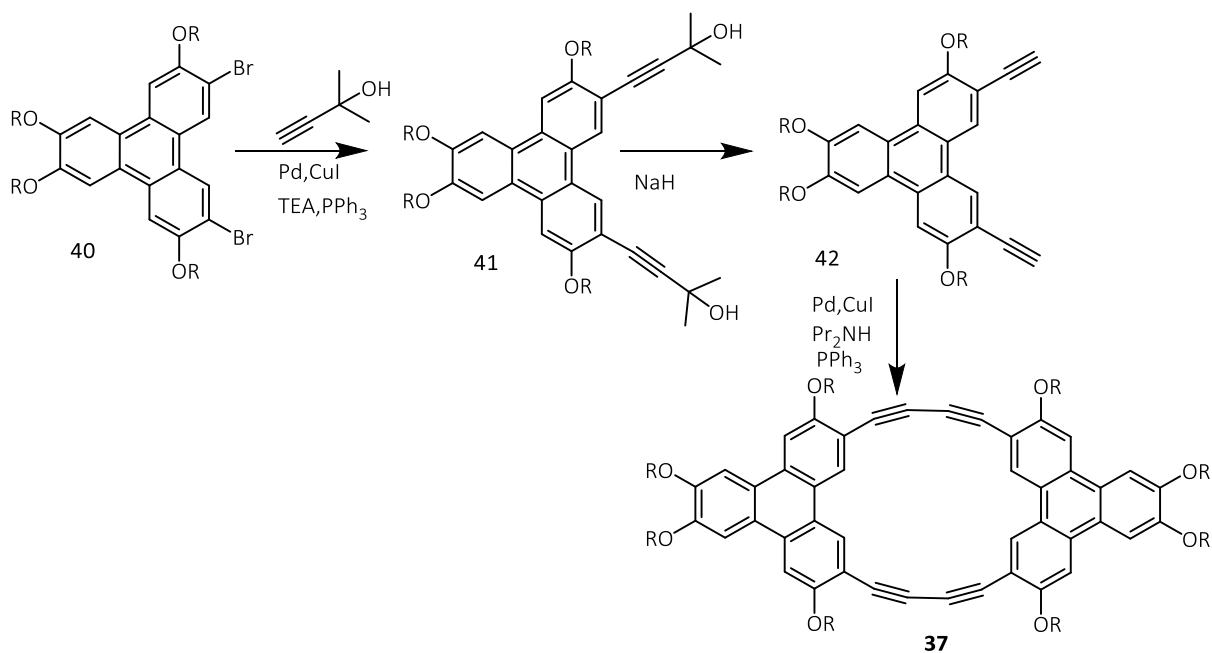
A new principle has been recognized for the design of discotic nematic liquid crystals. New types of discotic liquid crystal called “triphenylene twins” have been designed and synthesised. These have a mesogenic core consisting of two triphenylenes, which are covalently linked using a rigid spacer. These triphenylene twins are classified according to the length of their Beta-substituted chains (i.e  $R_2$  and  $R_3$ ) and their peripheral alkoxy or branched aliphatic chains ( $R_1$  and  $R_4$ ).<sup>41</sup>

Twinned macrocyclic structures with links at the 3, 6 positions have recently been made possible by improvements in synthesis techniques.<sup>5</sup>

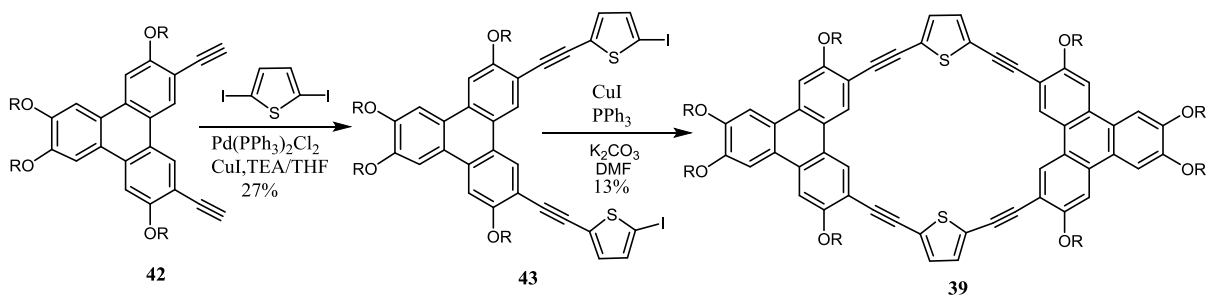
It has also been demonstrated that if triphenylene discogens are twinned using rigid linkers, nematic mesogen formation can occur, as opposed to the more commonly produced columnar mesophase.<sup>7</sup>



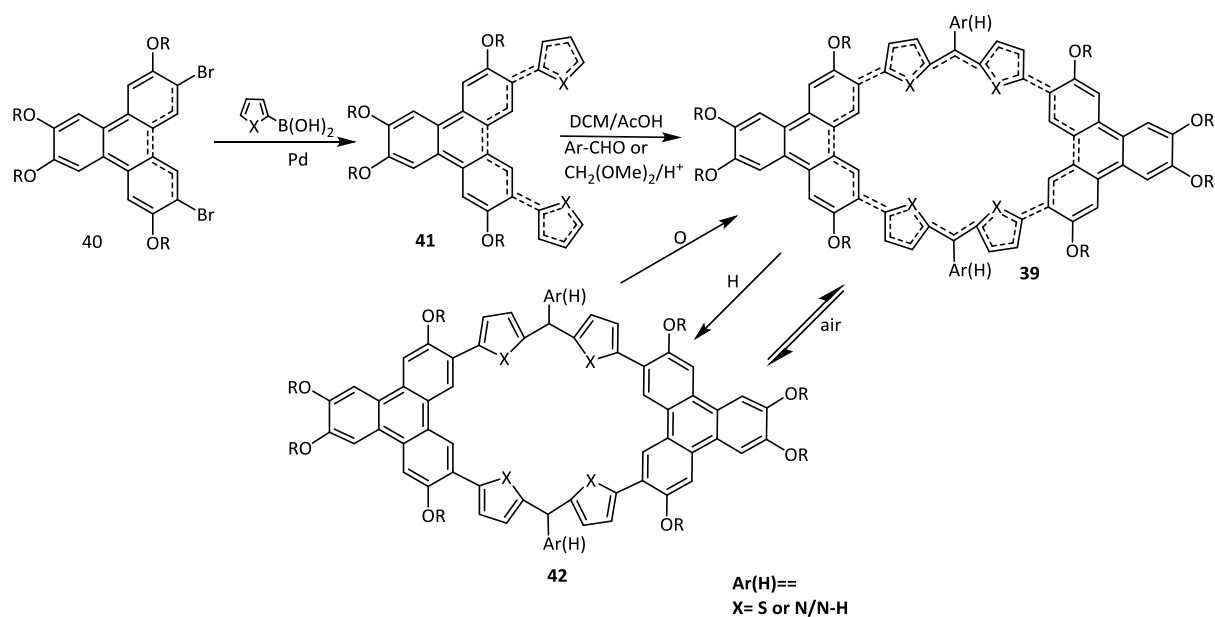
**Figure 1.21:** Some synthetic twinned triphenylenes.



**Scheme 22:** Synthesis of dehydroannulene-twinned triphenylenes linked through 3, 6 position.<sup>7</sup>

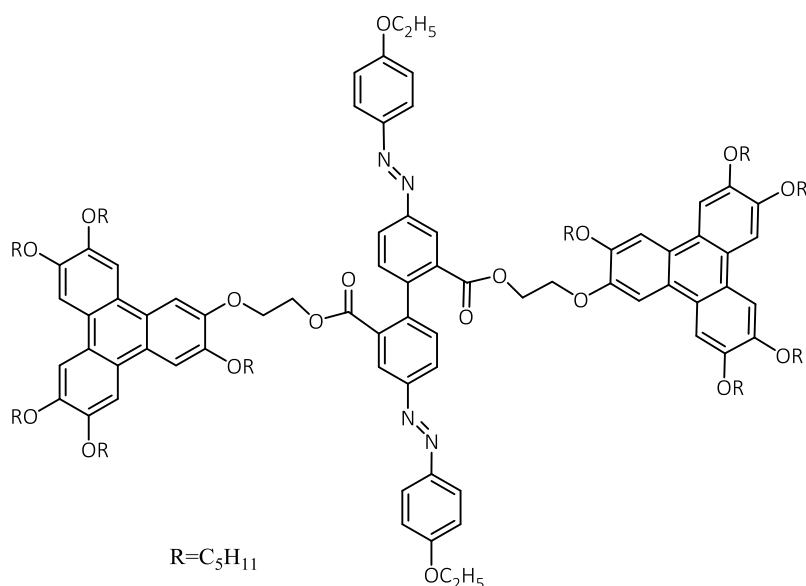


**Scheme 23:** Synthesis of thiophene-bridged twin.<sup>3</sup>



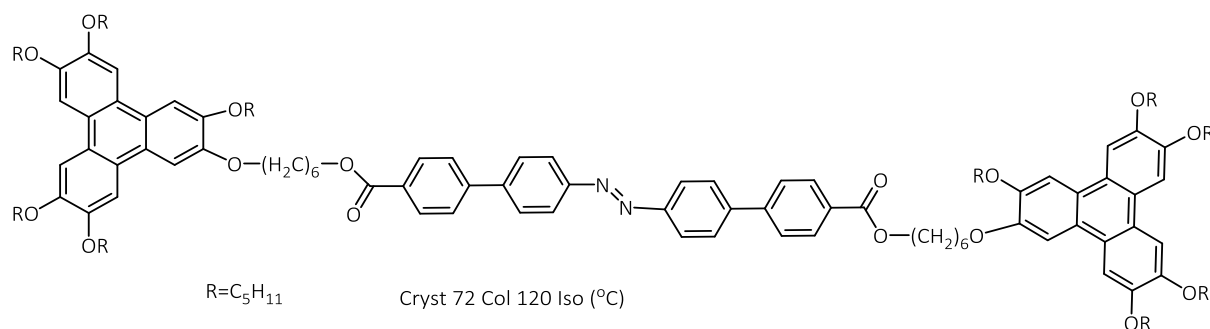
**Scheme 24:** Synthesis of expanded thiaporphyrin-like twins.<sup>27</sup>

Recent times have seen considerable progress in monofunctionalised triphenylene synthesis. As a result, various triphenylene based discotic dimers, oligomers and polymers have been produced. The easiest method for preparing a dimer is to attach two monomers using flexible spacers. Dimer chemistry includes a complex molecule, since a calamitic molecule is used to link the two triphenylene units.<sup>6</sup>



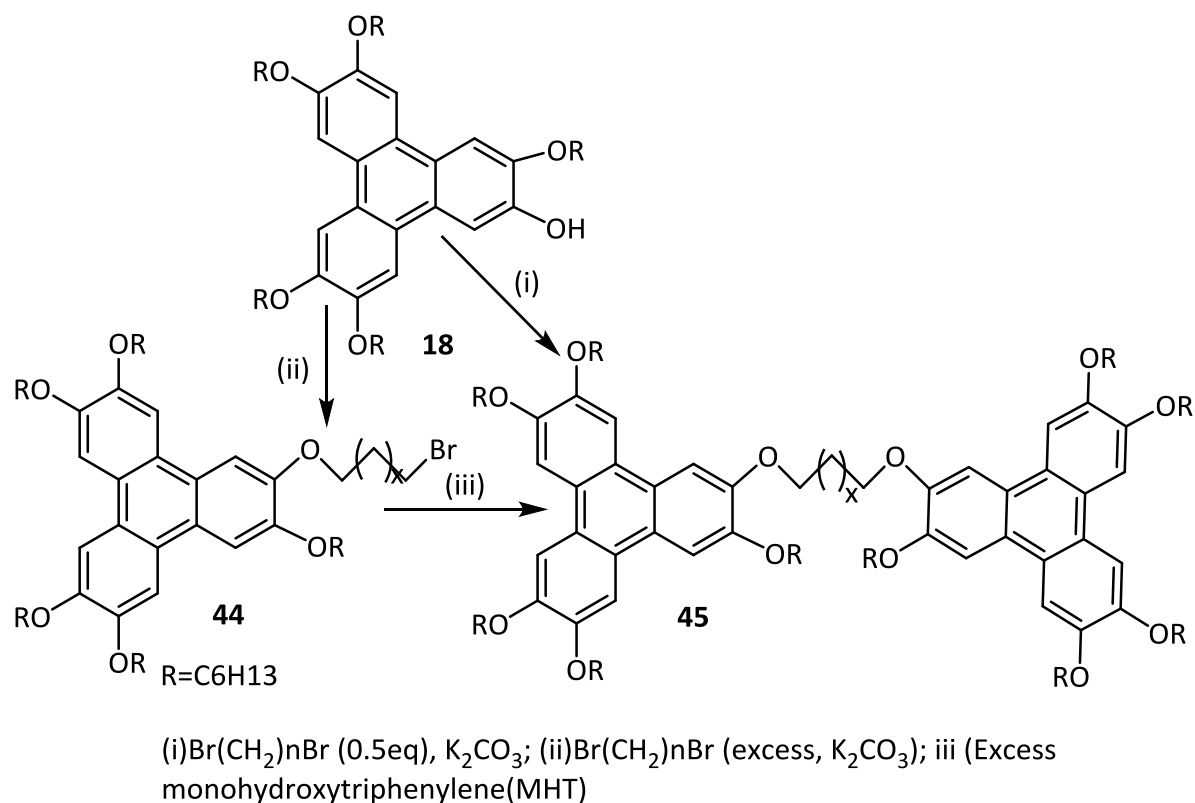
**Figure 1.22:** Dimer Ringsdorf et al's synthesis of a linked triphenylene.<sup>6</sup>

More liquid crystalline materials can be prepared by using a mesogenic azobiphenyl moieties instead of azobenzene. The resulting materials melt at 72°C to produce an extremely viscous mesophase which clears at 120°C.<sup>32</sup>



**Figure 1.23:** Discotic dimer with an azobiphenyl moiety.<sup>42</sup>

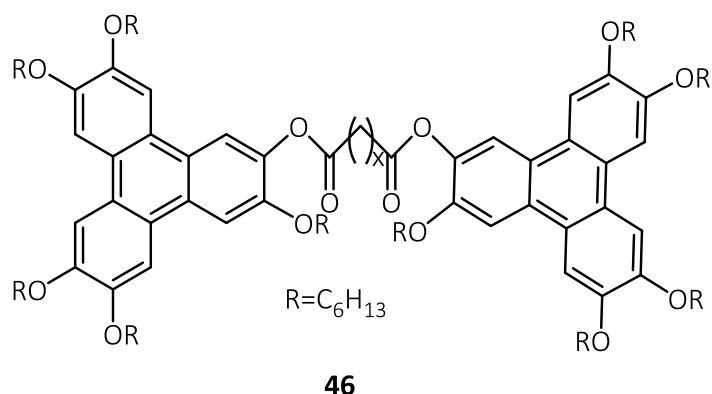
The most frequently prepared triphenylene dimers have two identical triphenylene moieties which are linked by means of a spacer. This spacer often consists of poly-methylene chains. However, esters or amide linkages are sometimes used at the centre of the spacer in the terminal positions. Illustrated below is one of the five triphenylene twins designed by Kumar and co-workers.



**Scheme 25:** Synthetic route for producing a symmetrical dimer.<sup>42</sup>

An unsymmetrical twin, in which a short methoxy chain was used to replace one of the long alkoxy peripheral chains, was reported by Boden et al. In this case, preparation of the starting material is by means of a phenyl-biphenyl coupling between tetrakoxy biphenyl and 2-methoxy phenol.<sup>42</sup>

In 1990, structures with liquid crystal properties were reported by Krag et al, using ester rather than ether linkages.



**Figure 1.24:** Discotic dimer with ester linkage.<sup>42</sup>

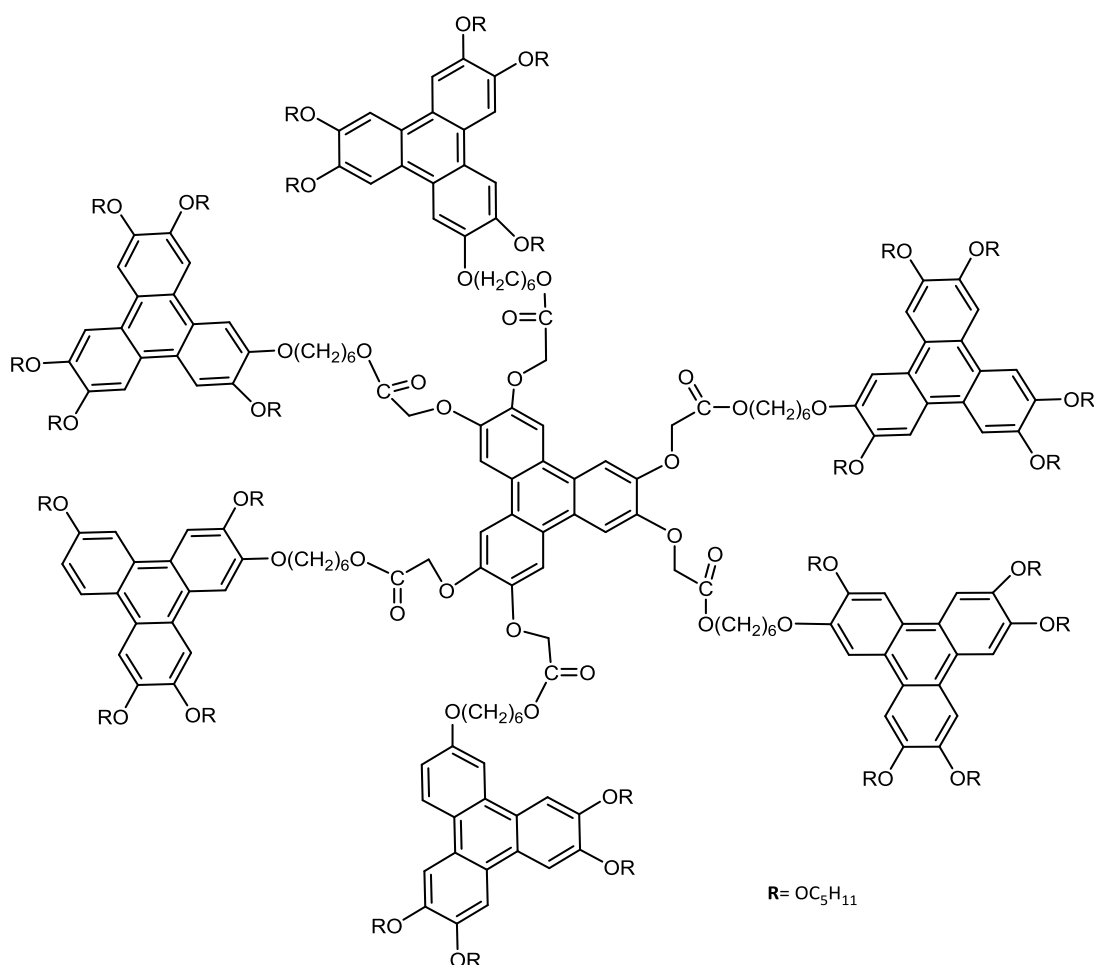
It has also been shown that two major factors to consider, when molecular self-assembly of the triphenylene twin is required, are rigid spacer length and beta substitution. Triphenylene twin which exhibit polymorphism, including the nematic phase have also been produced.<sup>15</sup>

Furthermore, research into the effects of linkages and functional groups has produced monomers which are joined by an alkyl chain, by means of either an ester linkage on one side or an ether linkage on the other. Discotic dimers and trimers have been designed and produced with triphenylene electron donor moieties and anthraquinone electron acceptor moieties, with different functional groups. These have various nematic and columnar mesophases which are stable at room temperature. It has been found that molecular assembly is affected by both the functional group at the core and the terminal linking group. Moreover, it has been demonstrated that the non-branched peripheral chains, which are common in DLCs can generate the nematic phase at room temperature.<sup>6</sup>

Columnar mesophases with star-like liquid crystals (Figure 1.29) are seen in cases where the discotic structure consists of a triphenylene core and six peripheral triphenylene units, this



architecture of this type have much potential for further development.<sup>5</sup>



**Figure 1.25:** Star-like liquid crystals with central triphenylene cores.

The mesomorphic tendency of the compounds is increased if the core is larger than benzene. Most discotic materials exhibit columnar phases, sometimes with a nematic phase ( $N_D$ ) as well.<sup>43</sup>

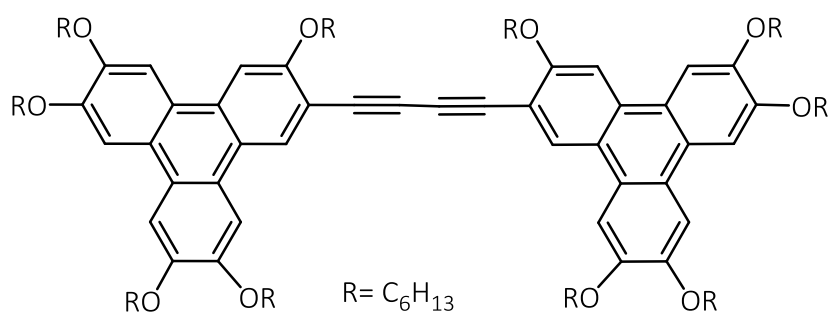
### 1.11.1 Triphenylene acetylene dimer

Compounds whose peripheral moieties are joined to the central, disc-like core using acetylene links, have the exceptional qualities of low melting points and the ability to exhibit just a nematic phase without a columnar phase.

Steric interaction between aryl rings can be prevented by introducing acetylene linkages. This also permits the rings to twist at 90° to each other. Furthermore, acetylene links are highly

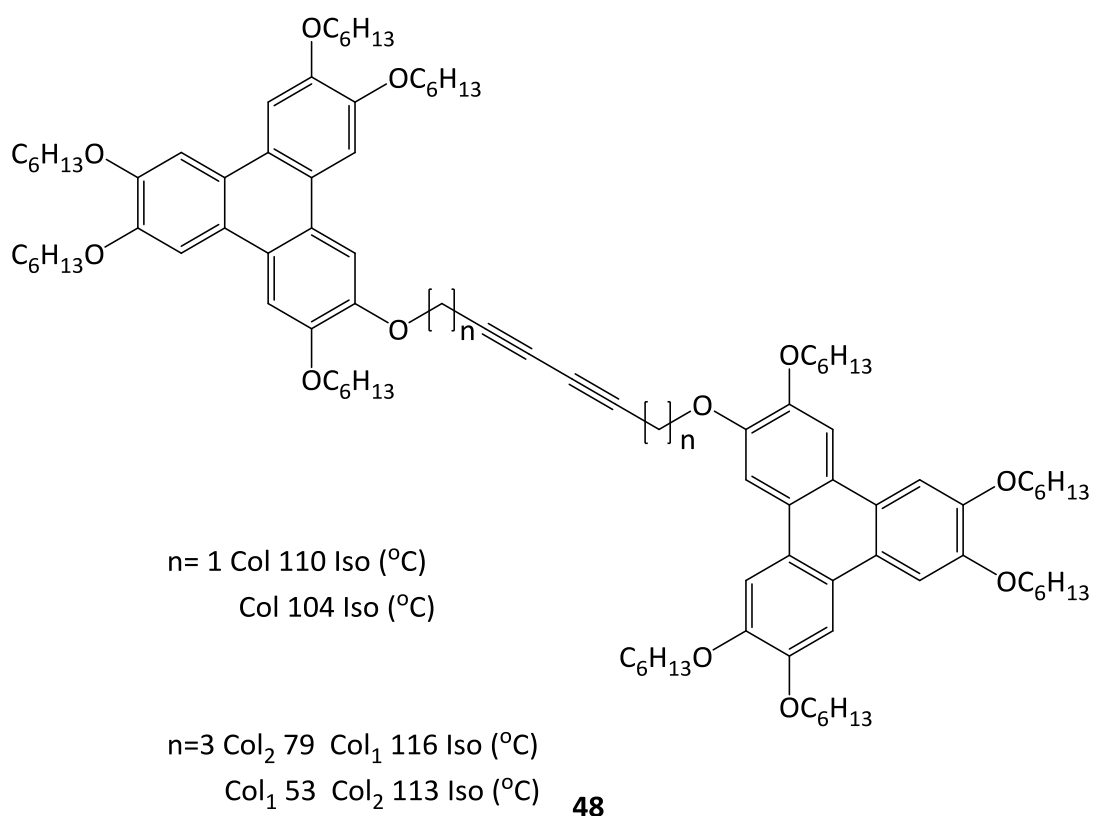
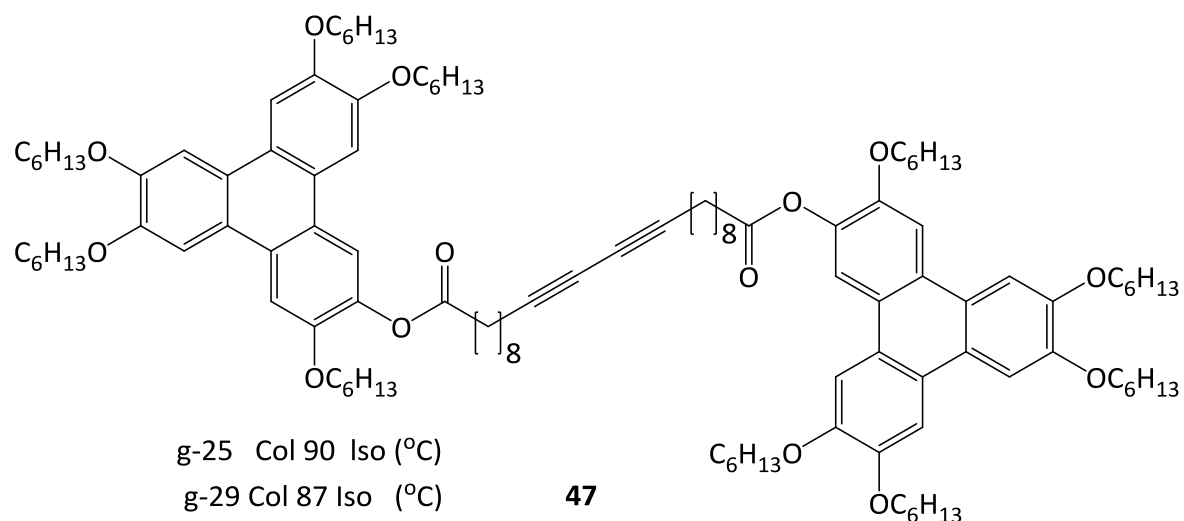
polarizable. This is because the molecules are face to face as they come together to form columns. Since they repel one another, they slide sideways, thus avoiding the columnar phase and forming a nematic phase.<sup>43</sup>

Triphenylene dimers, where a rigid  $\pi$ -conjugated diacetylene spacer was used to link two identical triphenylene units, were synthesised by Kumar et al. Preparation of these dimers, which exhibited discotic nematic mesophases over a wide range of temperatures, causes dimerization of the triphenylene derivatives using a free monoacetylene group.<sup>6</sup>



**Figure 1.26:** Diacetylene Bridge Triphenylene Dimer

A number of diads joined by acetylene units were synthesised in 2009. These dimers were shown to form more stable, more ordered columnar mesophases than their equivalent monomers. Furthermore, their semi conductive properties were enhanced.<sup>44</sup> It was also discovered that the high symmetry of **36** improved the  $\pi$ - $\pi$  interaction between the triphenylene cores. In addition, the formation of ordered columnar mesophases was enhanced.

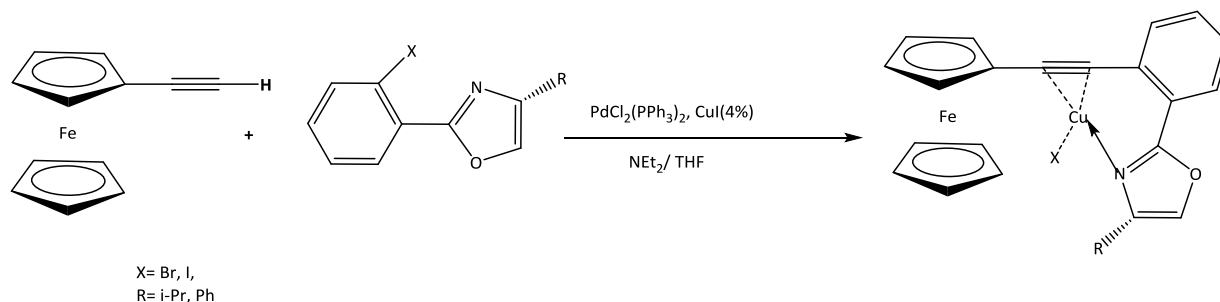


**Figure 1.27:** Acetylene linked triphenylene dimer.<sup>39</sup>

The most effective reaction method for coupling acetylenes with aryl and vinyl halides is Sonogashira coupling. This method has been used to synthesize numerous products, including polymers, pharmaceuticals and functionalised materials.<sup>45</sup>

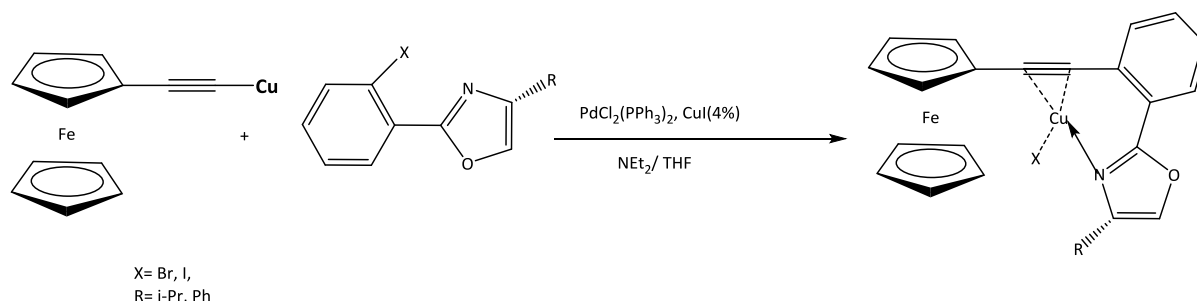
Deb et al.<sup>45</sup> conducted Sonogashira coupling of ethynyl ferrocene and oxazolinyll

bromobenzene. This experiment used a Pd catalyst with CuI. The result was a yield of both CuI and CuBr bound complexes Scheme 25. This suggests that the chiral ethynyl ferrocene ligand has a strong tendency to form Cu (I) complexes. Thus,  $\pi$ - complexes can be generated by more than one pathway.



**Scheme 26:** Synthesis of  $\pi$ - Cu complexes during the Sonogashira reaction

Investigation of the potential for isolating complexes which have similar ligands was undertaken. Cuprous Ferrocene acetylide was prepared. This was then reacted with oxazolonyl iodobenzene Scheme 26. Reaction conditions similar to those shown in Scheme 25 were used. The reaction took place, although the coloured compound, which was produced, was not sufficiently stable for isolation.

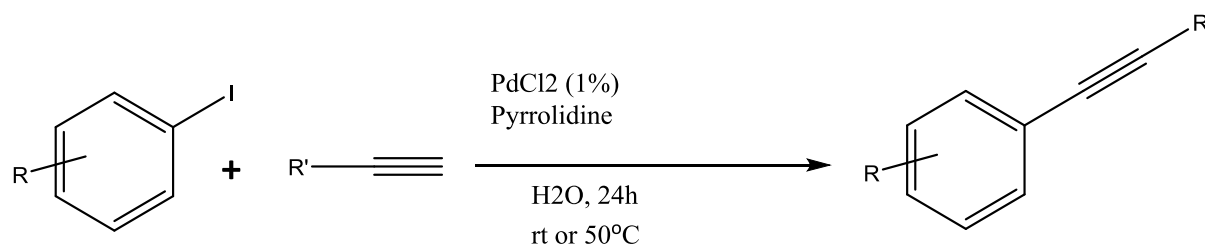


**Scheme 27:** Synthesis of  $\pi$ - Cu complexes using cuprous acetylide by Sonogashira reaction.

It is possible that the ferrocene unit is responsible for this effect. The Cu (I) centre might be protected by its steric bulkiness, thus providing a level of stability, which cannot be achieved using a phenyl group. This issue affects acetylene coupling when derivatives other than acetylene bonds coupled to themselves are used. Thus a dimer is the result, rather than the formation of the expected product.

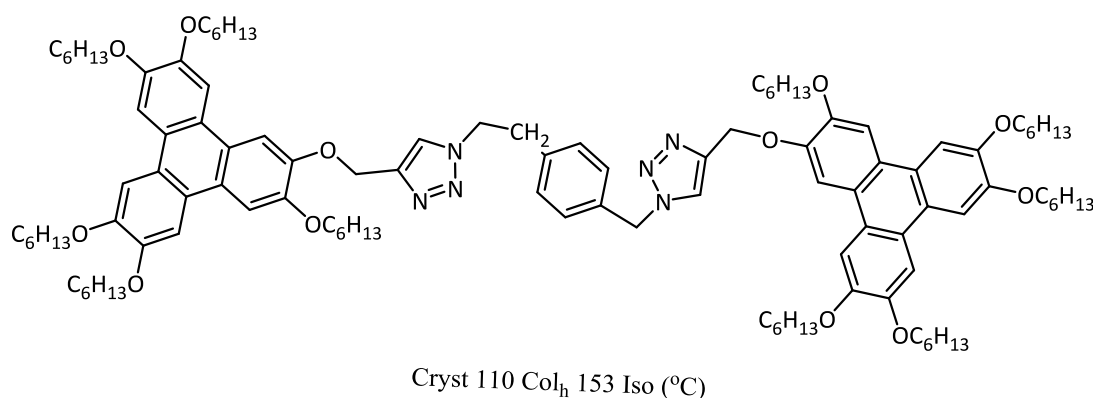
Numerous Sonogashira reactions were conducted without using copper salts. This avoids the copper mediated oxidative homocoupling of acetylene, making it possible to perform Sonogashira reactions under aerobic conditions. Many such reactions have proven successful.

Liang et al have developed a mild protocol for the copper-free Sonogashira coupling of aryl iodides with terminal acetylenes. This is conducted in water under aerobic conditions. The process is carried out at room temperature and uses 1 mol % PdCl<sub>2</sub> in the presence of pyrrolidine. Good or excellent yields have resulted.<sup>46</sup>



**Scheme 28:** Copper-free Sonogashira coupling of aryl iodides with terminal acetylenes.

Click chemistry has recently been used to produce a triphenylene diad. The triphenylene units are linked using a triazole.<sup>47</sup> Two diads were synthesized. One of these was linked using a -CH<sub>2</sub>-unit. The other was joined by means of a phenyl group. The intention was that the formation of columnar mesophases would be enhanced by the addition of an aromatic group.



49

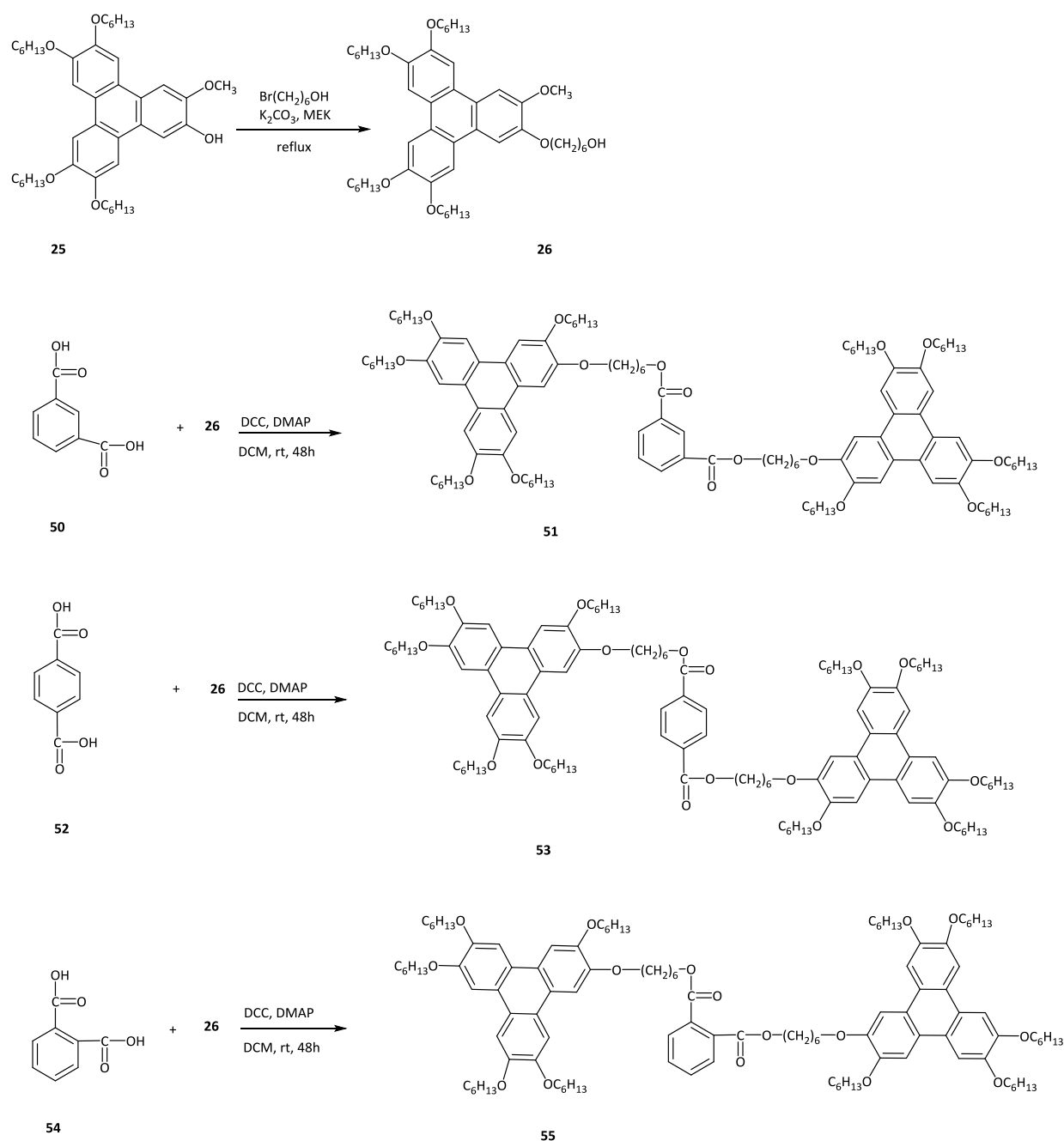
**Figure 1.28:** Triphenylene dimer linked through diazole link.

Analysis of the diads, however, revealed that it was only the -CH<sub>2</sub>-linked dimer which exhibited mesophase behaviour. It was suggested that the reason for this was, as Kumar had stated, that the flexibility provided by the spacer was reduced by the extra aromatic ring's rigidity. Thus, the stacking of the triphenylene cores is made more difficult.<sup>48</sup>

### 1.11.2 Synthesis of twinned triphenylene ester

Ester or amide linkages have also been used, either in the centre of the spacer or in the terminal positions.<sup>38</sup>

Synthesis of compound **26** was undertaken using the route illustrated in Scheme 19. This involved a potassium carbonate mediated esterification of monohydroxytriphenylene **25** with 6-bromohexanol-1 in ethylmethyl ketone. The required intermediate was thus produced.<sup>49</sup>



**Scheme 29:** Synthetic route of Ester dimers.

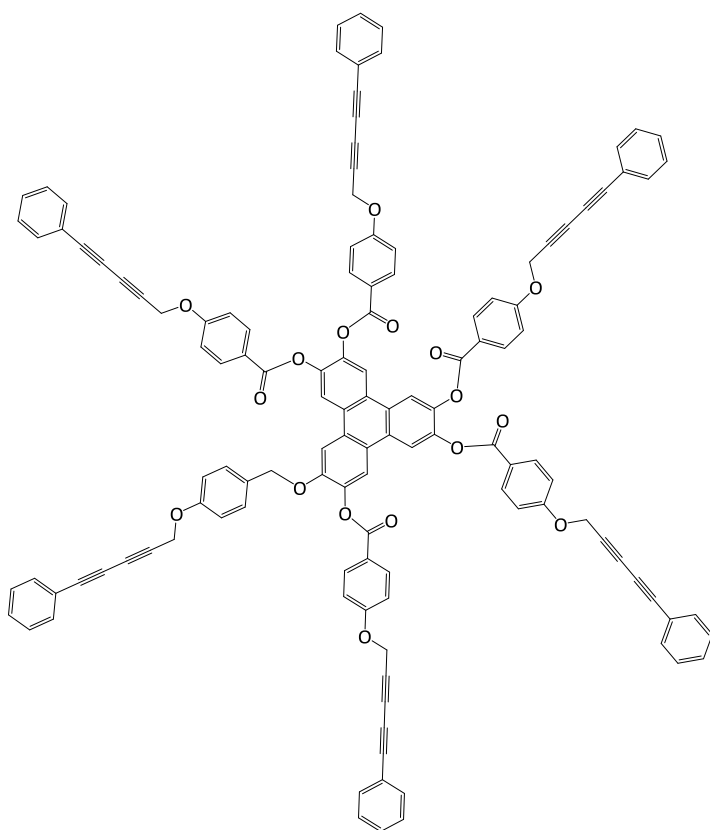
Esterification of hydroxyl functionalized triphenylene 26 was used to generate the ester dimers using benzene dicarboxylic acids. Ester dimer **51** was obtained using isophthalic acid, **53** with terphthalic acid and **55** with phthalic acid. This was carried out in the presence of N, N'- dicyclohexylcarbodiimide (DCC). The solvent used was a catalytic quantity of 4-dimethylaminopyridine (DMAP) in dry dichloromethane.<sup>25</sup>

## **1.12 Application of Triphenylene**

Triphenylene derivatives have many applications as listed below, many are due to the liquid crystalline properties of the compounds synthesised.

### **1.12.1 Optical Compensation Films for LCDs**

Liquid crystal display (LCD) devices have been dominated by calamitic LCs.<sup>49</sup> Mixture of twisted nematic and super twisted nematic displays were used, however there were a number of problems associated with these types of displays. In 1995 Fuji Photo Film Company filed a patent for a thin film comprising of a triphenylene-based discotic liquid crystal with diacetylene groups in the side chain.<sup>50</sup>



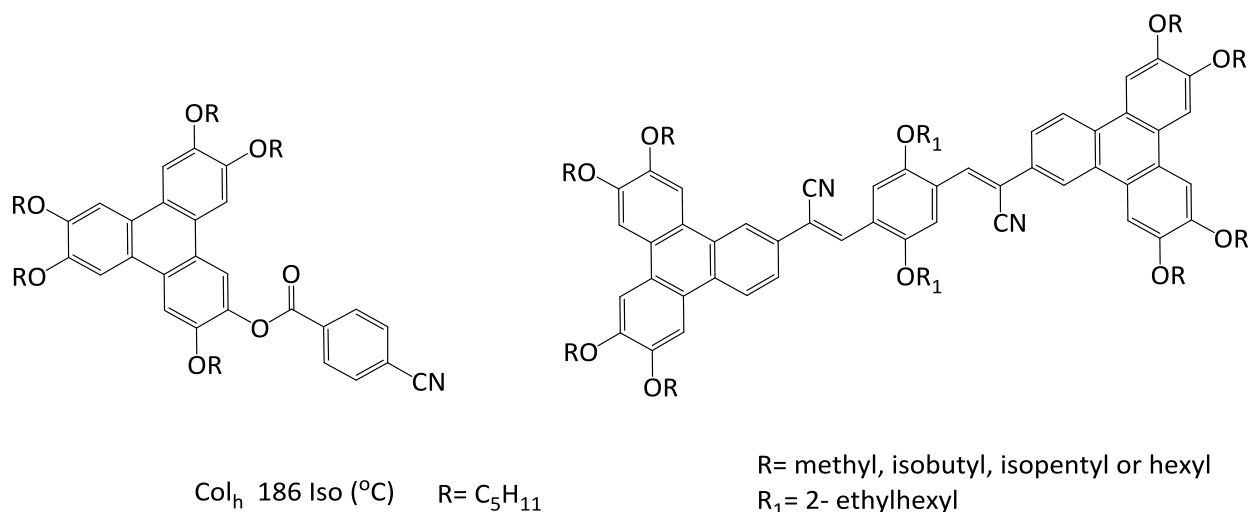
**Figure 1.29:** Example of TP based DLC patented by Fuji Photo Film Company

This negative birefringence optical compensation film was used to overcome the issues of the narrow viewing angle of the compounds utilised in the LCDs. A single discotic compensation film has also been found to reduce the cost of LCDs, lower the operating voltage and colour-shift, and raise the contrast ratio.<sup>51</sup>

### 1.12.2 Organic Light Emitting Diodes.

Conjugated bridged triphenylene derivatives show electroluminescent properties. These compounds could be used as the emissive layer in organic light-emitting diodes (OLEDs). OLEDs are devices that utilise a layer of organic material sandwiched between two electrodes, one a transparent anode and the other a metallic cathode.<sup>52</sup> These have two main benefits over liquid crystal displays (LCD), first they do not require a backlight so are much thinner and lighter, and secondly they can be viewed from a range of angles. Researchers showed that their triphenylene derivatives could be used in single and double layer displays.





**Figure 1.30:** Triphenylene derivatives use in OLED devices.

To create the organic layer, thermal evaporation is used; this process means that the thickness of the layer can be controlled under vacuum conditions. The energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) determines the colour of the photon, this is therefore controlled by the extent of the  $\pi$ -conjugation in the molecule.<sup>53</sup>

### 1.12.3 Gas Sensors

Devices used in the sensing of volatile gases were found to have a significant problem, their sensitivity to water vapour; in humid conditions, the signals from the volatile materials were unable to be detected. A solution for this was found by Clements *et al.* when they tested triphenylene systems.<sup>54</sup> These TP systems were highly sensitive to the presence of volatile substances, including non-polar molecules such as alkane hydrocarbons, and also alcohols, esters and aromatics. However, they showed no sensitivity to the presence of water vapour, making them ideal candidates for gas sensors.

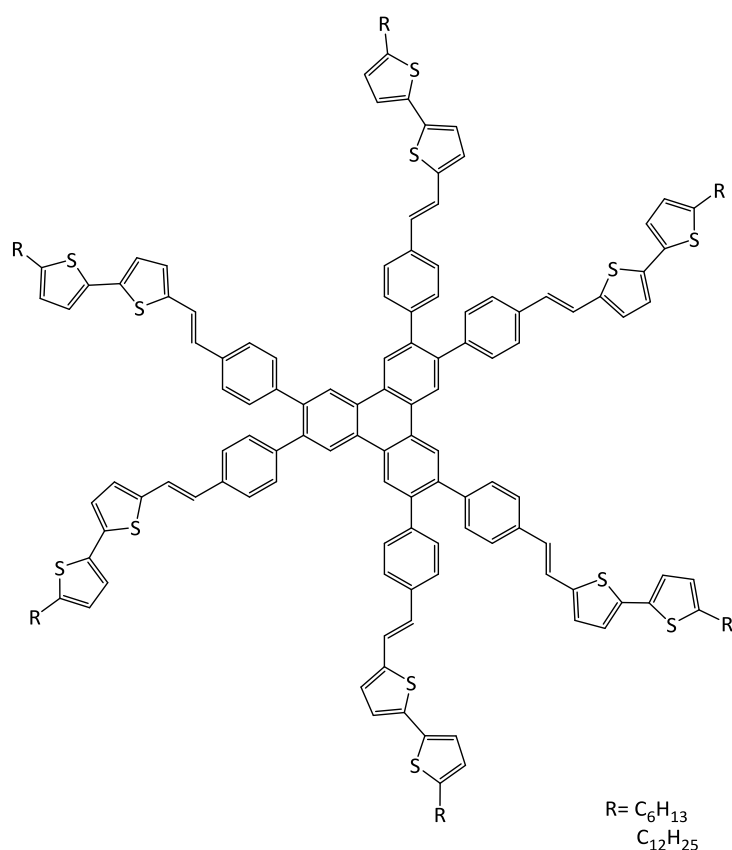
More recently, a triphenylene-tricarboxylate system has been incorporated into a metal-organic framework (MOF) which displayed highly selective absorption of gaseous  $\text{CO}_2$  over  $\text{CH}_4$  and  $\text{N}_2$ .<sup>55</sup> The TP-MOF could also selectively absorb the nitro explosive 2,4,6-trinitrophenol (TNP), giving the structure potential applications in the monitoring of TNP.

#### 1.12. 4 One-dimensional Energy Migration

Columnar liquid crystals have been reported as one-dimensional systems for electronic excitation transport since 1987.<sup>56</sup> The discotic mesogens stack in columns that act as molecular wires, allowing for conduction through the cores, with the peripheral chains insulating the columns. Triphenylene derivatives have been extensively studied for these properties.

#### 1.12.5 Organic Field-Effect Transistors

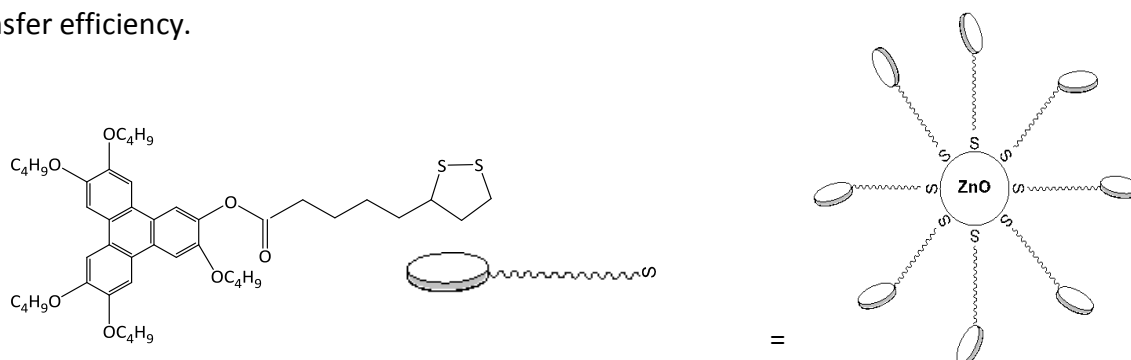
The first organic field-effect transistor (OFET) was designed using poly-thiophene as the active semiconducting material. The OFET had two major advantages, the cost of materials and manufacturing were reduced and the device became more environmentally friendly. The compounds synthesised are thiophene-based  $\pi$ -extended triphenylenes (Figure 1.36). They were shown to have good film forming properties, a high degree of crystallinity and lower optical bandgap energies



**Figure 1.31:** Structure of thiophene based  $\pi$ -extended triphenylene for OFET fabrication.

### 1.12.6 Photovoltaic Solar Cell

Triphenylene moieties have also been utilised in photovoltaic solar cells. Chen *et al.* modified zinc oxide nanoparticles to introduce dithiol-functionalised triphenylene ligands (Figure 1.37).<sup>57</sup> They found that the modified nanoparticles enhanced the charge separation and transfer efficiency.



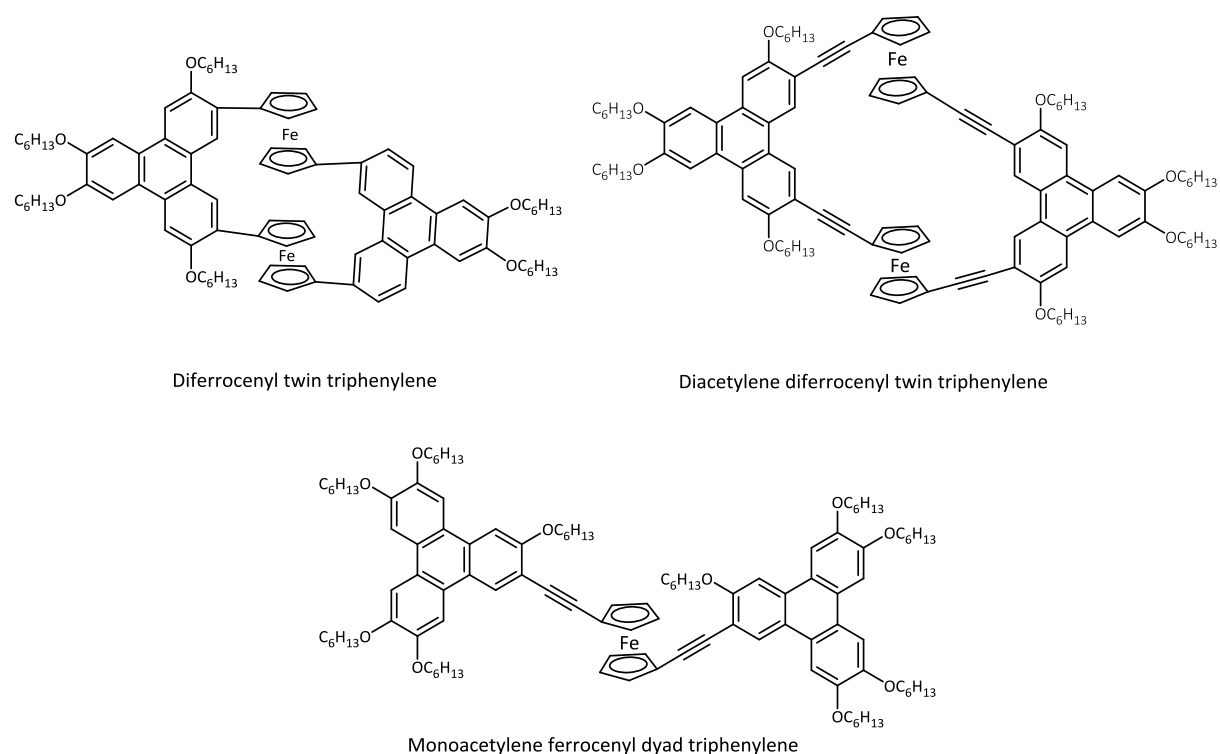
**Figure 1.32:** Structure of dithiol-triphenylene ligand, structure of ZnO Nanoparticle modified with triphenylene ligands.

### 1.13 Aims and objectives

The aim of this research is to explore approaches to the synthesis of triphenylene mesogens that are linked through staggered ferrocene bridges. This type of molecular architecture for discogens is new and intriguing and follows the group's recent discoveries concerning flat, twinned systems.

A general observation is that linking two triphenylene units through an appropriate length, rigid spacer will give distinctive architecture that can yield rare Nematic mesophases.<sup>48</sup> More conventional, flexible spacers give columnar phases. The spacer could be a polymethylene chain but in some cases, there could be an ester or amide linkage in the middle of the spacer or at the terminal positions.<sup>6</sup>

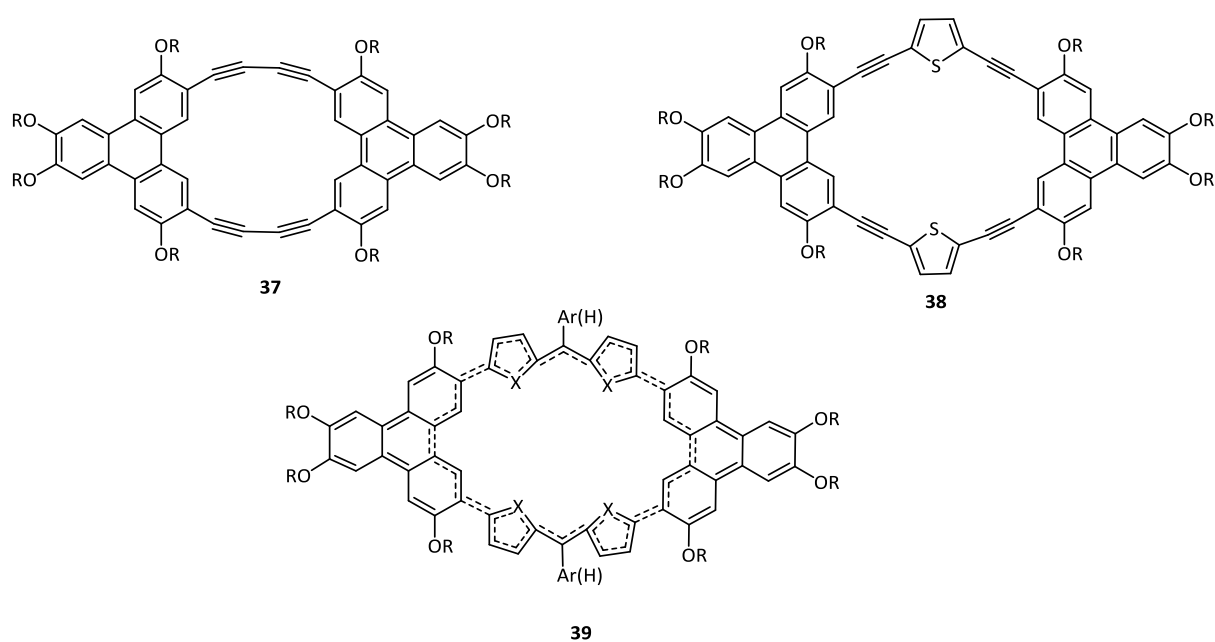
The triphenylene derivatives used for discotic liquid crystals are often 2, 3, 6, 7, 10 and 11 substituted (Figure 1.1). The target compounds in this research will be linked to one or two of this substituted position/s (Figure 1.33)



**Figure 1.33:** Triphenylene dimers

Our initial aim was to use a 3,6-dibromotriphenylene discogen as a common intermediate for the synthesis of staggered twins. A new synthesis of this important precursor was therefore planned to be initially investigated. Two different approaches were originally planned, direct linking and via acetylene units using Suzuki and Sonagashira couplings as key steps. Model compounds (monomers and more flexible dyads) were planned to be prepared for comparison.

However, previous work in our group has shown that twinning triphenylene discogens through rigid linkers gives rise to nematic mesophase formation compared to the formation of columnar mesophases that are normally observed. Some twinned triphenylenes synthesised from our group are as in Figure 1.34.

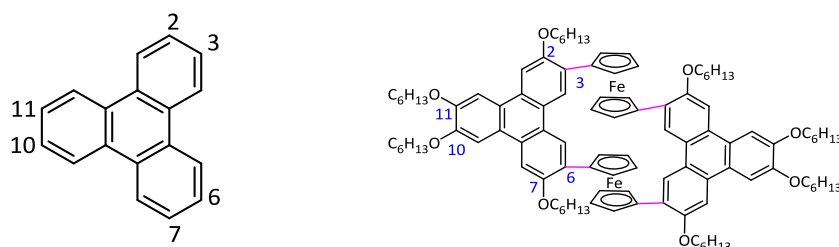


**Figure 1.34:** Some synthetic twinned triphenylenes.

## CHAPTER 2 RESULTS AND DISCUSSION

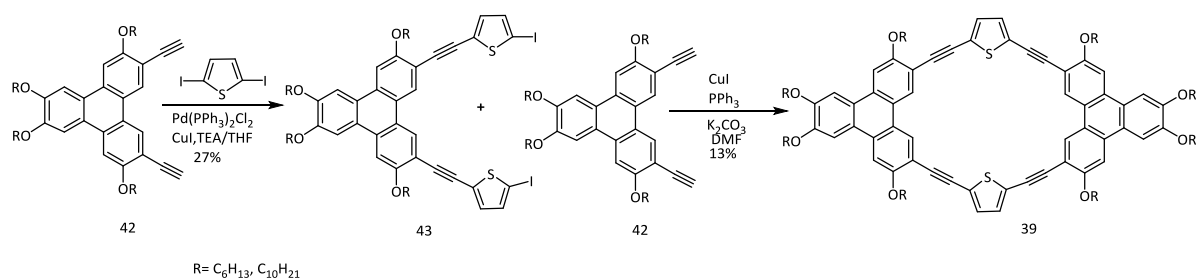
### 2.1 Synthesis of Staggered Triphenylene Twins Linked Through Ferrocene Bridge.

Our research work focuses on the synthesis of new twinned triphenylenes. The two triphenylenes are staggered with respect to each other. This architecture is new, and intriguing. The simple twinned triphenylene is the recent focus. The general observation is that linking two discotic triphenylene units through an appropriately lengthed, rigid spacer can yield nematic materials,<sup>48</sup> an important observation. Interestingly, our group have successively synthesised some discotic liquid crystals showing nematic phase. This research therefore initially focuses on the synthesis of twinned triphenylene with staggered ferrocene bridge because the product may have unusual liquid crystal properties because the bridging mode gives a unique architecture. Triphenylene linking position for discotic liquid crystals is 2, 3, 6, 7, 10 and 11 (Figure 2.1). We are therefore interested in the link and properties of the staggered ferrocene unit because the molecule or shape is unique. The target triphenylene twin will be linked by two ferrocenes, linking at position 3 and 6 of the triphenylene, other peripheral units ( $-OR$  where  $R$  is  $C_6H_{13}$ ) will occupy the remaining positions. The gap between positions 2 and 3 is smaller than the gap between position 3 and 6 in triphenylene Figure 2.1.



**Figure 2.1** Triphenylene linking sites and Ferrocenyl triphenylene twin.

### 2.1.1 Previous work

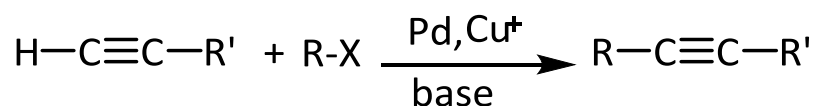


**Scheme 30:** Synthesis of thiophene acetylene dimer **39**.

This thiophene triphenylene twin **39** is one of the twinned triphenylenes synthesised from our group. The thiophene unit is used because it allows communication throughout the two triphenylene cores forming the twin and the strain in the structure is less due to its matching bond angles. The synthetic route is as seen in Scheme **26**. The thiophene unit was added by Sonogashira coupling, and the common method for coupling alkynes / acetylene linking group to form acetylene derivatives. The diiodo thiophene was used in excess; further coupling using **43** and more acetylene triphenylene **42** gave the resulting product **39**.

#### 2.1.2 Sonogashira Coupling Reaction

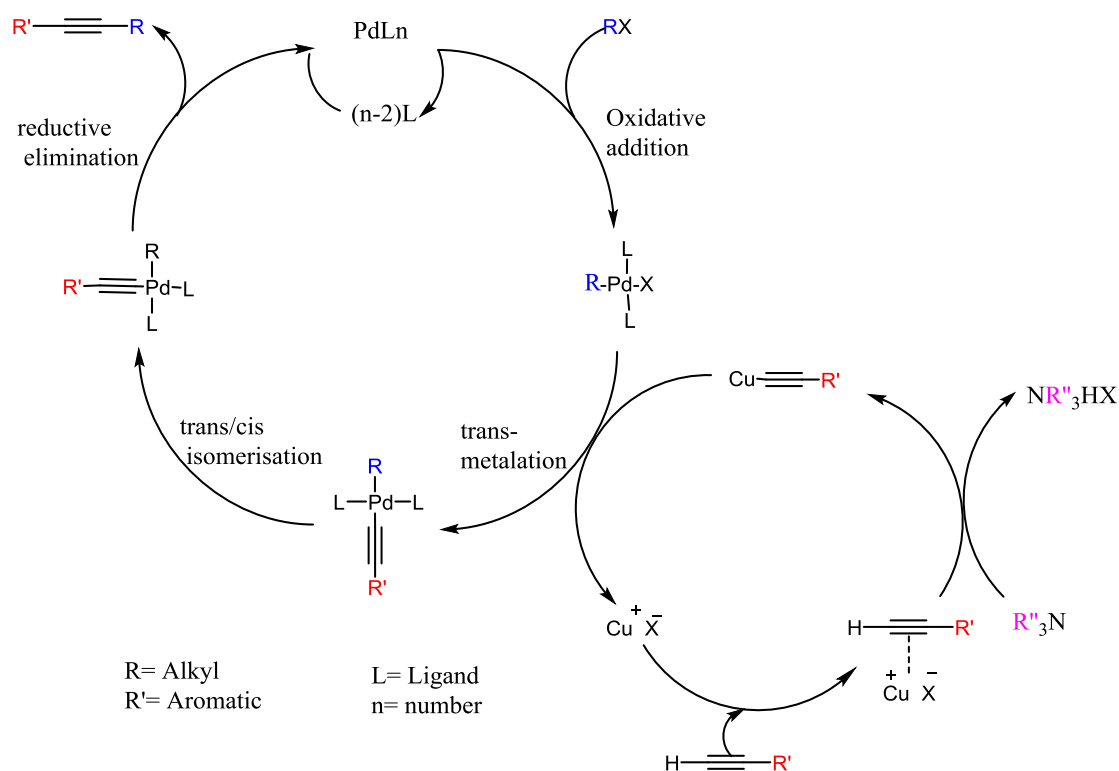
The reaction occurs by palladium-catalysed cross-coupling between a terminal sp-hybridised carbon of an alkyne with an sp<sup>2</sup> carbon of an organohalide (or triflates) is commonly termed as a Sonogashira coupling (Scheme 27).<sup>59</sup>



**Scheme 31:** Summary of Sonogashira reaction

The Sonogashira reaction takes place through two independent catalytic cycles (palladium cycle and copper cycle) Figure (2.2). The palladium cycle (cycle A) starts with the catalytically active species Pd<sup>0</sup>L<sub>2</sub>. The first step in the catalytic cycle is initiated by oxidative addition of the organohalide to form a Pd(II) complex. The complex is then transformed into a [Pd(II)L<sub>2</sub>] after transmetalation with a copper acetylide that is generated in the copper cycle. The complex

undergoes reductive elimination, after cis/trans- isomerisation, to the final alkyne, regenerating the catalyst  $[Pd^0L_2]$ . The base (organic or inorganic) is assumed to assist the copper acetylide formation with the help of a  $\pi$ -alkyne copper complex, which would make the alkyne terminal proton more acidic.<sup>59,60</sup>



**Figure 2.2** Sonogashira coupling mechanism<sup>61</sup>

## 2.2 A new Synthesis of Triphenylene Precursors

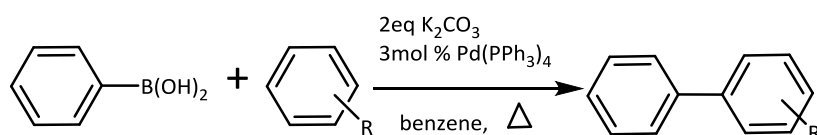
The early stages of our project concerned the development of improved synthesis of important unsymmetrically substituted triphenylene intermediates. As previously discussed, there are many types of synthetic process used for the synthesis of triphenylenes, most of the ways used are classified into six types by Perez and coworkers.<sup>17</sup> The six types (1-6) are characterised by preparation and isolation of terphenyl (type1), biphenyl (type2) naphthyl (type 3), phenanthryl (type 4), three units benzene ring (type 5) and one benzene ring (type 6) respectively as key intermediates. These synthetic routes are all important but what we considered is the availability of the starting materials and reagents and also the yield of the



product. The most commonly used routes are the trimerisation of dialkoxy-benzene and biphenyl route using electron rich precursor to yield hexaalkoxy substituted triphenylenes, oxidative trimerisation of benzene in type 5 and cyclisation of ortho terphenyl in type 1 to synthesise symmetrical and unsymmetrical triphenylenes. The most commonly synthesised triphenylenes are the alkoxy symmetrical and unsymmetrical substituted triphenylenes. Different literature shows that the synthesis of mono and disubstituted symmetrical and unsymmetrical triphenylenes, and the triphenylenes cores are possible, from terphenyl using some of these available routes as discussed by Perez and co-workers (type 1 route) examples, shown in Scheme 1 and 2 using oxidative cyclisation and photocyclisation.

### 2.2.1 Suzuki Reaction for the Preparation of Terphenyl, the key Intermediate

Suzuki-Miyaura coupling is said to represent one of the most widely used methods in organic synthesis. Suzuki coupling is the palladium-catalysed cross coupling between organoboronic acid and halides. The first Suzuki coupling reaction (Scheme 28).<sup>63</sup>

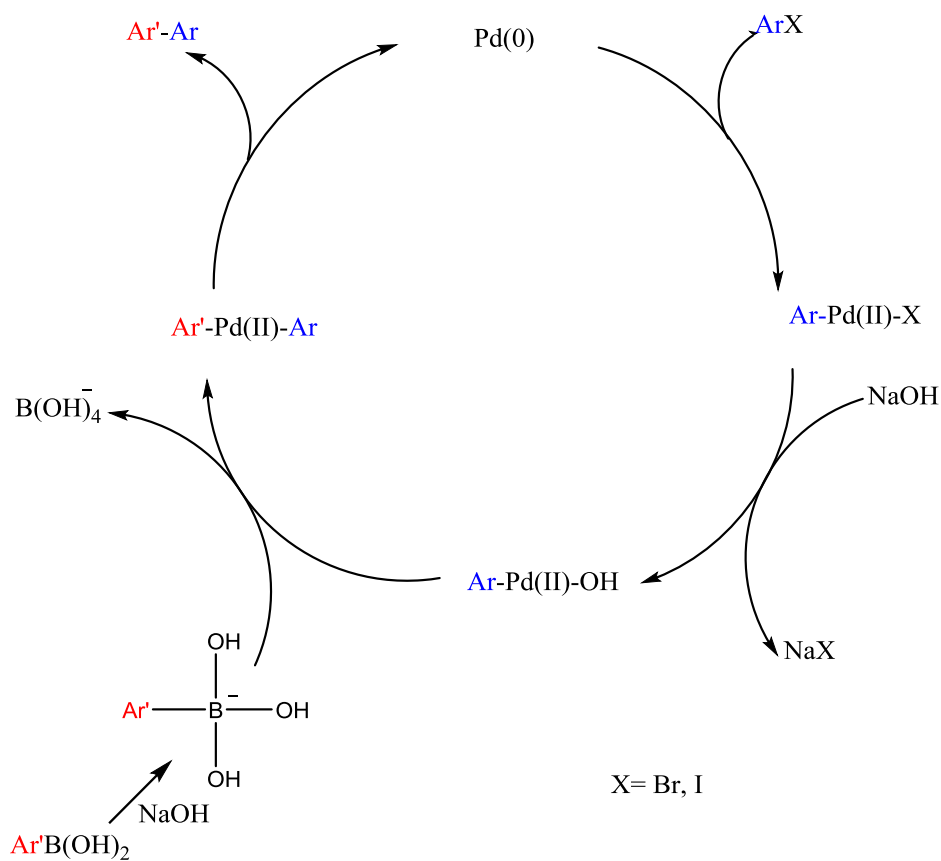


**Scheme 32:** First Suzuki coupling reaction.<sup>63</sup>

Recent catalyst and methods developments have broadened the possible applications enormously; that the scope of the reaction pattern is not strictly on aryls, but it includes alkyls, alkenyls and alkenyls. Other borane compounds are also used such as organoboranes, potassium trifluoroborates, organoboranes or boronate esters instead of boronic acid. With these developments, we still consider the availability of the materials. Triflate (pseudohalides) are also used as coupling partners.<sup>64</sup> Also, that the boronic acid must be activated, for example with base, that makes it different from Stille coupling (palladium catalysed cross coupling between an organotin or alkenyl, arylhalide or triflate).

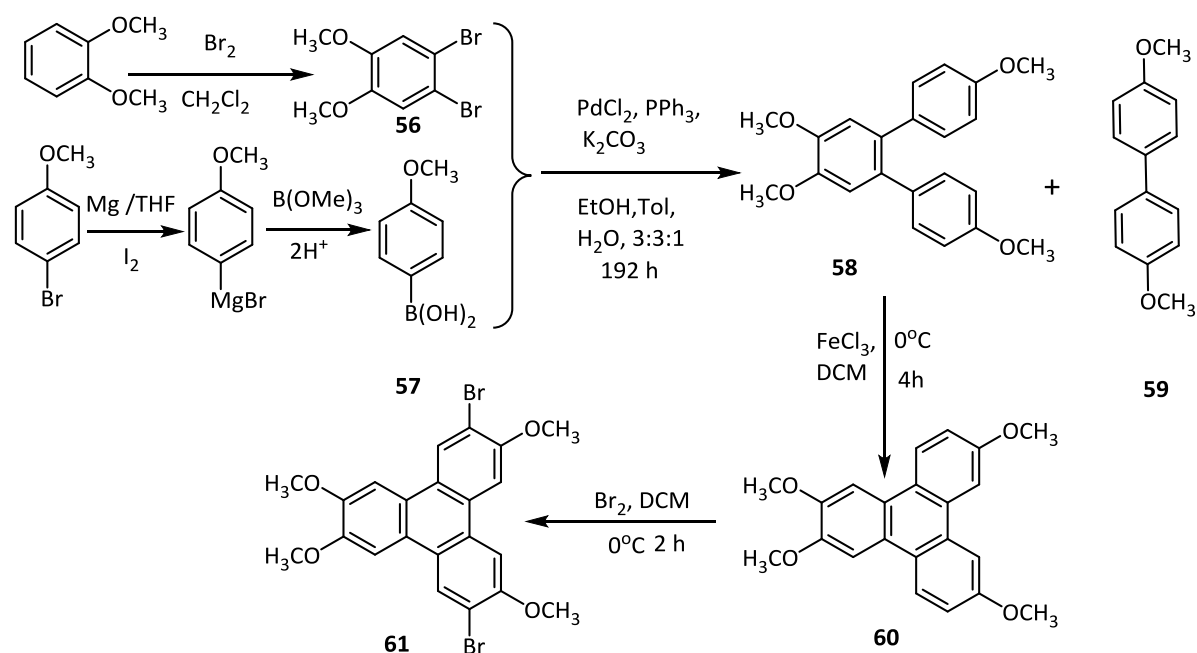
In the Suzuki coupling reaction the metal/ ligand systems that facilitate the cross coupling with different electrophiles have been the most extensively studied ranges from Pd<sup>0</sup>, Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd<sub>2</sub>dba<sub>3</sub> or Pd(II)[PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>] in the absence of ligands to very elaborate catalyst/ligand system has been applied, it is also said that recently the successful use of air stable catalyst has been reported to improve the catalyst turnover, to achieve the coupling with less reactive electrophiles or to permit coupling with hindered substrate.<sup>65</sup>

### 2.2.2 Mechanism of Suzuki coupling reaction



**Figure 2.3** Mechanism of Suzuki coupling reaction.<sup>63</sup>

### 2.2.3 Synthesis Tetramethoxy Triphenylene 60

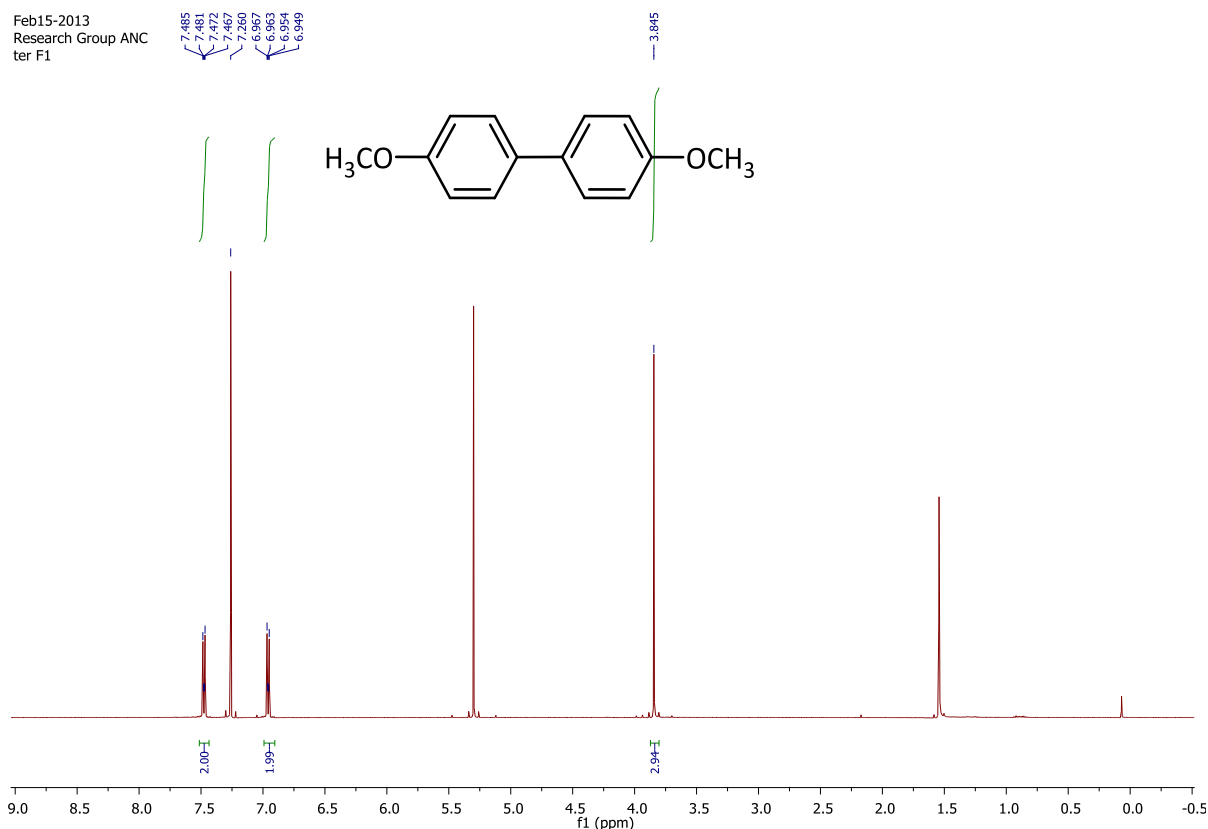


**Scheme 33:** Synthesis of the Triphenylene core **61**

Compound **56** was synthesised according to the procedure described by Fanta.<sup>58</sup> Veratrole was brominated in dichloromethane at 0°C using bromine. After workup, the residue was recrystallized from isopropanol giving needle-like colourless crystals in 90% yield. Compound **57** was prepared by forming the Grignard reagent from 4-bromoanisole using Magnesium turnings and a crystal of iodine in dry THF. The cooled Grignard reagent was then added gently to mixture of dry THF and trimethylborate cooled at -78°C. The mixture was allowed to warm up overnight at room temperature. The mixture was worked up and recrystallised from hot water slowly. The product obtained was off white solid.

The two precursors **56** and **57** were coupled by a double Suzuki-Miyaura reaction. Compound **56**, 4-methoxyphenyl boronic acid **57**, palladium (II)dichloride (PdCl<sub>2</sub>), triphenylphosphine (PPh<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were reacted under standard conditions using toluene, ethanol, water (3:3:1) solvent mixture under Nitrogen atmosphere. The reaction was monitored by TLC and NMR of aliquots, and after 3 days, some bromide starting materials remained. More boronic acid and catalyst were added, and reflux continued for 5 more days. However, the reaction was still not complete. It was

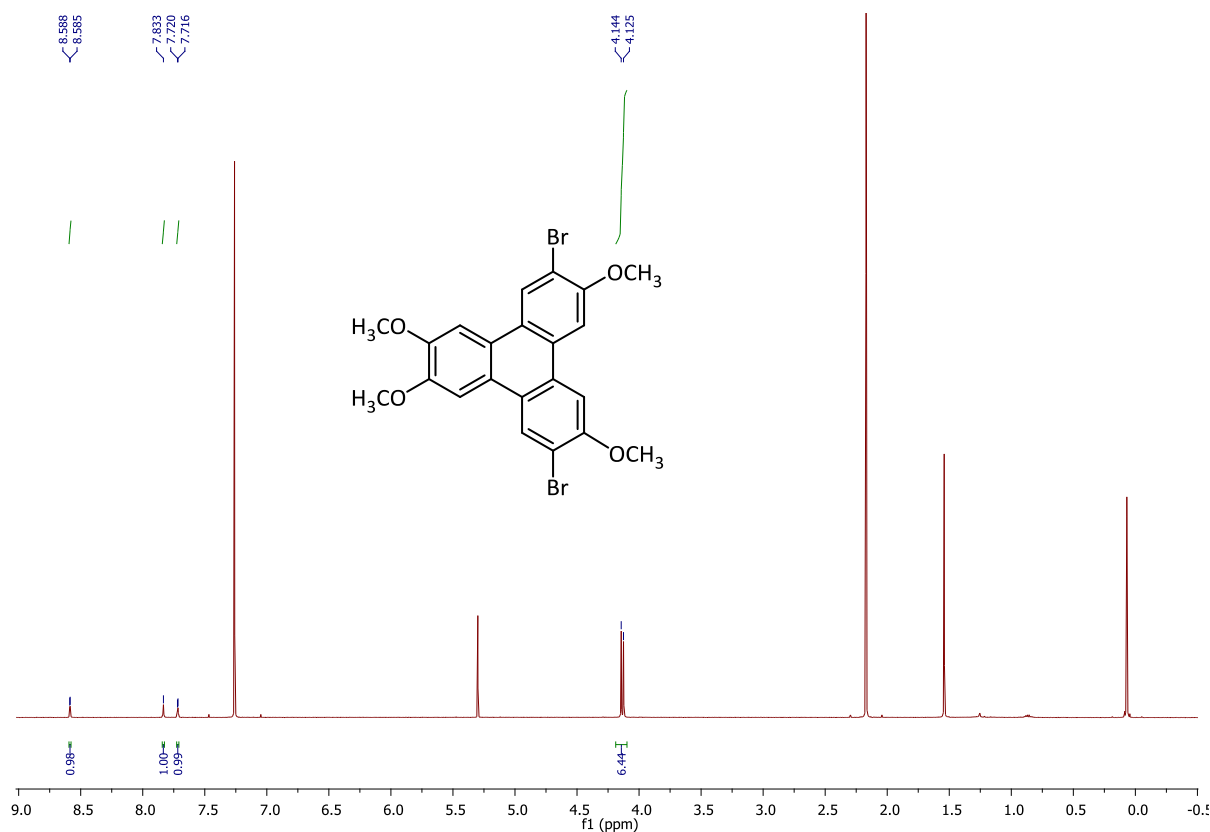
stopped and worked up and separated by column chromatography eluting with 7:3 DCM/PE to give **58** as a colourless solid in yield of 75%. Dimethoxybiphenyl **59** was formed as a by-product in the reaction because of adding excess boronic acid to the reaction mixture. This by-product, proved to elute to the same level with the starting material, complicating the analysis of the reaction.  $^1\text{H}$  NMR of dimethoxybiphenyl **59** in  $\text{CDCl}_3$  is as shown in Figure 2.4.



**Figure 2.4:**  $^1\text{H}$  NMR of dimethoxybiphenyl **59** in  $\text{CDCl}_3$

Terphenyl **58** was stirred in DCM and nitromethane ( $\text{CH}_3\text{NO}_2$ ) and  $\text{FeCl}_3$  was added slowly over 2 h and further stirred for 2 h. The desired product was obtained by this oxidative cyclisation of **58** as seen in Scheme **33** is obtained as a colourless solid **60** in 52% yield by slow recrystallisation in DCM/MeOH.

Compound **60** was stirred in dichloromethane, cooled at  $0^\circ\text{C}$  and Bromine added dropwise and stirred for 2h. The solid obtained was purified by column chromatography (eluting 7:3 DCM: Pet ether) and the solid obtained was recrystallized from DCM and isopropanol giving colourless solid **61** in 61% yield.



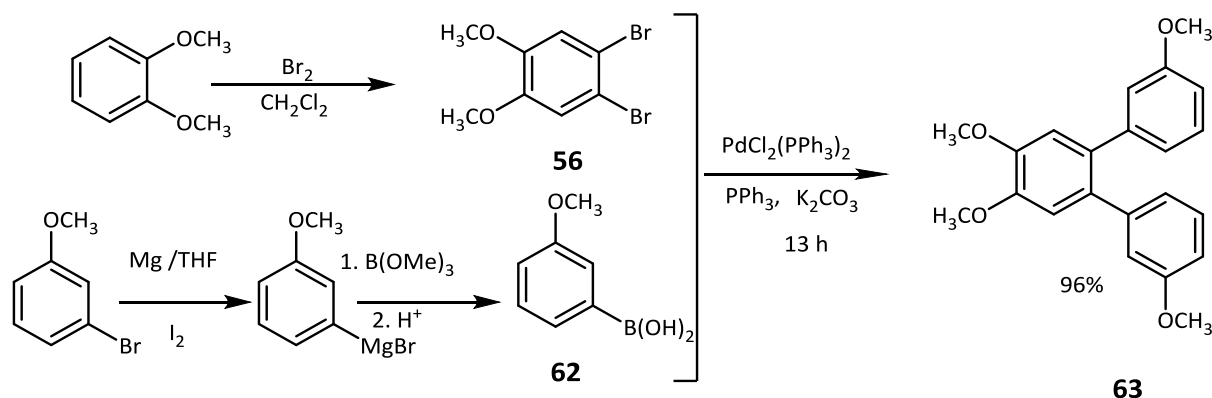
**Figure 2.5** <sup>1</sup>H NMR of dibromotetramethoxy triphenylene **61** in CDCl<sub>3</sub>.

Figure 2.5 shows the <sup>1</sup>H NMR spectrum of triphenylene **61**. As seen on the NMR spectrum, three resonances are present, each of the singlets are related to two aromatic protons. Triphenylene **61** has two bromines having leading to a classic isotopic pattern as seen on the mass spectrum. Triphenylenes with 4-6 long alkoxy chains are known to have columnar liquid crystal phases. Research findings shows that, to get triphenylene discotics, at least four C-atoms are required for the peripheral units. We reasoned that a convenient synthesis of the tetramethoxy intermediate could provide (after hydrolysis) a useful, common tetrahydroxy triphenylene intermediate that could be alkylated or acylated to modify the liquid crystal properties of the final twin material.

Surprisingly our group observed mesogenic behaviour in this triphenylene **61**. On heating, a mesophase is formed at 188°C. The mesophase has a moderate range; it forms the isotropic liquid at 267°C. On cooling, a columnar hexagonal mesophase texture was observed with optical polarising microscopy. These findings show that triphenylene with just methoxy (-OCH<sub>3</sub>) chains can also form a discotic liquid crystal phase.<sup>67</sup>

## 2.2.4 Synthesis of Tetramethoxyterphenyl **62** and Optimisation

Terphenyls are most often synthesised among the famous routes by the use of palladium-catalysed cross coupling reactions as mentioned. Both symmetrically and unsymmetrically substituted triphenylenes can be produced using this form of synthesis. This is the most often route used in our group, and a version was used to synthesise terphenyl (Scheme **34**)



**Scheme 34:** Synthesis of Terphenyl **63**

The starting materials **56** and **62** were prepared for the synthesis of triphenylene in our lab, although they are also commercially available. Compound **56** was synthesised according to the procedure described by Fanta.<sup>62</sup> Veratrole was brominated in dichloromethane at  $0^\circ\text{C}$  using bromine. After workup, the residue was recrystallized from isopropanol giving needle-like colourless crystals in 90% yield.

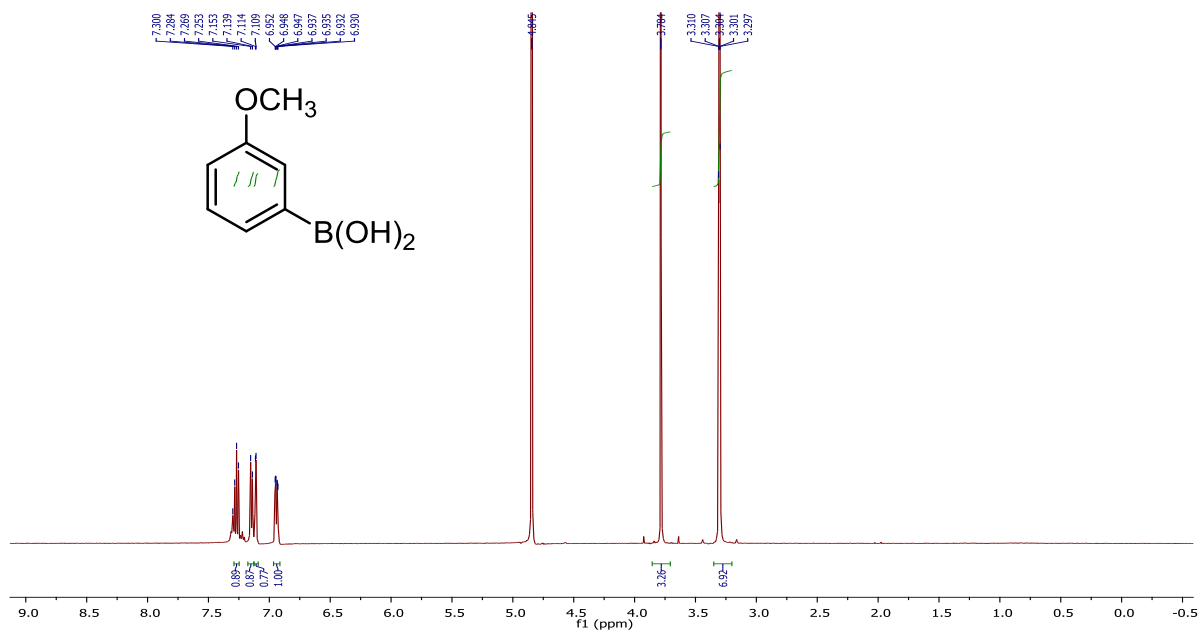
Compound **62** was prepared by forming the Grignard reagent from 3-bromoanisole using Magnesium turnings and a crystal of iodine in dry THF. The cooled Grignard reagent was then added gently to mixture of dry THF and trimethylborate cooled at  $-78^\circ\text{C}$ . The mixture was allowed to warm up overnight at room temperature. Workup and recrystallization from water (a slow process) gave the product as an off-white solid.

Attempts were then made to couple the two precursors through a double Suzuki-Miyaura reaction. We therefore experienced some difficulties in this reaction. However, at the end we were able to get a suitable condition that gave us high yield within a short reaction time. The summary of the result of the different reactions is summarised in Table 2.1 as entries 1 to 5.

Entry	Catalyst	Solvents	time	base	%yield <b>63</b>	Ref.
1	PdCl <sub>2</sub>	Tol/ EtOH/H <sub>2</sub> O 3:3:1	336 h	Na <sub>2</sub> CO <sub>3</sub>	15%	78
2	PdCl <sub>2</sub>	DME	240 h	Ba(OH) <sub>2</sub>	52%	64
3	PdCl <sub>2</sub>	DME	168 h	CsF	42%	64
4	PdCl <sub>2</sub> (dppf)	DME	168 h	CsF	59%	77, 79
5	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Toluene	13 h	K <sub>2</sub> CO <sub>3</sub>	96%	80

**Table 2.1:** Optimisation of the Synthesis of Terphenyl **63**.

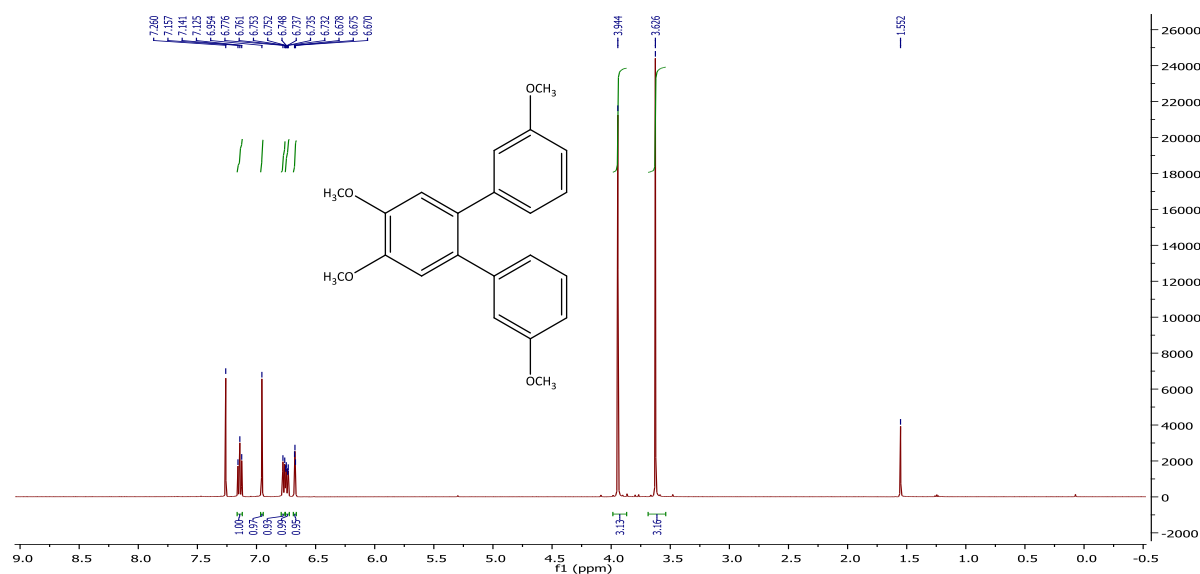
In all cases, the solid **63** was recrystallized from EtOH and DCM, and no column chromatography is involved in the isolation. This is a convenient method for the synthesis of terphenyl, particularly because it avoids chromatographic separation.



**Figure 2.6:** <sup>1</sup>H NMR of boronic acid **62** in CDCl<sub>3</sub>.

In the first experiment, compound **56**, 3-methoxyboronic acid, palladium (II) dichloride (PdCl<sub>2</sub>), triphenylphosphine (PPh<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were reacted under standard conditions using toluene, ethanol, water (3:3:1) solvent mixture under nitrogen atmosphere. After 4 days, there was no evidence for product formation (NMR of an aliquot). More boronic acid and catalyst were added, and reflux continued for 3 more days. However, the reaction was still not complete. It was stopped and the solvent exchanged for DME and heated under reflux (total days for the reaction 10 days). Starting material was still present in the mixture, which was worked up and separated to give a low yield of terphenyl (15%).





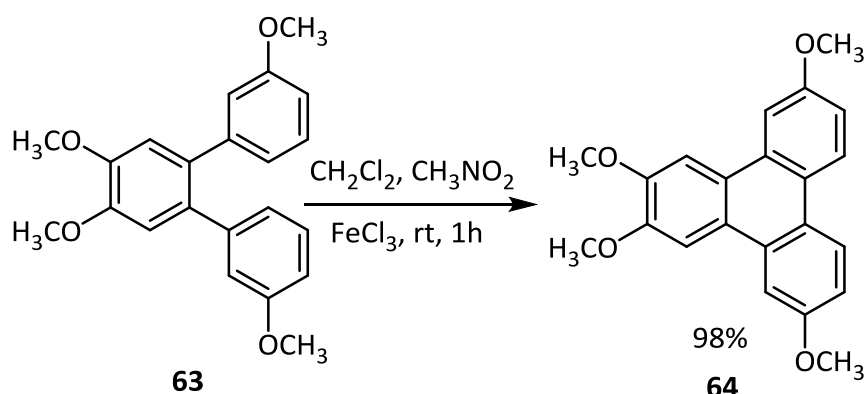
**Figure 2.7:** <sup>1</sup>H NMR of tetramethoxyterphenyl **63** in CDCl<sub>3</sub>.

Subsequent experiments were therefore performed in attempts to improve the transformation.

In one experiment compound **56**, 3-methoxyphenylboronic acid, PdCl<sub>2</sub>, PPh<sub>3</sub> and Barium hydroxide (Ba(OH)<sub>2</sub>) were stirred with DME solvent. Analysis of the reaction after refluxing for 7 days again showed remaining starting material. More of 3-methoxyphenylboronic acid PdCl<sub>2</sub>, PPh<sub>3</sub> was added to the mixture and stirring continued for another 3 days. An improved yield of terphenyl was obtained (off-white crystals, 52%) alongside a significant quantity of 4,4-dimethoxybiphenyl side product.

Subsequent coupling employed caesium fluoride in DME solvent (7 days, 42 %), caesium fluoride in DME solvent under nitrogen (PdCl<sub>2</sub>(dppf), 7days, 59 %). However, the best outcome employed K<sub>2</sub>CO<sub>3</sub> in toluene where reflux for 13 h have a 96% yield using (PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>).

### 2. 3. Synthesis of Tetramethoxytriphenylene **64**



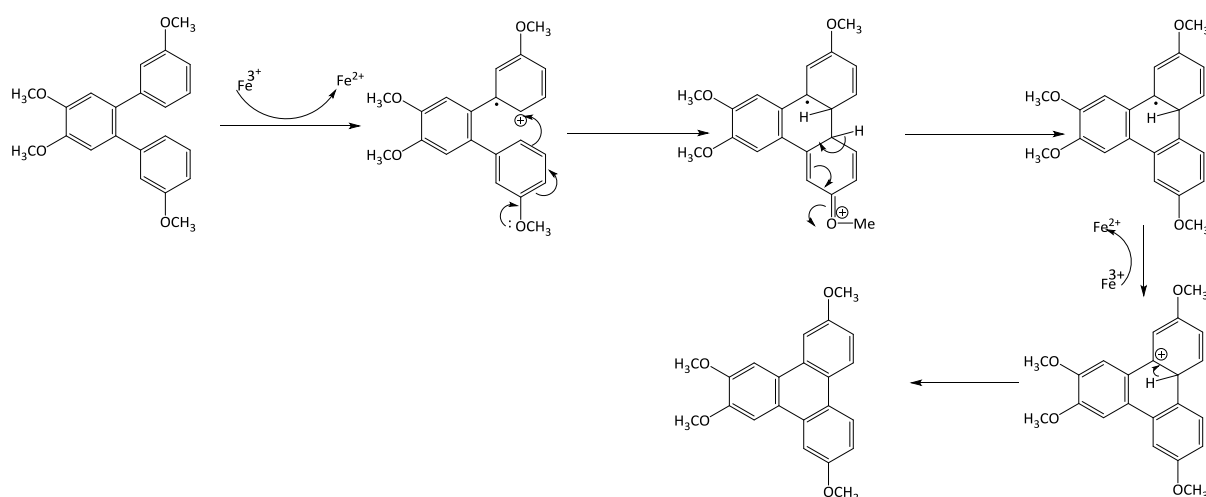
**Scheme 35:** Synthesis of triphenylene core **64**

Terphenyl **63** was stirred in DCM and nitromethane (CH<sub>3</sub>NO<sub>2</sub>). FeCl<sub>3</sub> was added slowly within 2 h and further stirred for 2 h. The desired product **64** was obtained by oxidative cyclisation of **63**, following the procedure of Artal and co-workers.<sup>64</sup> This process involve the repeated cycles of electron removals, C-C bond formation and deprotection. MeOH was used for quenching the excess FeCl<sub>3</sub>, from the procedure developed by Klaus Bechgaard. Nitromethane (CH<sub>3</sub>NO<sub>2</sub>) was added to increase the solubility of the FeCl<sub>3</sub>. The FeCl<sub>3</sub> in DCM is a very satisfactory oxidant, the FeCl<sub>3</sub> –DCM/ MeOH workup protocol provides the best route to a wide range of systems.<sup>68, 69</sup>

The resulting product was obtained without any further purification, except washing several times with methanol and drying under vacuum. The low solubility of the product initially caused problems for isolation, but this protocol proved effective.

### 2.3.1: Oxidative Cyclisation of Terphenyl

Oxidative coupling of aromatic or heterocyclic compounds provides a method for creating aryl-aryl bonds which is sometimes cheaper, quicker and easier than the palladium based routes.<sup>69</sup> An insight from electrochemical studies of oxidative aryl coupling given by Boner and co-workers<sup>68</sup> that there is the need for a full sufficiency of oxidant, in the mechanism apart repeated cycles of electron removals, C-C bond formation and deprotection; the product from each of the cycles has a more extended conjugated system than its precursor, however the electron removal steps gets quicker with every cycle while the radical-cation intermediates become less reactive and the C-C bond forming reaction becomes slower. This process continues cycle to cycle, building larger and larger oligomers until a stable radical cation is formed.<sup>66</sup> (Scheme 36)

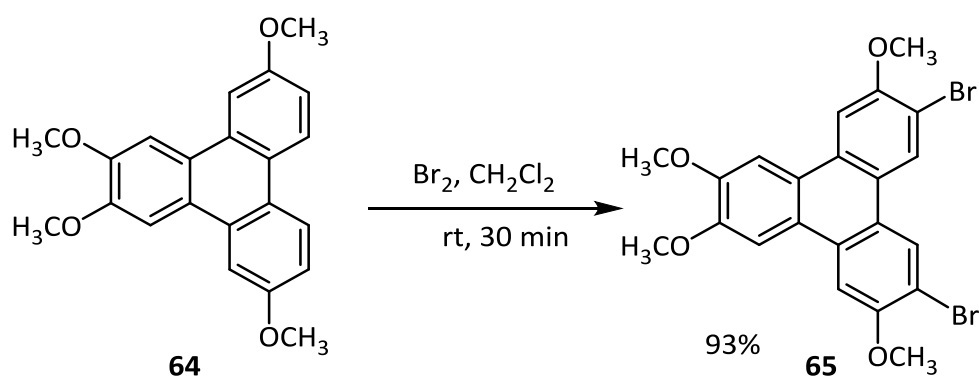


**Scheme 36:** Mechanism of Oxidative Cyclisation of Terphenyl

It is advised that it is best to use excess oxidant to convert all of the substrate through to this ultimate cation; if less oxidant is used a complex mixture will be formed. It is also important to use a solvent that is not nucleophilic because the product is a radical cation/di-cation that uses radical cation intermediates, for this reason the presence of water or other nucleophilic substance gives mixture of phenols and quinones. The work up procedure should involve one or two electron reduction because the use of water in the work up leads to mixture of addition product as mentioned.<sup>70</sup>

#### 2.4. Synthesis of 3,6-dibromo-2,7,10,11-tetramethoxy triphenylene 65

2,3,7,10-Tetramethoxytriphenylene **64** was stirred in dichloromethane, cooled at 0°C and bromine added drop wise and stirred for 2 h. The resulting compound was seen as a precipitate, washed with sodium thiosulphate, filtered and washed several times with ethanol and dried, giving a solid in 93% yield. This is a good yield, collected as a precipitate from the reacting mixture; there was no further workup required apart from refluxing for 24 h in DCM for further purification. Pure solid **65** was obtained (Scheme 37).



**Scheme 37:** Synthesis of Dibromotetramethoxy Triphenylene **65**

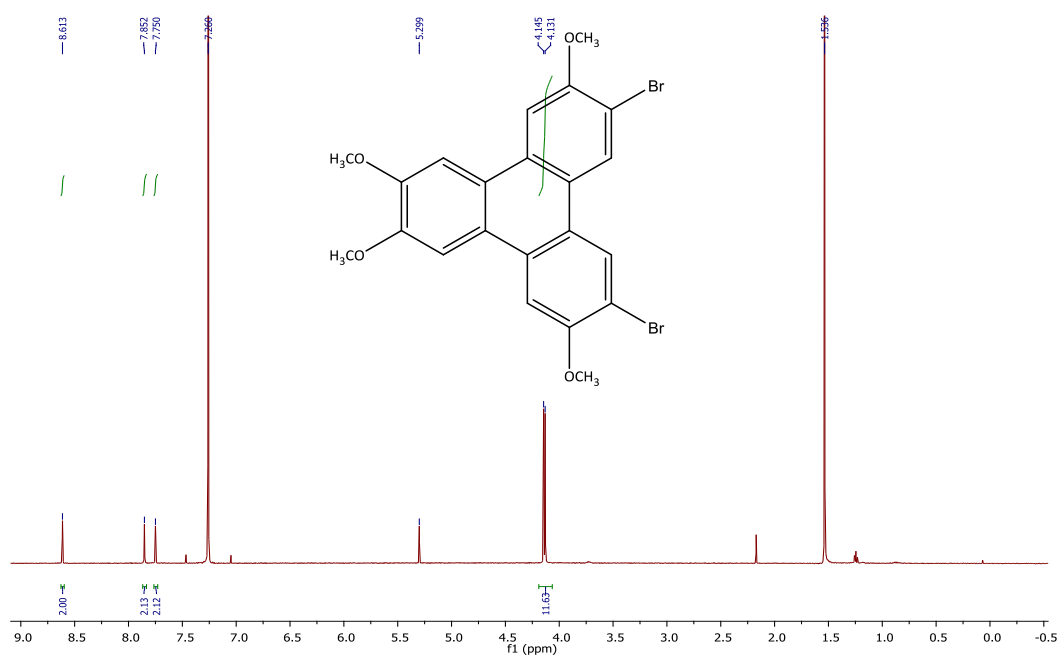


Figure 2.8:  $^1\text{H}$  NMR of dibromotetramethoxy triphenylene **65** in  $\text{CDCl}_3$ .

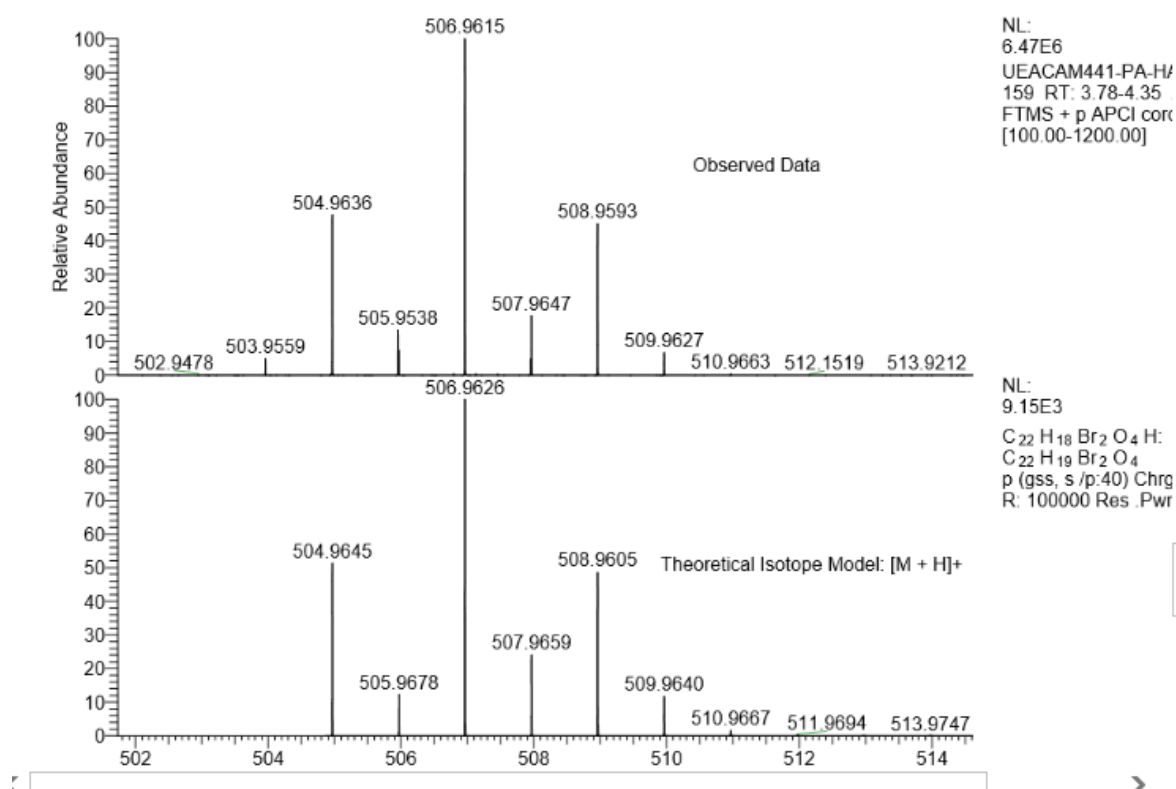
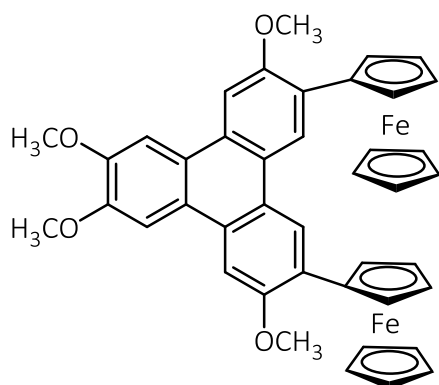


Figure 2.9: HRMS (ESI) of triphenylene **65**

No clear melting point was observed as the compound decomposed on heating at 90°C. The unfortunate situation with this compound is its high melting point, the isomer **61** was found to be a liquid crystal but this compound **65** is not.

#### 2.4.1 Attempted Synthesis of Ferrocenyl (methoxy) Triphenylene) **66**

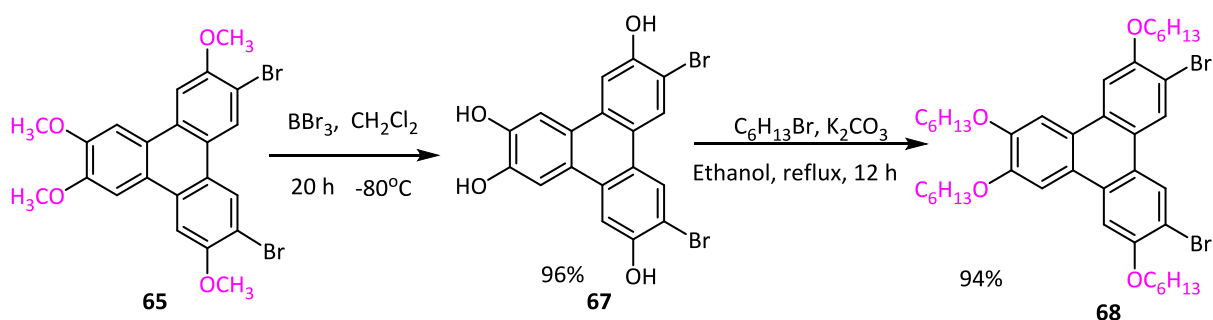


As a model reaction, the synthesis of Ferrocenyl triphenylene **66** was attempted using compound **65** and ferrocene boronic acid.

We deduced that its non-reactivity was due to its poor solubility, because for any reaction to occur, the reacting compound must dissolve. The compound is not in the solution for reaction to occur. Neither the MALDI-TOF MS nor the NMR spectrum showed the presence of the expected compound. Instead, the boronic acid is consumed through side reactions.

#### 2.5 Conversion of Methoxy-triphenylene to Hexyloxy-triphenylene (Demethylation and Alkylation)

At this stage of the work we realised that the long (hexyl) chains needed to be installed before the coupling to ferrocene. However, with a simple synthesis of the methyl derivative already developed, we explored its use as a precursor to other, longer chain derivatives. The product **65** proved still very useful because it was effectively converted to long chain alkoxytriphenylene by demethylation **65** and alkylation of **67** (Scheme **37**). The desired product formed was the known hexyloxy-triphenylene **68**.



**Scheme 38:** Conversion of Methoxy-triphenylene **65** to Hexyloxy-triphenylene **68**

### 2.5.1 Demethylation of Dibromotetramethoxy Triphenylene **65**

3,6-dibromo-2,7,10,11-tetramethoxy triphenylene **65**, hydrobromic acid and acetic acid in ratio (1:1) were stirred and refluxed for 48 h but gave no product. Another reaction was set up with  $\text{BBr}_3$  in dichloromethane and initially stirred at  $-80^\circ\text{C}$ . The reaction was allowed to stir and warmed up overnight to room temperature. It was quenched slowly with ethanol and evaporated without further purification; a grey solid **67** was obtained.

Entry	Solvent	Reagent	temp	time	% yield of <b>67</b>	Ref
1	DCM	HBr, Acetic acid 1:1	rt	96 h	----	68, 82, 84,
2	DCM	$\text{BBr}_3$	$-80^\circ\text{C}$	22 h	96%	68, 71, 83

**Table 2.2-** Demethylation of dibromotetramethoxy triphenylene **67**

The reaction was allowed to stir and warmed up overnight to room temperature. It was quenched slowly with ethanol and evaporated without further purification; a grey solid was obtained. The mixture was quenched with ethanol immediately, to remove excess  $\text{BBr}_3$  that will form  $\text{HBr}_3$  and boric acid that can interfere with the product (Scheme 39).



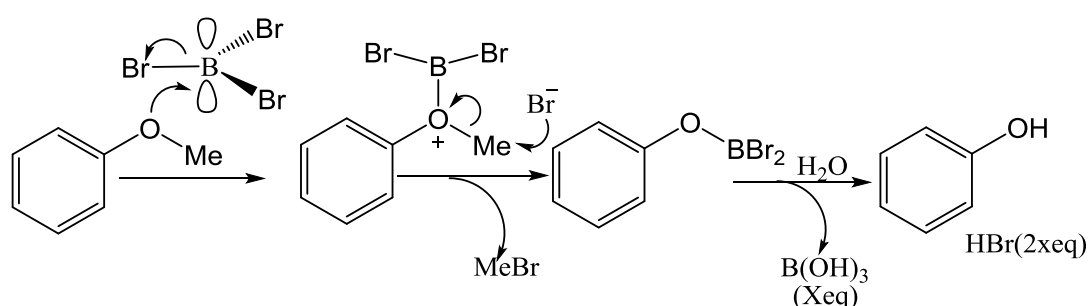
**Scheme 39:** Quenching Reaction Borontribromide using Ethanol.

The mixture did not go through rigorous isolation because compound **67** is air sensitive which may result to phenolic coupling/radical oxidative process forming polymer.

Also,  $\text{BBr}_3$  is best known for its ability to cause selective cleavage of aryl methyl ethers in the presence of other functional groups in the molecules. It has been reported by Paliakov and co-worker that using  $\text{BBr}_3$  a methoxy group can be demethylated selectively.<sup>71</sup>

Compound **67** was effectively synthesised by the use of  $\text{BBr}_3$  instead of using the common acetic acid/ $\text{HBr}$  reaction, although there are some setbacks enumerated on the demethylation reaction by Lee and Kee<sup>72</sup> as harsh reaction conditions, long reaction times, difficulty in manipulation, use of the exotic reagents and low reaction yields.  $\text{BBr}_3$  is the classical reagent for the de-alkylation of methyl aryl ethers. The mechanism goes through with the formation of complex between the boron centre and the ether oxygen then elimination of alkyl bromide to give dibromo organo borane. The dibromo organoborane then become hydrolysed given alcohol/phenol, boric acid and hydrogen bromide.

### 2.5.2 Mechanism of Demethylation with $\text{BBr}_3$



**Scheme 40:** Demethylation Reaction Mechanism of  $\text{BBr}_3$



### 2.5.3. Alkylation Reaction of Hydroxyltriphenylene to Hexyloxy Triphenylene.

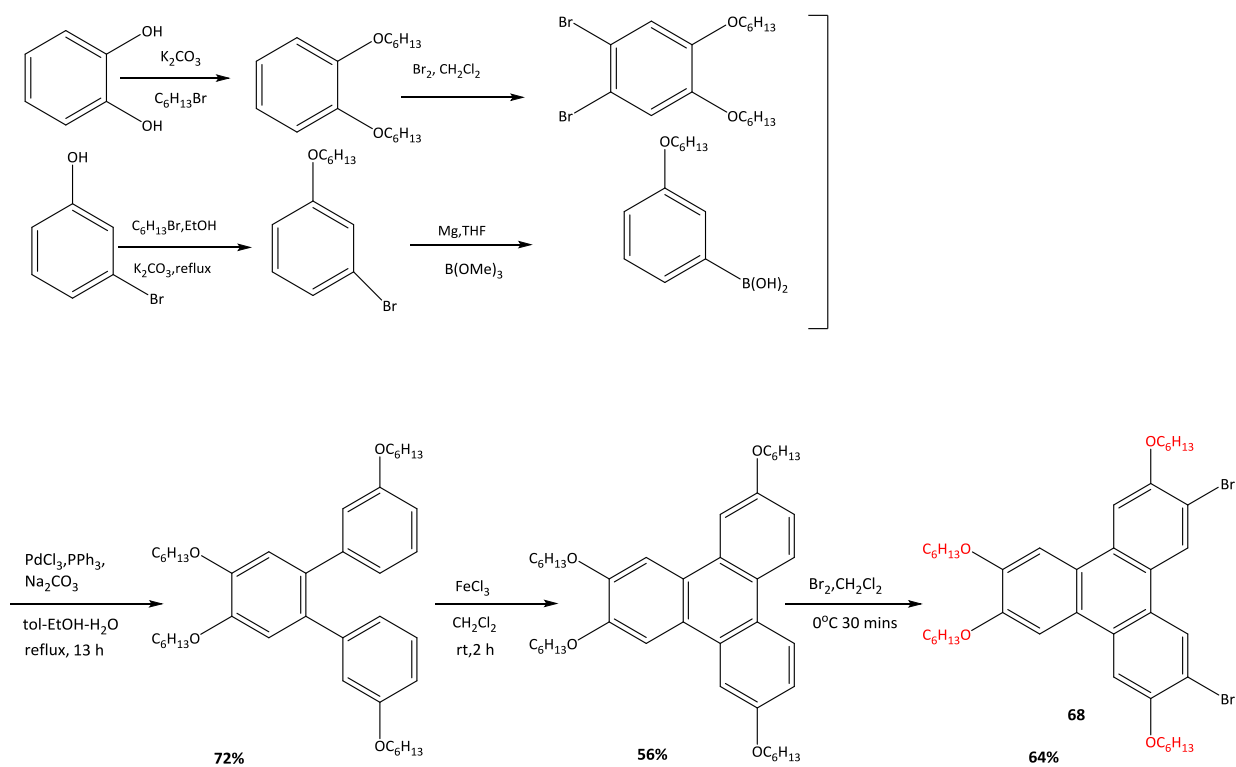
#### 2.5.3.1 New route for the Synthesis of Alkoxy-Triphenylene.

Compound **68** is formed by alkylation reaction of **67**. The preparation of this compound was necessary using this route because compound **65** was found unsuitable for further reaction due its low solubility. Since the reaction was not possible, the compound **65** was dealkylated to convert it into the suitable and common long-chain (hexyl chain) often used for the synthesis of triphenylene derivatives used for liquid crystals.

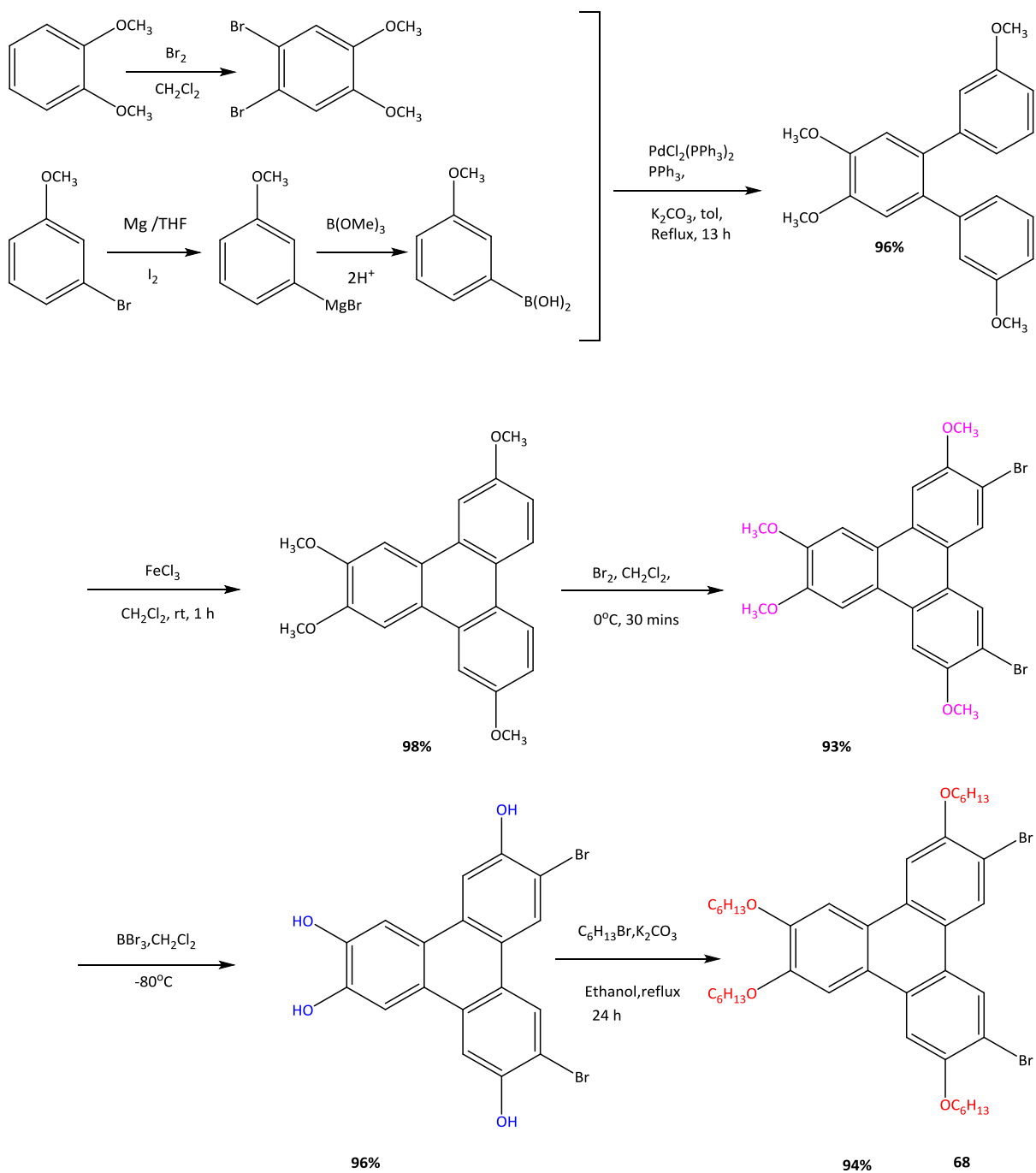
#### 2.5.3.2: Comparison of the two Routes (Normal and New) to Synthesise of Alkoxy-Substituted Dibromo-Triphenylene **68**.

By the normal route (Scheme **41**) **68** is synthesised by the procedure developed from our group in 2001 by Cammidge and Gopee.<sup>18</sup> Catechol and 1-bromohexane were stirred in ethanol and allowed to reflux to yield the diether and subsequent bromination yielded 1,2-dibromo-4,5-bis-hexyloxybenzene. The 3-bromophenol undergoes alkylation with bromohexane under same conditions as above yielding bromohexyloxybenzene. Both compounds were purified by distillation. The boronic acid was synthesised by reacting the bromide compound with magnesium turnings forming a Grignard reagent which was reacted with trimethylborate. Suzuki coupling reaction was carried out between 1,2-dibromo-4,5-bis-hexyloxybenzene and bromohexyloxybenzene yielding terphenyl the main precursor. FeCl<sub>3</sub> was used to induce ring closure of the terphenyl giving the corresponding triphenylene and further bromination of the triphenylene gave 3,6-dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene at lower yield.<sup>73</sup> In the second route (Scheme **42**) **68** is synthesised as described and discussed in Schemes **34**, **35**, **37** and **38**.

Comparing these two routes, the Scheme **42** route that started from shorter alkoxy triphenylene derivative (tetramethoxy triphenylene) starting materials saves time and no column chromatography is required. The product yield is high. This method appears more convenient to the common method in Scheme **41** because of the advantages mentioned.



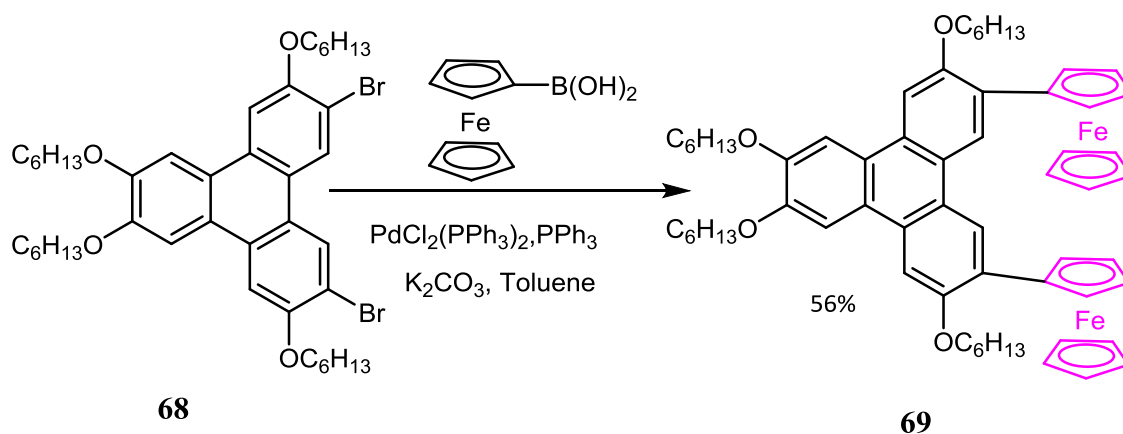
**Scheme 41:** Normal Route to Synthesis of Alkoxy-substituted Dibromo-triphenylene **68**



**Scheme 42:** New Route to Synthesis of Alkoxy-substituted Dibromo-triphenylene **68**

## 2.6: Synthesis of Ferrocenyl Triphenylenes from Hexyloxy Triphenylene

Compound **69** was synthesised by Suzuki coupling of **68** with ferroceneboronic acid (Scheme 37). The starting material compound **68**, excess ferrocene monoboronic acid, triphenylphosphine (12% mol) and  $K_2CO_3$  were stirred in degassed toluene for 20 mins. Bis (triphenylphosphine)palladium(II)dichloride (3% mol) was added and the reaction was allowed to reflux under  $N_2$  atmosphere for 1 hour. The resulting Solid after work up was recrystallised from DCM: ethanol (2: 3) given orange product of 56% yield: MALDI MS:  $m/z$  996.86 (M+H)<sup>+</sup>; HRMS; calculated For  $C_{62}H_{77}Fe_2O_4$  997.4519 found: 997.4516 (Isotope pattern Figure 2.11). The resulting product compound **69** was formed as a result of addition of excess ferrocenedicarboxylic acid. The resulting product **69** is a new compound formed with excess of ferrocenedicarboxylic and it was characterised with the result as seen in Figure 2.10 and 2.11.



**Scheme 43:** Synthesis of Ferrocenyl Triphenylene **69**.

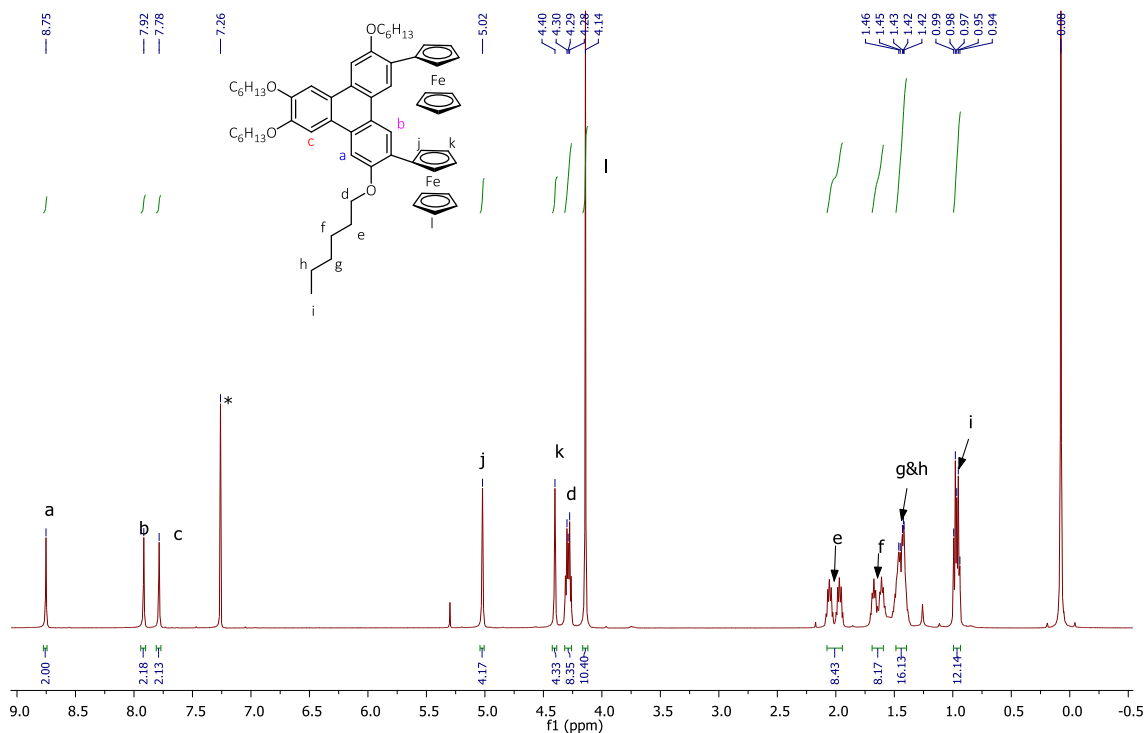


Figure 2.10  $^1\text{H}$ NMR of Ferrocenyl Triphenylene in  $\text{CDCl}_3$ .

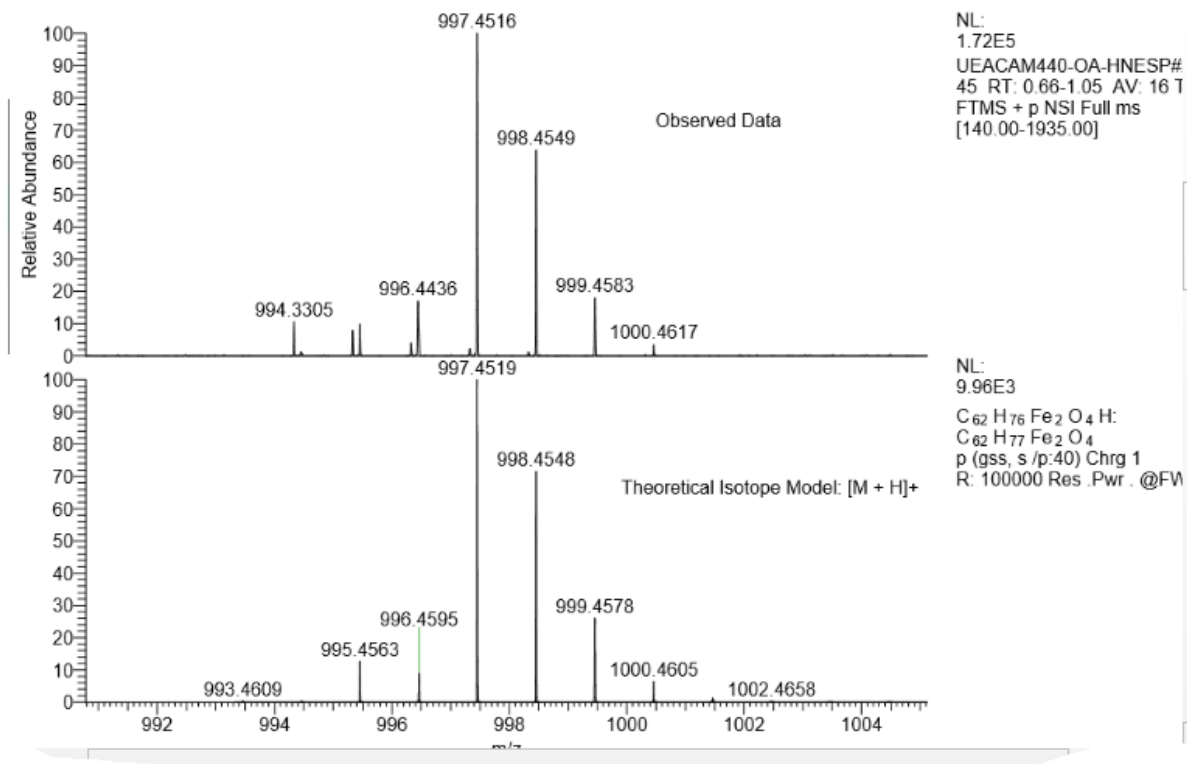
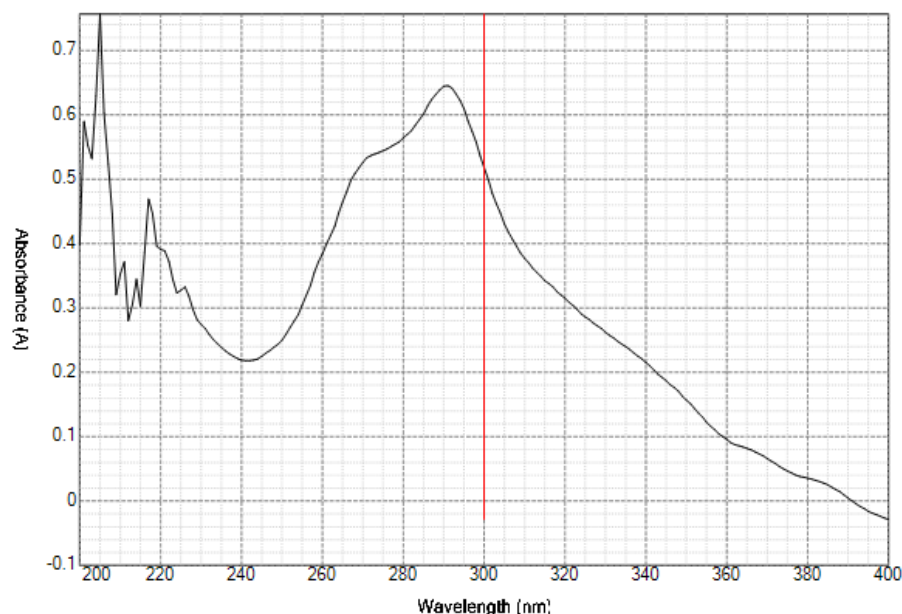


Figure 2.11: HRMS (ESI) of Ferrocenyl triphenylene **68**

The proton NMR spectrum of compound **69** Figure 2.10 corresponds to the desired structure. The aromatic region has three singlets at chemical shifts  $\delta$  of 8.75, 7.92 and 7.79 having two protons each. The alkoxy protons attached to the aromatic ring are found at the middle near to the ferrocene protons. The alkoxy proton is represented as two triplets at 4.28 and 4.30 with four protons each (8H). The three other peaks are of ferrocene, 2 peaks on the Cp ring on position j and k (2H each x 2 Cp rings) found at 5.02 and one peak on g (5H each x 2 Cp ring) found at 4.14. The protons at the aliphatic region correspond to the number of protons (8H, 8H, 16H and 12H respectively) found on the remaining 5-Hexyl long chain after the first (-OCH<sub>2</sub>-) (Figure 2.10). The reaction was effective and the resulting product **69** is a new compound. Compound **69** melts at 202°C and decomposed. Unfortunately, **69** did not show mesogenic behaviour.

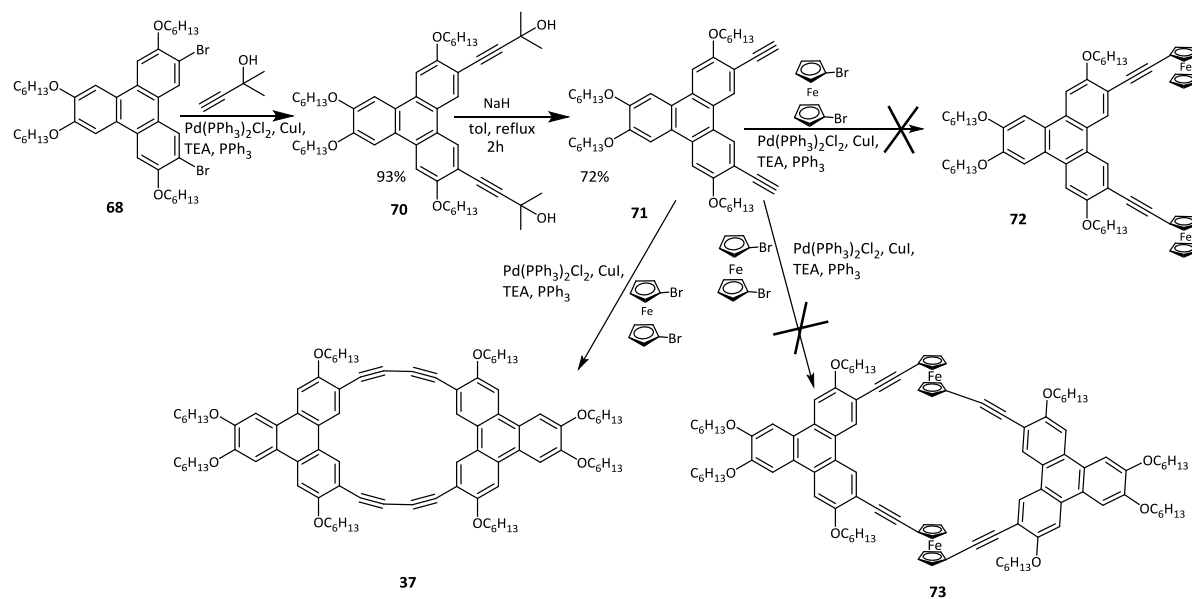
The synthesis of this model compound was not straightforward and, in practice, required a large excess of ferrocene boronic acid. Unfortunately this means that it will be impossible to use a related synthetic strategy to form our required “staggered twin” efficiently. For this reason, the twin was not attempted.

Compound **69** was obtained as an orange solid for this reason the UV/Vis spectrum was also measured. Peak detection for the compound was at 217 nm and 291 nm (Figure 2.12)



**Figure 2.12:** Uv-Vis of the Ferrocenyl triphenylene **69**.

## 2.7 Attempted synthesis of Ferrocenyl triphenylene **73** from triphenylene diacetylene compound **71**.



**Scheme 44:** Synthesis of Ferrocenyl diacetylene triphenylene **73**

Our strategy was therefore changed to select a twinning reaction that could potentially be more efficient for this reason acetylene bridges were chosen. Reaction from **68** to the diacetylene triphenylene **71** proceeded smoothly. A trial test was carried out using excess dibromoferrocene on the diacetylene triphenylene to prepare Ferrocenyl diacetylene monotriphenylene **72** as seen in entries 1-2 of Table 2.3 but the product formed is the triphenylene diacetylene dimer **37**, furthermore, other experiments were carried out by adding excess of the diacetylene triphenylene derivative to the reacting mixture dropwise by syringe pump at rate 5 ml per hour to prepare Ferrocenyl diacetylene triphenylene twin derivative **73** (entries 3-7), instead a dimer **37** was formed.

However, reaction with dibromoferrocene gave no expected product, the acetylene coupled to the acetylene of another triphenylene forming dimer in all cases. Despite many attempts under high-dilution conditions, dimer formation (homocoupling) was always observed.

Entry	SM DAcTP (eq)	Reagents		Catalyst PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Solvent/ base THF: TEA 1: 2	Reaction time	% yield of <b>73</b>	% yield of <b>37</b> (Dimer)	Ref.
		FcBr <sub>2</sub> (eq)	CuI (eq)						
1	1	4	0.2	0.05	1: 2	4 days	0	12	48
2	1	6	0.3	0.10	1: 2	4 days	0	15.5	48
3	6	2	0.3	0.10	1: 2	5 days	0	14	48
4	6	4	0.3	0.10	1: 2	5 days	0	14.7	48
5	6	4	0.3	0.10	1: 2	7 days	0	15	48
6	6	2	0.3	0.10	1: 2	8 days	0	15.9	48
7	6	2	0.3	0.20	1: 2	8 days	0	16	48

DAcTP- diacetylene triphenylene derivative      FcBr<sub>2</sub>- dibromoferrocene

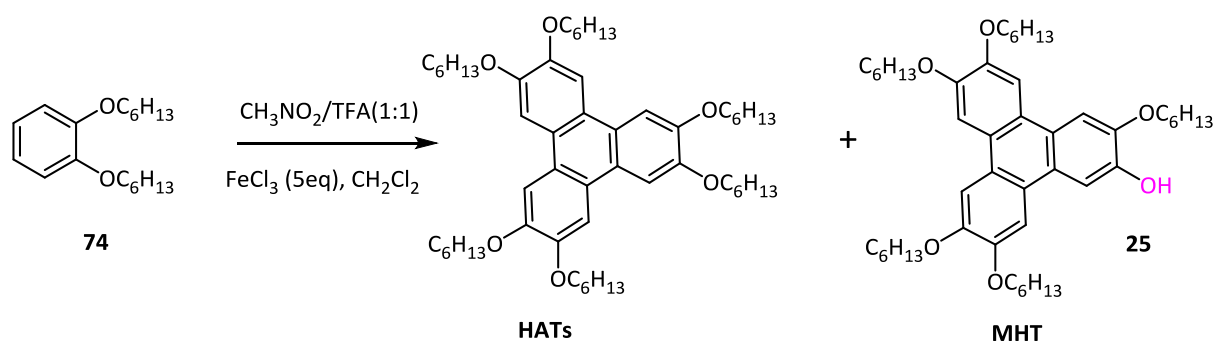
**Table 2.3** Attempted synthesis of Ferrocenyl diacetylene triphenylene **73**

## 2.8 Synthesis of mono-hydroxy-penta-hexyloxytriphenylene (MHT) key precursor to the target compound.

The synthesis of the initial target compound through a disubstituted triphenylene was therefore not successful; for this reason, we moved focus to a route to twin formation using monosubstituted triphenylene derivative monohydroxy-triphenylene (MHT) **25**. MHT is a useful intermediate for many structural designs. The active hydroxyl group is a useful point of attachment to form other triphenylene derivatives.

The synthesis of this compound has many routes already developed by other researchers but we used the route developed in part from our group (Scheme 45).<sup>30</sup>





**Scheme 45:** Synthesis of MHT **25**.

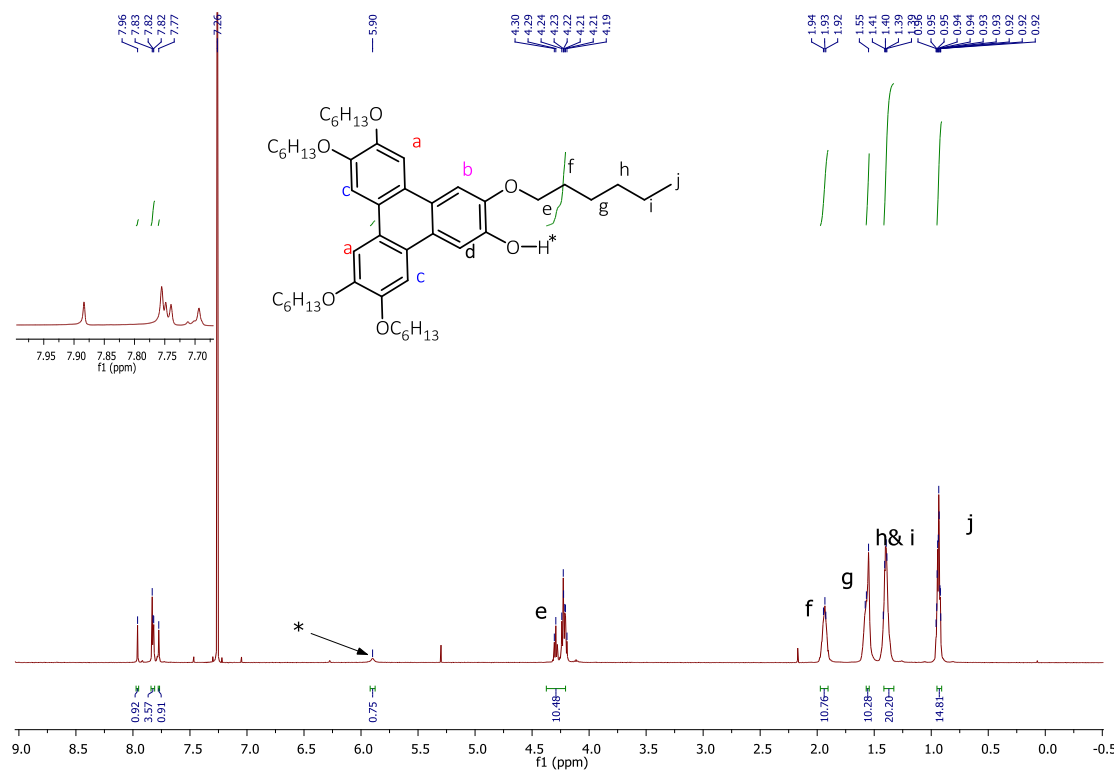
3,6,7,10,11-Pentakis(hexyloxy)triphenylene-2-ol **25** was synthesised by two-step procedure used by Cammidge group.<sup>30</sup> 1,2-Dihexyloxybenzene (DHB) **74**,  $\text{CH}_3\text{NO}_2$ ,  $\text{FeCl}_3$  and TFA were stirred in dry DCM at  $0^\circ\text{C}$  for 90 mins. The DHB was synthesised from our lab by alkylation of catechol. The addition of  $\text{CH}_3\text{NO}_2$  was to improve the solubility of the  $\text{FeCl}_3$  used, the reaction took less time than expected and gave high yield. The TFA was used as catalyst to speed up the reaction.  $\text{FeCl}_3$  is a weak Lewis acid and oxidant responsible for the oxidative cyclisation of **74** forming the MHT.

Entry	SM	Solvent	Reagent	Reaction time	% yield ( <b>25</b> ) MHT	Ref.
1	DHB	$\text{CH}_2\text{Cl}_2$	$\text{FeCl}_3(3\text{eq})$ $\text{FeCl}_3(2\text{eq})$	48 h	20 %	86
2	DHB	$\text{CH}_2\text{Cl}_2$	$\text{FeCl}_3(3\text{eq})$ $\text{FeCl}_3(2\text{eq})$ $\text{H}_2\text{SO}_4$	28h	32%	85
3	DHB	$\text{CH}_2\text{Cl}_2$	$\text{FeCl}_3$ , $\text{CH}_3\text{NO}_2$ , $\text{H}_2\text{SO}_4$	4 h	46 %	28
4	DHB	$\text{CH}_2\text{Cl}_2$	$\text{FeCl}_3$ , $\text{CH}_3\text{NO}_2$ , TFA	1.5 h	66.6%	-----
5	$(-\text{OC}_6\text{H}_{13})_6$ TP (by product)	$\text{CH}_2\text{Cl}_2$	$\text{BBr}_3$	10min	60%	-----

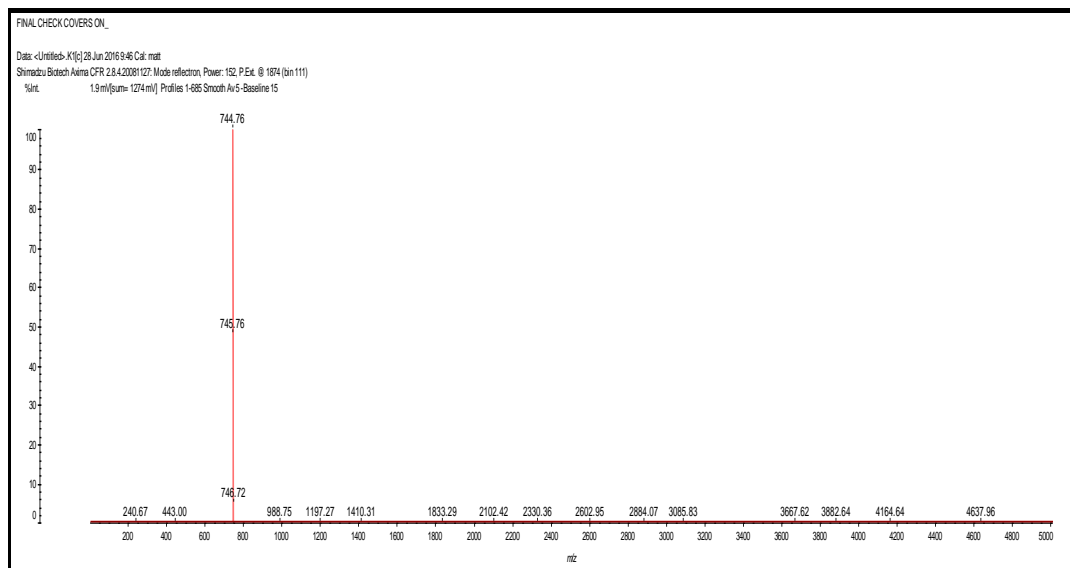
**Table 2.4** Synthesis of Monohydroxytriphenylene (MHT) **25**.

The difficulty experienced in the experimental procedure used in our lab was the formation of the desired product alongside the symmetrical HAT6; the symmetrical product is the higher yield from the reaction. Fortunately, later we are able to convert the symmetrical to the desired product **25** by reacting with  $\text{BBr}_3$  for 10 mins. Typically, when the reaction is left longer it will result in more unwanted products. Also the purification stage is laborious because column chromatography was using 1:80 EtOAc / PE and the MHT solid obtained is always in low yield/recovery. The time used to get the desired product was long and required much solvent during chromatography, although the addition of  $\text{CH}_3\text{NO}_2$  and TFA helps to some extent. However, the condition for the reaction could be improved in future to rectify these problems.

This key product **25** was synthesised and used as pure compound for the synthesis of other triphenylene monosubstituted derivatives. The NMR spectrum of **25** shows that the aromatic region has 6 protons represented with 5 visible peaks, then the peak with chemical shift 7.83 has 4 protons (4 singlets fused together like triplets but it is not, because of the size of the peaks), The -OH- proton is seen at 5.90 (\*) the  $-\text{OCH}_2-$  proton of the hexyloxy long chain is multiplet (e) with 10H, the remaining proton (f, g, h, i, j) of the hexyloxy long chain has 10H, 10H, 20H and 15H as multiplet each and mass spectrometry is  $m/z$  744.76 (Figure 2.13)



**Figure 2.13:**  $^1\text{H}$ NMR of MHT 25 in  $\text{CDCl}_3$ .

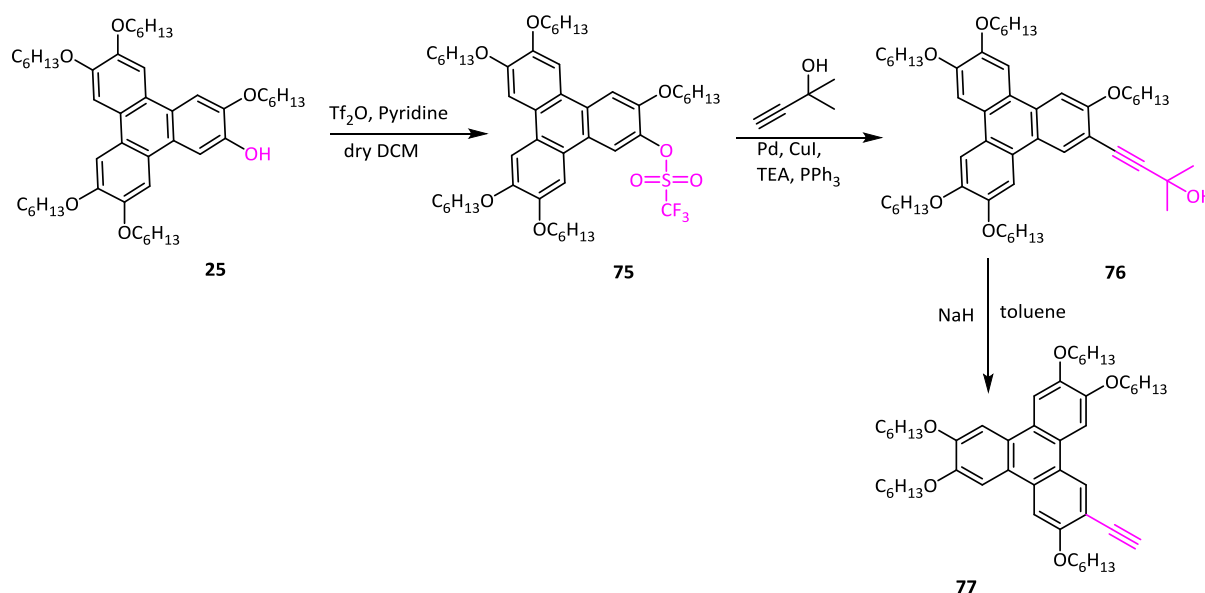


**Figure 2.14:** MALDI-TOF MS of MHT 25

The result above clearly shows how pure the compound is and it represents the correct structure. It was a compound with good properties for the reaction. The method used as in Scheme 39, to synthesise **25** is an effective way to synthesise unsymmetrically substituted triphenylene. Compound **25** is an important triphenylene derivative that can be widely used to synthesise many mesogenic and other derivatives that can be used to link or twin structures because of their versatility.

## 2.9 Synthesis of Ethynyl-3,6,7,10,11-pentakis(hexyloxy)triphenylene **75**

Triphenylene **77** derivative was synthesised from MHT **25** (Scheme 46).



**Scheme 46:** Synthesis of Monoacetylene triphenylene **77**

### 2.9.1: Synthesis of 3,6,7,10,11-pentakis(hexyloxy)triphenylene-2-yl trifluoromethanesulfonate **75**

3,6,7,10,11-Pentakis(hexyloxy)triphenylene-2-ol **25** was treated with trifluoromethanesulphonic acid anhydride in dry and pyridine. Workup gave the triflate product as a solid after recrystallization in DCM: ethanol (2:1), with 98% yield. The proton NMR and MALDI-TOF MS spectrum as shown below represent the compound (Figure 2.15 and 2.16 respectively).

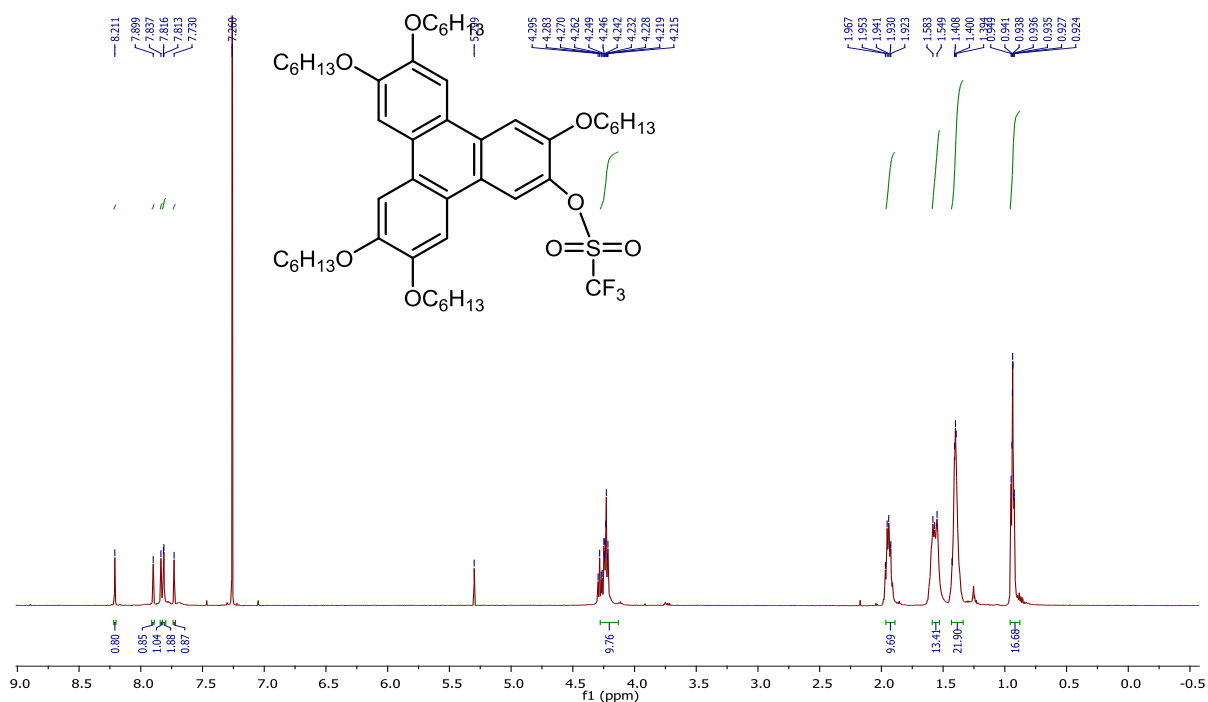


Figure 2.15  $^1\text{H}$  NMR of triphenylene triflate **75** in  $\text{CDCl}_3$ .

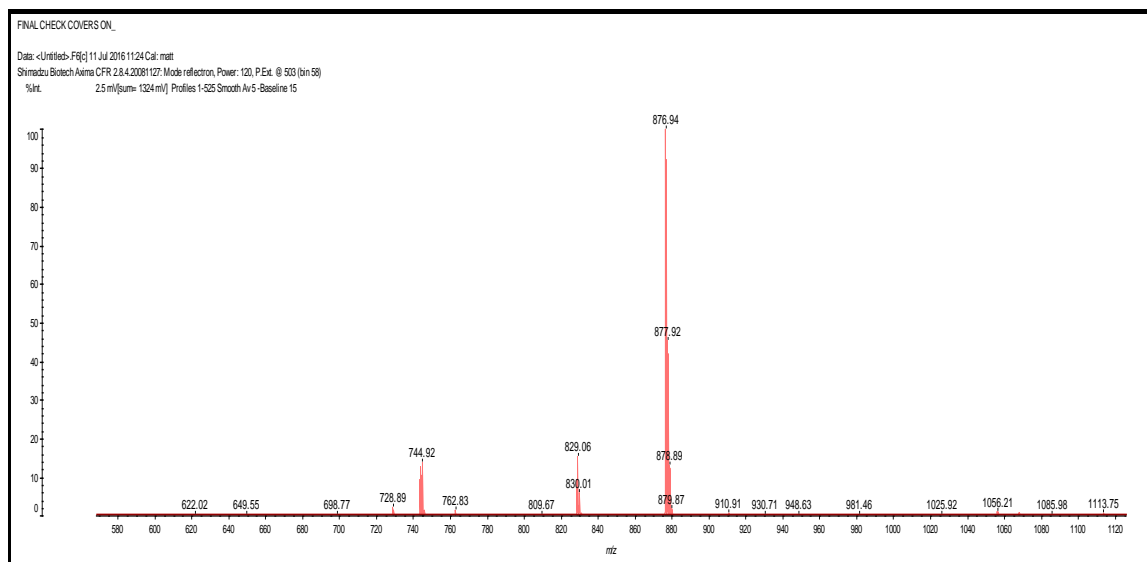


Figure 2.16: Maldi-TOF MS of triphenylene triflate **75**

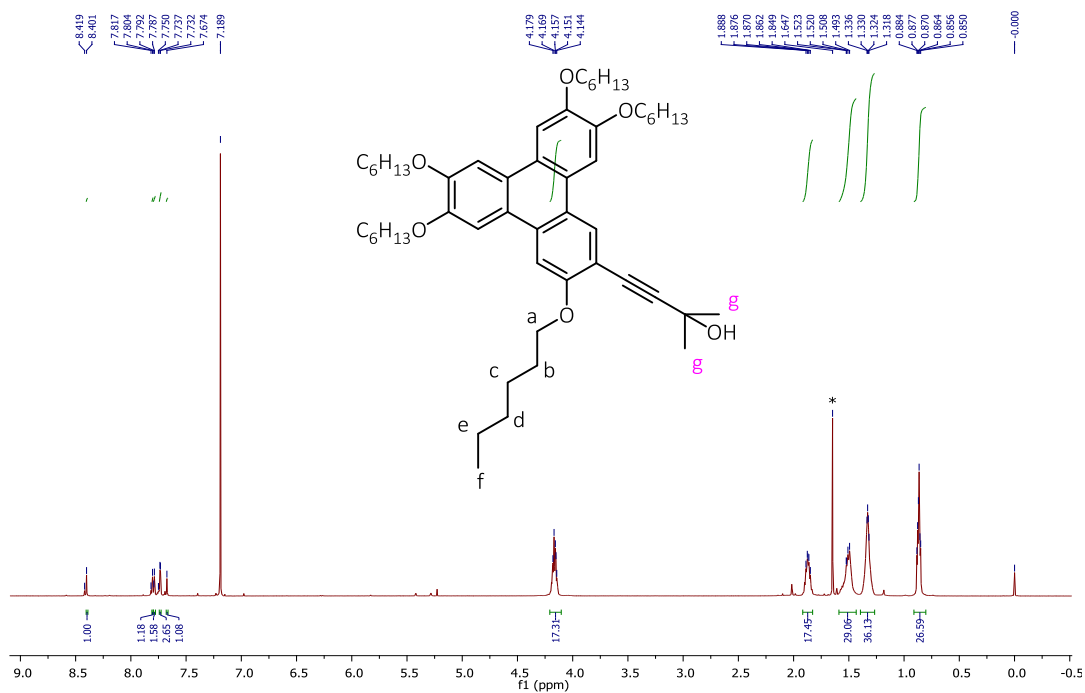
### 2.9.2. Synthesis of 2-methyl-4-(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)but-3-yn-2-ol **76**

For the Sonogashira coupling, initial reaction under standard conditions gave low yields (presumably due to competing homocoupling of the acetylene). Reactions were performed as shown in Table 2.5, normal Sonogashira coupling conditions with Cu were used in entries 1 and 2 but gave low yields. Entry 3 did not give any yield, maybe because of the solvent (water) used. The suitable condition is entry 4 that gave high yield of **74** using pyrrolidine base under copper free Sonogashira coupling. Compound **75**, PPh<sub>3</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, pyrrolidine and TEA (2:3) were stirred under argon. Excess 2-methyl-but-3-yn-2-ol was added dropwise into the mixture, and it was allowed to reflux for 15 h. After workup, a solid was obtained which was recrystallised in DCM/EtOH, giving a pale yellow solid **76** in 89% yield.

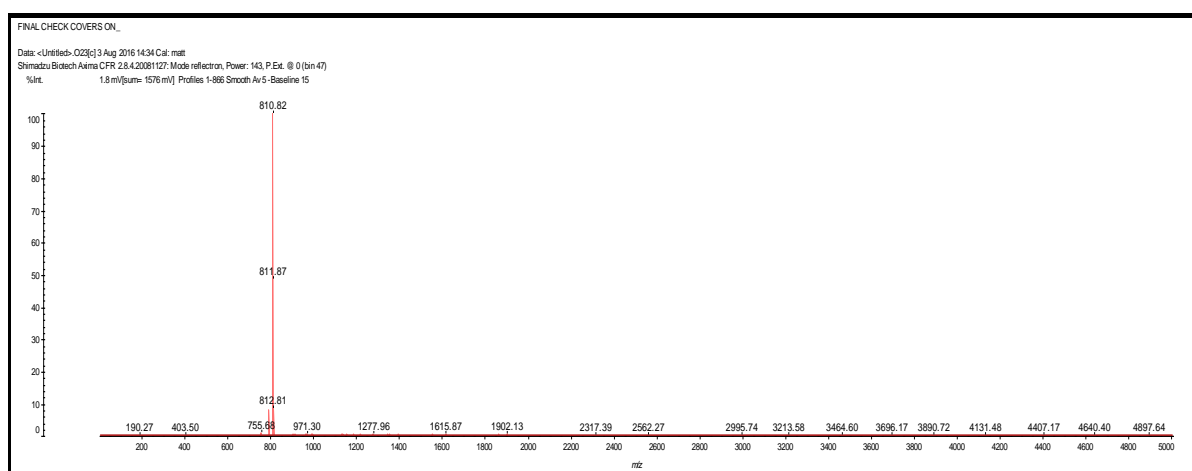
Entry	Catalyst	Reagent	Solvent	Reaction time	% yield of <b>76</b>	Ref.
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TEA, CuI	TEA	168 h	25 %	48
2	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TEA, CuI	TEA	72 h	47 %	48
3	PdCl <sub>2</sub>	Pyrrolidine (Cu free)	H <sub>2</sub> O	24 h	0 %	89, 90
4	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Pyrolidine (Cu free)	TEA	15 h	89 %	87 88

**Table 2.5** Optimisation of condition for the synthesis of Monoacetyol-Tp **76**

We selected 2-hydroxyprop-2-yl reagent was preferable to TMS-acetylene for the synthesis of **76** because it is cheaper and, importantly, much less volatile. Among the various experiment carried out as shown in entries 1-4 in Table 2.5, Copper-free conditions with appropriate base instead of water proved best, as seen in entry 4 having the highest yield.



**Figure 2.17**  $^1\text{H}$  NMR of monosubstituted triphenylene **76** in  $\text{CDCl}_3$ .

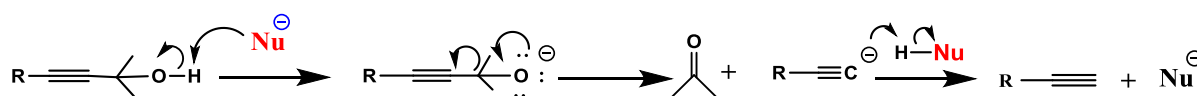


**Figure 2.18.** MALDI-TOF MS of monosubstituted triphenylene **76**.

$^1\text{H}$  NMR spectroscopy as shown in fig 2.14 shows a singlet peak designated with (\*) at 1.72 ppm is related to the two methyl groups protons (6H) represented as (g). Figure **2.17** reveals the mass peak as provided by MALDI-TOF MS, this gives true representation of the product **76**.

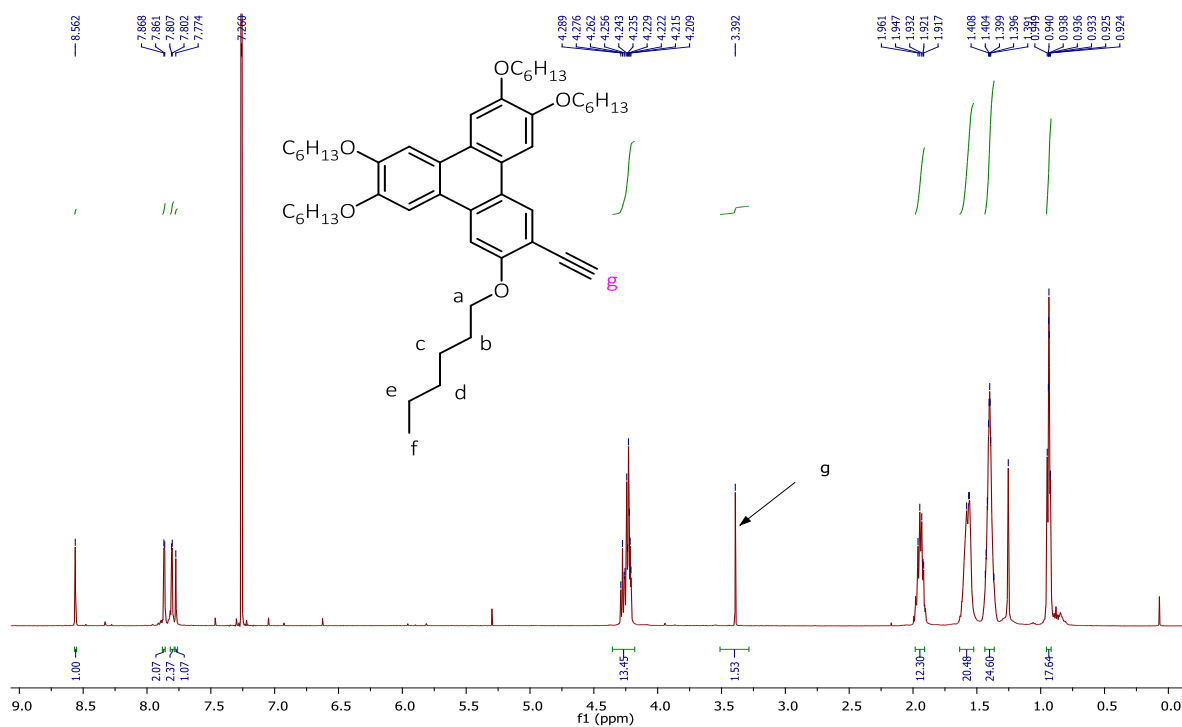
### 2.9.3. Synthesis of Ethynyl-3,6,7,10,11-pentakis(hexyloxy)triphenylene **77**

Compound **77** was synthesised by deprotecting of 2-methyl-4-(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)but-3-yn-2-ol **76** using sodium hydride (60% dispersion in oil) stirred in dry toluene. The crude product (a yellowish oil) was then recrystallised in DCM/EtOH giving a pale yellow solid in 97% yield. This reaction mechanism is shown in Scheme 47.



**Scheme 47:** Deprotection mechanism of **76**

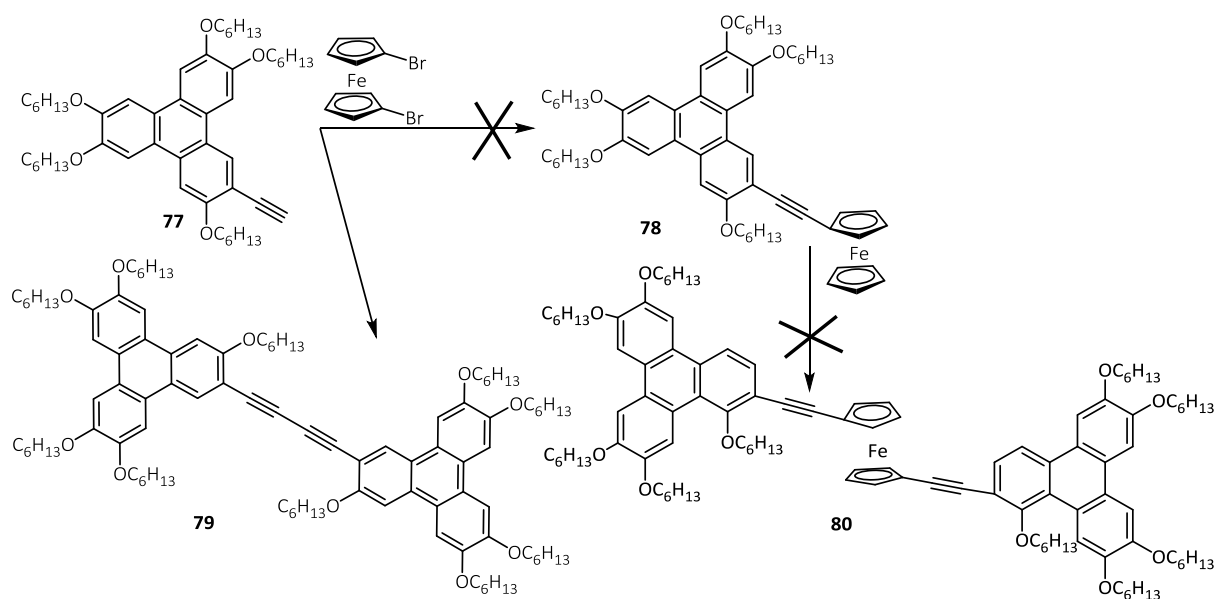
The  $^1\text{H}$  NMR spectrum of **77** is shown in Figure 2.19. The peak at 3.39 ppm is the ethyne proton resonance seen as label g on the structure and the isopropyl protons seen in Figure 2.17 for **76** are no longer seen.



**Figure 2.19**  $^1\text{H}$  NMR of Monoacetylene Triphenylene **77** in  $\text{CDCl}_3$ .



## 2.10 Attempted synthesis of Ferrocenyl Acetylene Twin Triphenylene 80

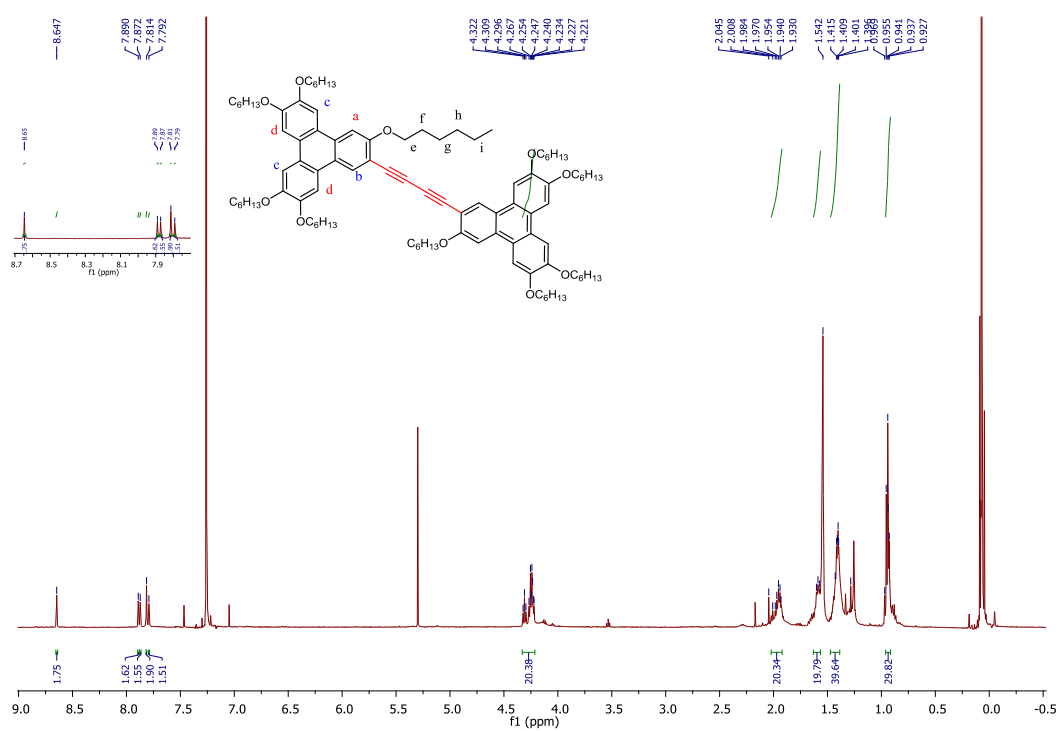


**Scheme 48:** Sonogashira coupling reaction of **77** with dibromoferrocene

1,1'-Dibromoferrocene was stirred in a mixture of freshly distilled TFA and THF under nitrogen atmosphere at room temperature and was CuI added. A THF solution of acetylene **77** was then added slowly by syringe pump over 5 h, and then heated at 50°C for 48 h. The triphenylene starting material was consumed. After workup, the crude solid was separated by column chromatography with (ethylacetate/hexane 1:9). The resulting compound was yellow solid. Analysis of compound revealed the following data: MALDI-TOF MS:  $m/z$  1505.46 ( $M^+$ , 100%). This sample was reanalysed by MALDI-TOF MS, in positive-reflectron mode with DCTB matrix. Expected ions for the newly proposed formula were not also observed. The sample appears to give a mixture of minor components of very low intensity, and one major component  $m/z$  1504, does not provide evidence of containing either Fe or Br elements. However, if two of the bulky alkyne groups are joined together, without the ferrocene unit, you get the formula  $C_{100}H_{142}O_{10}$ , which provides a good  $M^{+}$  match for the major species. For  $C_{100}H_{142}O_{10}$  1504.10: found 1504.10 as seen on the isotope pattern (Figure 2.22). We conclude, therefore, that unfortunately this reaction yields only the dimer even with different conditions applied as seen in Table 2.6

Entry	SM	Reagents	Catalyst	Solvent/ base	Reaction time	% yield of <b>79</b> (Dimer)	% yield of <b>80</b>	Ref.
1	MAcTp	FCBr <sub>2</sub> , CuI	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	THF: TEA 2: 1	24h	47	0	48
2	MAcTp	FCBr <sub>2</sub> (Cu free)	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Pyrolidine/ pyrolidine	5hr	80	0	87

**Table 2.6:** Cu and Cu free reaction attempted for synthesis of Ferrocenylacetylene-TP **80**



**Figure 2. 20.** <sup>1</sup>H NMR of monoacetylene dimer **79** in CDCl<sub>3</sub>

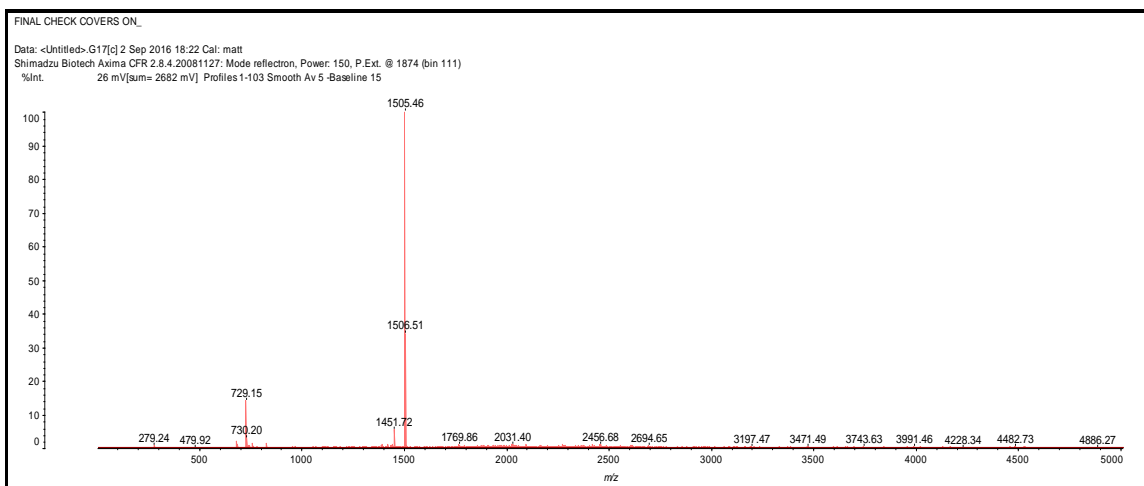


Figure 2.21. MALDI-TOF MS monoacetylene dimer 79.

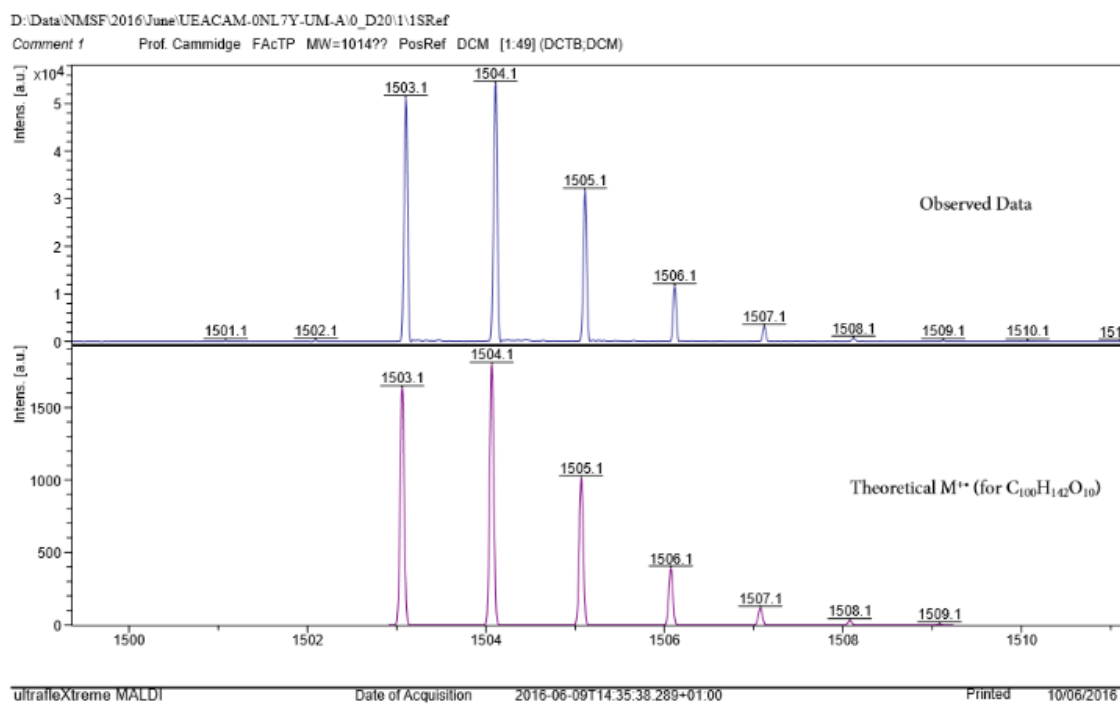
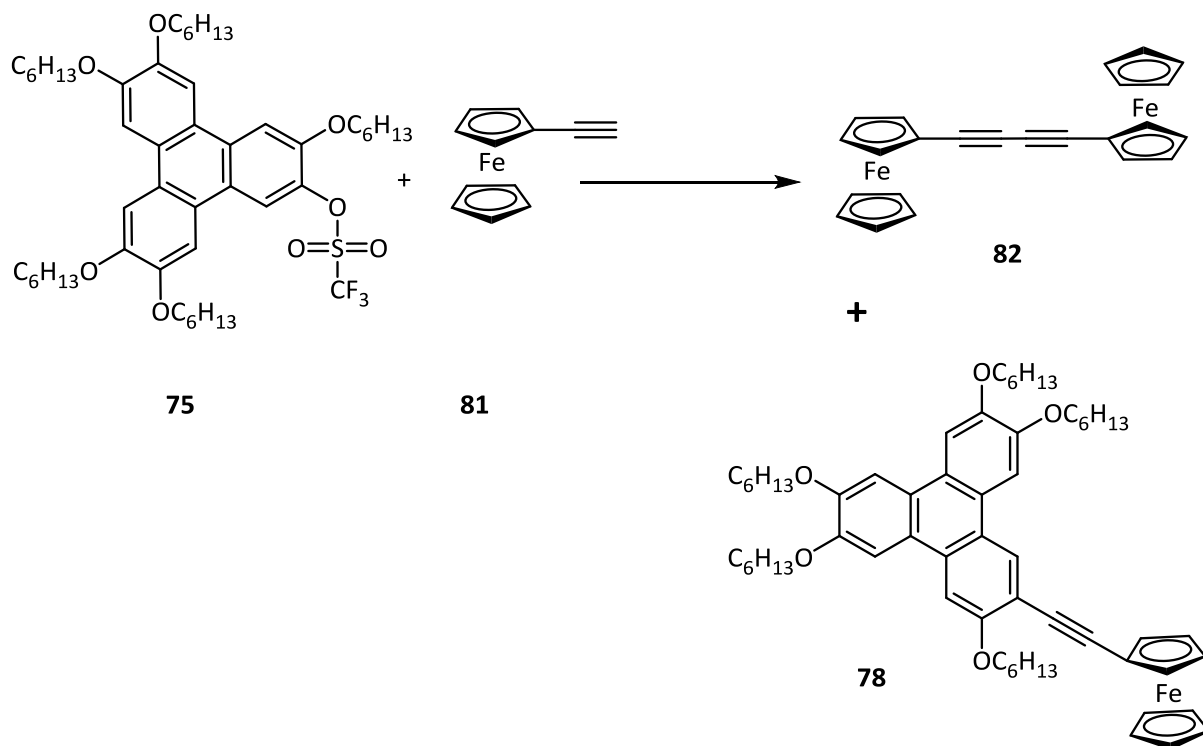


Figure 2.22. HRMS (ESI) of monoacetylene dimer 79.

## 2.11 Attempted Synthesis of Monoacetylenoferrocenyl Triphenylene **78** using Ferrocene acetylene **81**.



**Scheme 49.** Synthesis of Monoacetylene Ferrocenyl Triphenylene **78**

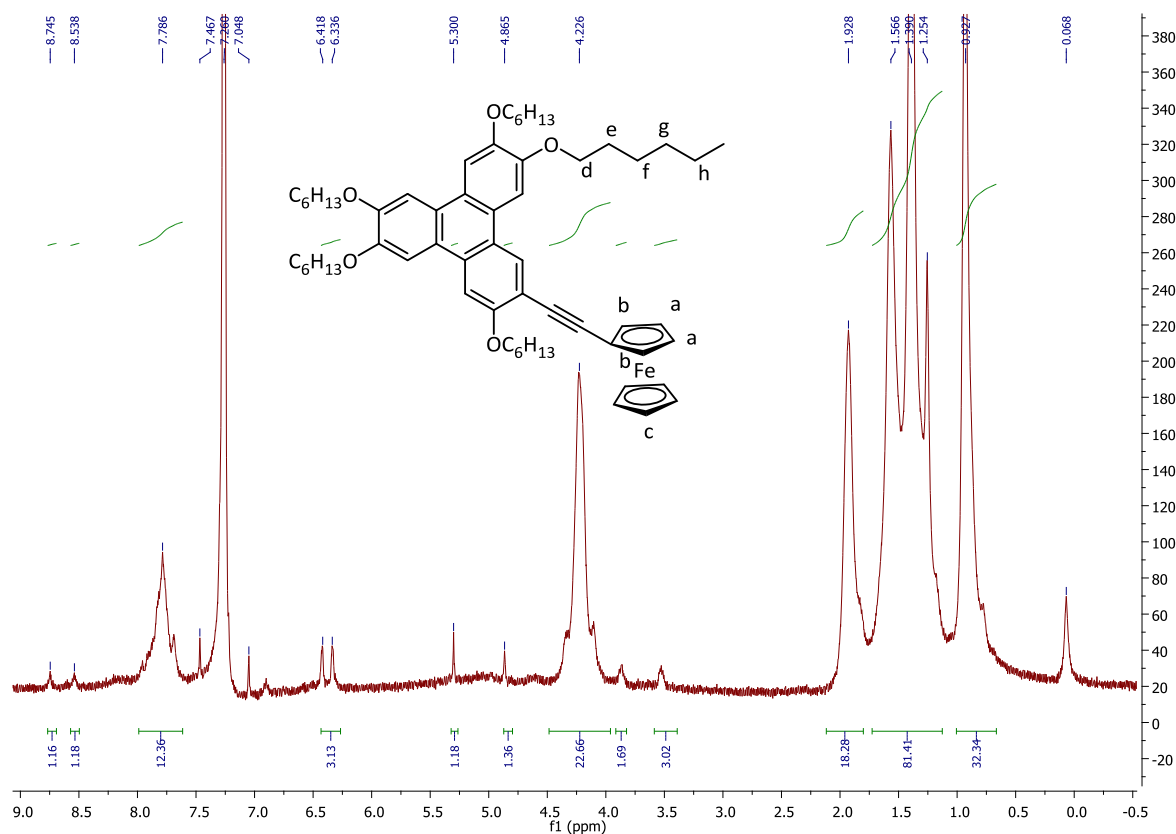
The synthesis of **78** was not possible using the procedure in Scheme **49**, so another procedure was attempted using ethynylferrocene **81**. PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI and dry TEA were all stirred under nitrogen atmosphere at 50°C and **81** was added slowly with syringe pump at 1 ml/h over 10 h. Solid obtained was recrystallized in DCM / EtOH. Resulting amorphous solid **78** was orange of low yield of 4%. No liquid crystal phases were observed on heating. The proton NMR data was also not clear (Figure 2.20) but such observations are common for ferrocene derivatives. In the MALDI-TOF MS: *m/z* C<sub>60</sub>H<sub>81</sub>FeO<sub>5</sub> (M<sup>+</sup>, 100%) 937.57. The MALDI-TOF MS result confirms the presence of the product (Figure 2.24). The main product, in high yield, in this synthesis was the ferrocene acetylene dimer **82**. MALDI-TOF MS of this product is shown in Figure 2.25.

However, the reaction attempted using triflate-Tp **75** under Cu and Cu free condition dimerization still occur with the acetylene precursor **81** used (Table 2.7). This seems to be the problem of using acetylene precursor for the synthesis of the acetylene triphenylene derivatives, same dimerization occur in the first attempt (Scheme 49).

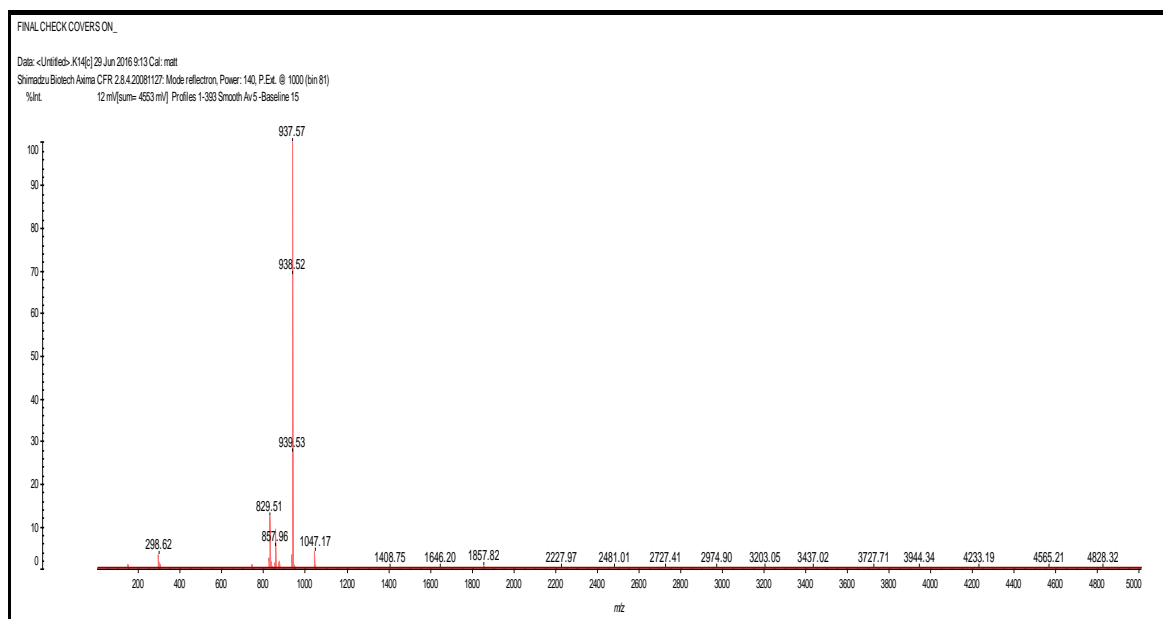
Entry	SM	Reagents	Catalyst	Solvent/ base	Reaction time	% yield of <b>78</b>	% yield of <b>82</b> (dimer)	Ref.
1	TrifTp	FcMAct, CuI	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TEA (excess)	5 h	4	82	45
2	TrifTp	FcMAct (Cu free)	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TEA, K <sub>2</sub> CO <sub>3</sub>	28 h	0	75	91

**TrifTp**- Triphenylene triflate **75**; **FMAcTp**- Ferrocene-monoacetylene **81**.

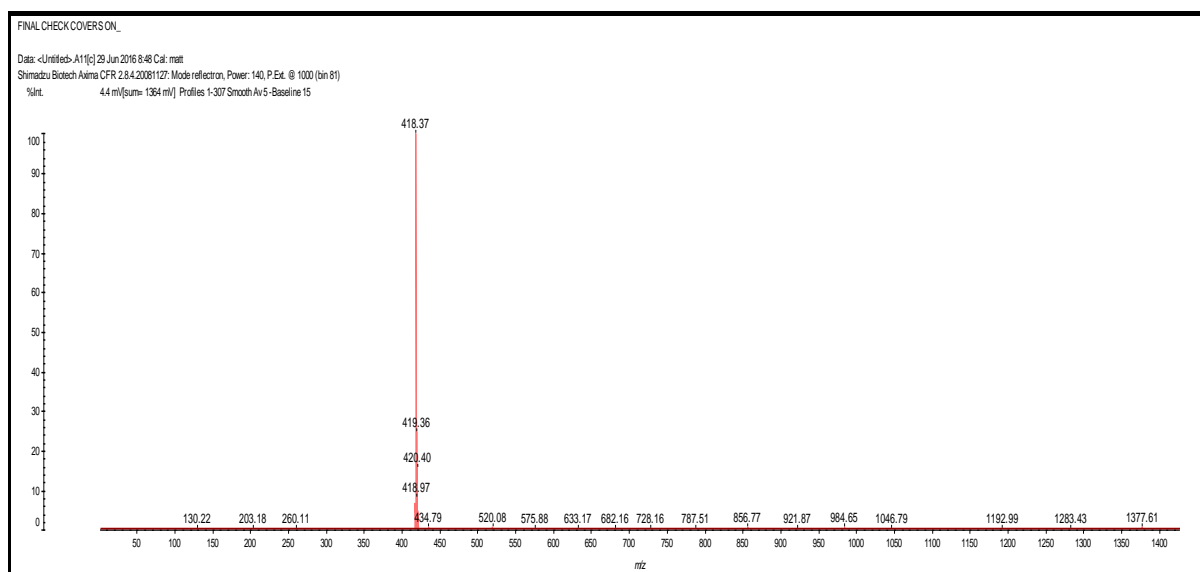
**Table 2.7:** Optimisation of the synthesis of Ferrocenylacetylene-TP



**Figure 2.23:** <sup>1</sup>H NMR of monoacetylene Ferrocenyl triphenylene **78** in CDCl<sub>3</sub>



**Figure 2.24:** MALDI-TOF MS of monoacetylene Ferrocenyl triphenylene **78**.



**Figure 2.25:** MALDI-TOF MS of the ferrocene acetylene Dimer **82**.

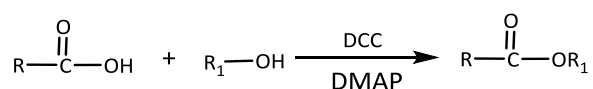
The inefficiency of this general coupling strategy using ferrocenes meant that it was unlikely to give a satisfactory result if extended to the twin. Alternative twins were therefore designed.

## 2.12 Synthesis of twinned triphenylene esters

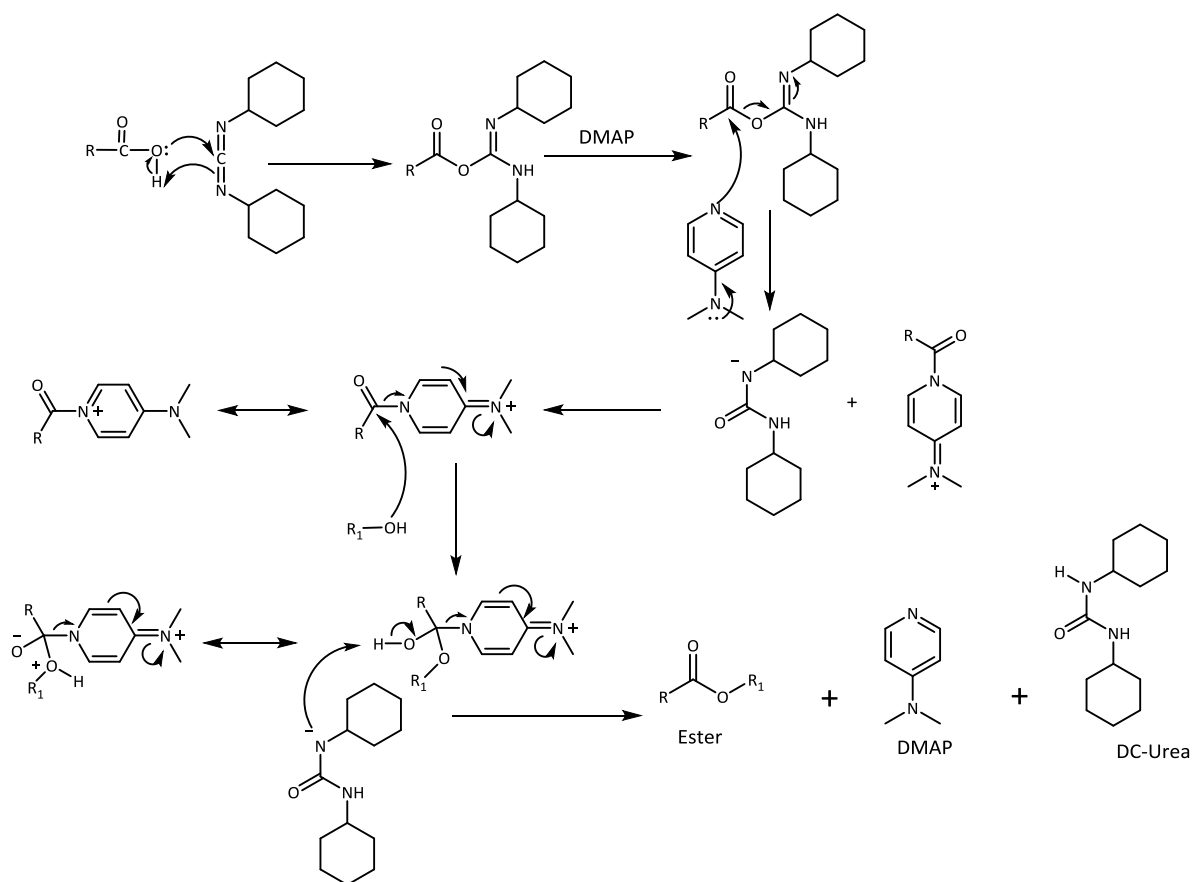
The esterification reaction using DCC and catalysed by DMAP is known as Steglich esterification. The amount of DMAP required is around 10 mol % in conjunction with at least one equivalent of DCC when carboxylic acid is used directly.<sup>78</sup>

### 2.12.1 Proposed mechanism of DCC /DMAP

It is said that DMAP is used as an acyl transfer reagent in the Steglich esterification. The alcohol is less nucleophilic than DMAP. The reaction between an alcohol and *N*-acyl isourea intermediate generated from carboxylic acid and DCC is slow, but is fast with the presence of DMAP. The mechanism (Figure 2.26.2) shows the reaction between a general carboxylic acid, DCC/DMAP and a general alcohol.



**Scheme 50:** General reaction of Steglich esterification

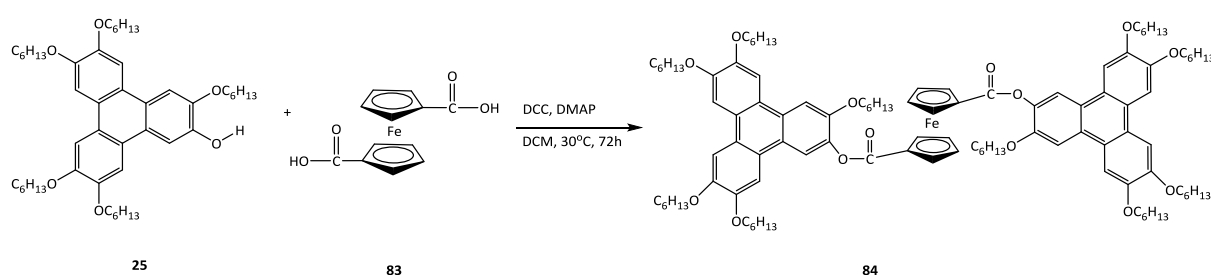


**Scheme 51:** Reaction mechanism of Steglich esterification.<sup>98</sup>

The same mechanism (Scheme 51) applies to the reaction in this section using monohydroxytriphenylene (MHT) and the different dicarboxylic acids in the presence DCC/DMAP for the preparation of the twin triphenylene esters.

### 2.12.2: Synthesis of Ferrocenyl Triphenylene Ester 84

The esterification reaction of MHT **25** with the ferrocenedicarboxylic acid is catalysed by DMAP and uses DCC (Scheme 52).



#### Scheme 52: Synthesis of Ferrocenyl triphenylene ester **84**

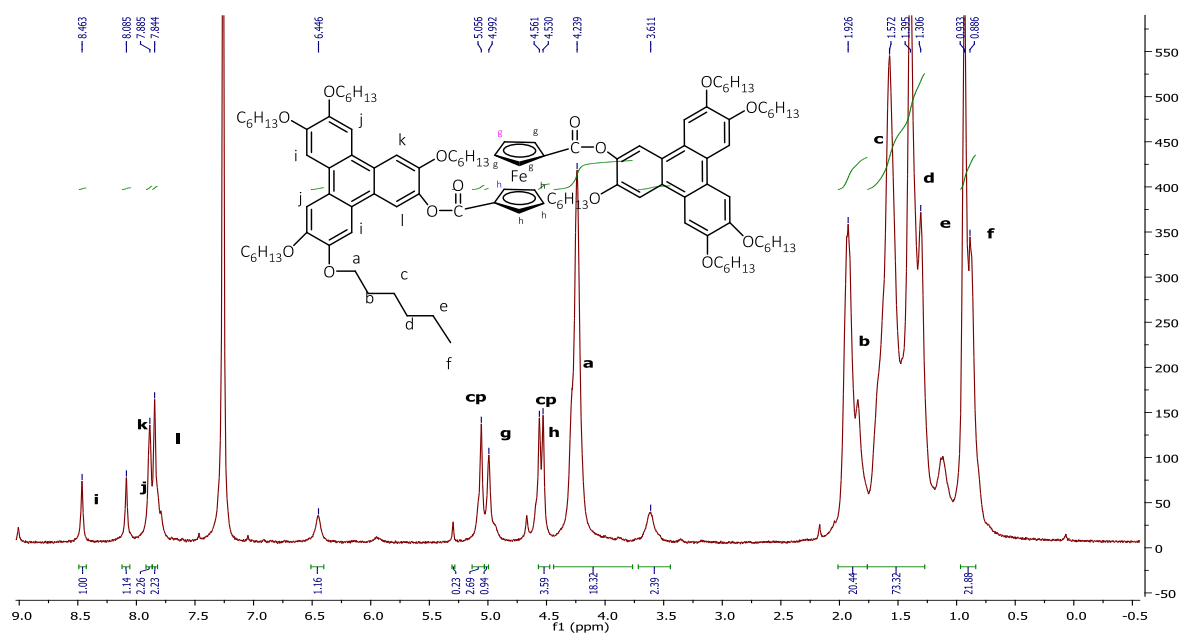
Compound **25** (MHT), 1,1'-ferrocenedicarboxylic acid **83**, *N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP) were stirred in dry DCM for 48 h. After work-up the crude product was separated by column chromatography and recrystallised from EtOH/DCM to give an orange solid in 41% yield. Different conditions were used to improve the yield as seen in Table 2.8 entries 1 to 6, entries 5 and 6 are the most convenient conditions for the synthesis of **84**.



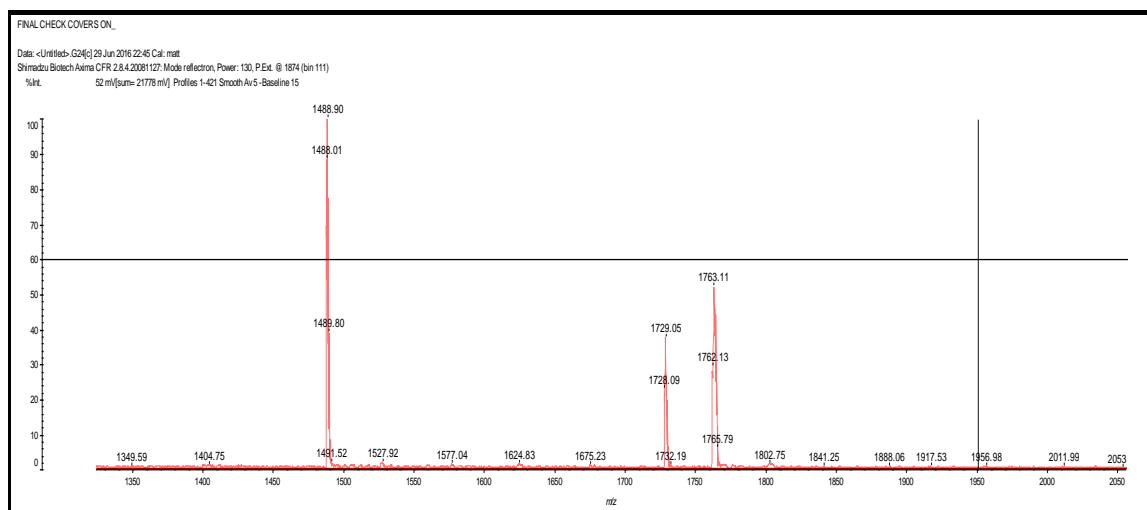
Entry	SM	Reagents		Catalyst	Solv.	temp (0°C)	time	% yield of <b>84</b>	Ref .
	MHT (eq)	Fc(COOH) <sub>2</sub> (eq)	DCC (eq)	DMAP (%)					
1	1	0.4	1	0.05	DCM	rt	72	0	10, 28, 92
2	1	0.4	2	0.05	DCM	30	72	28	-
3	1	0.4	2	0.10	DCM	30	48	30	-
4	1	0.4	2	0.05	THF	30	72	20	-
5	1	0.4	4	0.20	DCM	30	24	40	-
6	1	0.4	4	0.25	DCM	30	24	40.9	-

**Table 2.8:** Optimisation of the synthesis of Ferrocenyl Triphenylene Ester **84**

Ferrocene dicarboxylic acid proved to be an effective reagent for the preparation of Ferrocenyl triphenylene ester **84**. MALDI-TOF MS:  $m/z$ , calculated for C<sub>108</sub>H<sub>151</sub>FeO<sub>14</sub> (M+H) 1729.05 found 1729.05 (Figure 2.27). Proton and carbon NMR was not clear (Figure 2.26) but the product was identified by MALDI-TOF MS. Further purification of the product by recrystallization and chromatography has so far proved unsuccessful.



**Figure 2. 26:**  $^1\text{H}$  NMR of Ferrocenyl Triphenylene Ester **84** in  $\text{CDCl}_3$



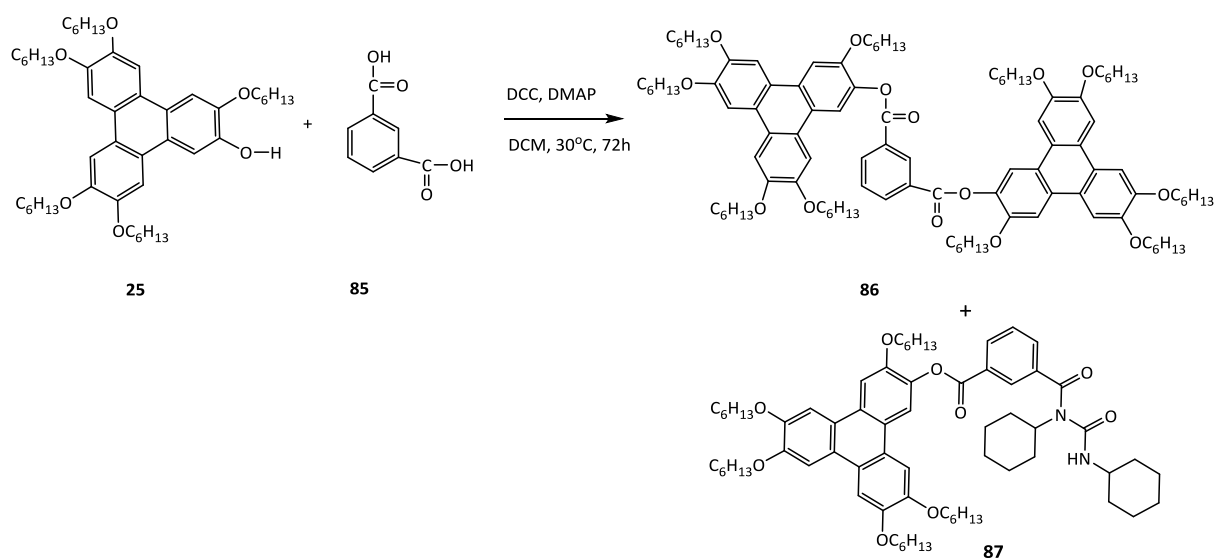
**Figure 2. 27.** MALDI-TOF MS of Ferrocenyl triphenylene ester **84**.

The poor solubility of the ferrocene dicarboxylic acid reagent seems to be an issue affecting the reaction. Equal amount of the MHT was isolated as a product because excess of the MHT was used for the twinning and much was left unconverted. Most DCC/DMAP reactions occur

with just stirring at room temperature but the desired product did not form at room temperature but at 30°C.

### 2.12.3 Synthesis of Benzoyl Ester twins

#### 2.12.3.1 Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)isophthalate **86**



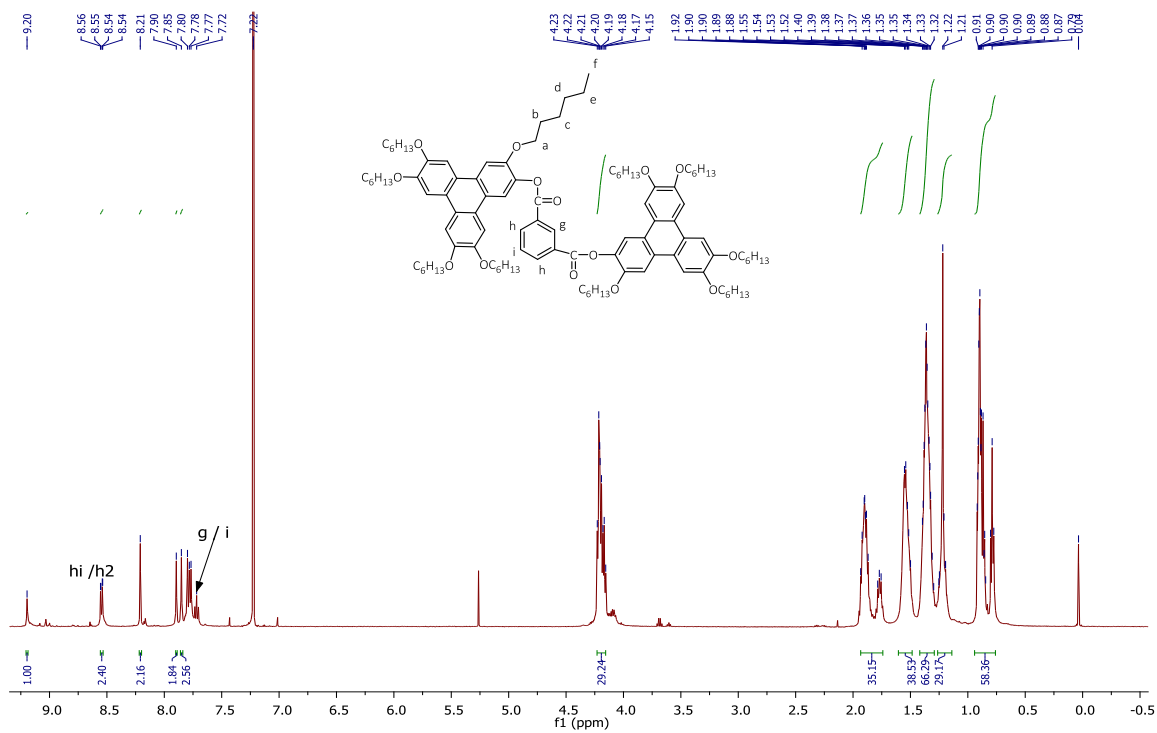
#### Scheme 53: Synthesis of Isophthalate twin triphenylene **86**

Compound **25**, benzene-1,3-dicarboxylic acid **85**, *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) were stirred in DCM at 30°C for 72 h. The isolated crude solid was columned and recrystallised in EtOH/DCM. Resulting off-white solid **86** was obtained in 29% yield alongside with a by-product that was characterised as **87** with higher yield of 52%. Different conditions were applied for the synthesis to for better yield, however the result is as shown in Table **2.9** with entry 4 as the best yield and higher yield of the undesired byproduct.

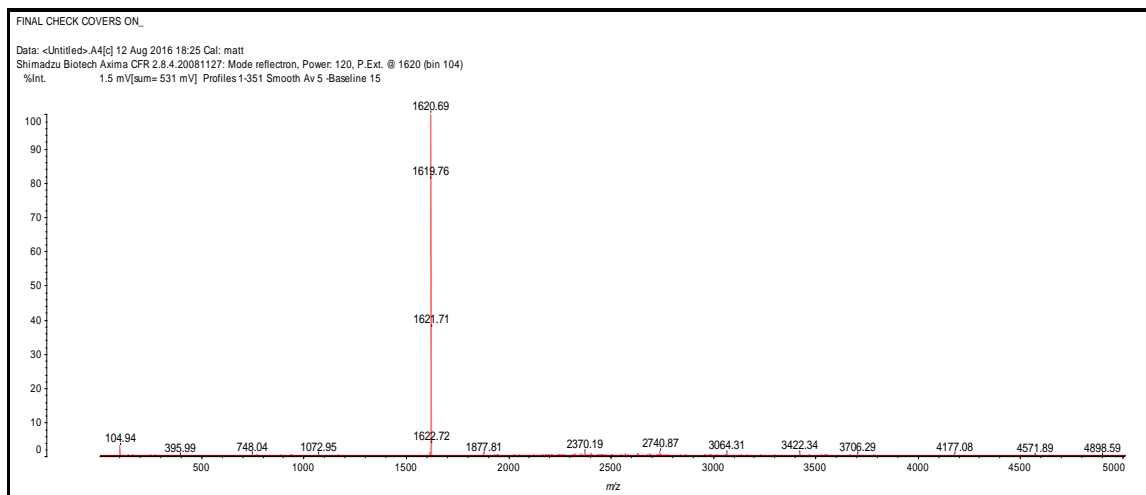
Entry	SM	Reagents		Catalyst	Solv.	temp (°C)	time (h)	% yield of <b>86</b> .	% yield of <b>87</b>	ref
	MHT (eq)	Isophthalic acid (eq)	DCC (eq)	DMAP (%)						
1	1	0.4	1	0.05	DCM	rt	72	0	-	10, 28, 92
2	1	0.4	2	0.05	DCM	25	48	18	46%	--
3	1	0.4	4	0.10	DCM	30	48	20	50%	--
4	1	0.4	4	0.20	DCM	30	48	28.6	52%	--

**Table 2.9** Optimisation of the synthesis of Isophthalate twin triphenylene **86**

The NMR result as shown in Figure 2.28 represent the compound. MALDI-TOF MS:  $m/z$  calculated for **86**  $C_{104}H_{147}O_{14}$  (M+H)<sup>+</sup> 1620.07 found 1620.38 (Figure 2.29). Preliminary evaluation of the thermal behaviour revealed the solid appears to convert from an amorphous material to a mesophase at around 155 °C. On cooling, a mesophase appears at 150 °C with a texture characteristic of a columnar hexagonal phase. The mesophase cools to form a glass, and crystallisation did not occur even at room temperature overnight.

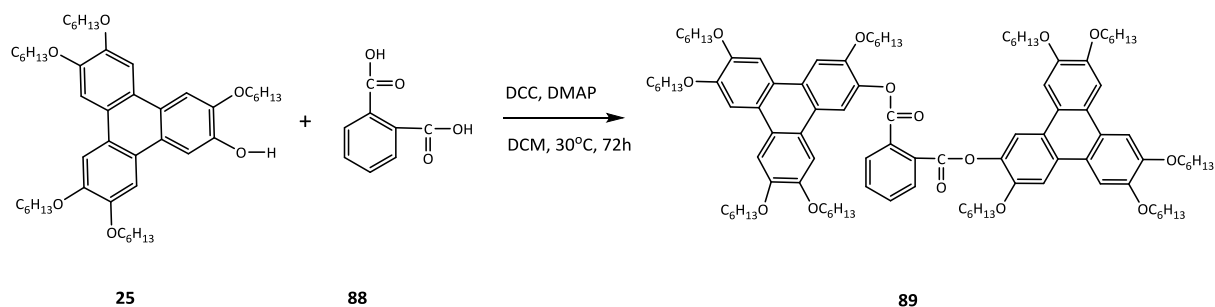


**Figure 2.28.** <sup>1</sup>H NMR of Isophthalate twin triphenylene **86** in CDCl<sub>3</sub>



**Figure 2.29.** MALDI-TOF MS of pure Isophthalate twin triphenylene **86**.

### 2.12.3.2 Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)phthalate **89**



#### Scheme 54: Synthesis of phthalate twin triphenylene **89**

Isomeric triphenylene twin **89** was prepared using same conditions for **86** but using phthalic instead of Isophthalic acid. The solid obtained was colourless and in 41% yield. The following reaction was carried out (Table 2.10), results shows that entry 3 is most favourable condition for the synthesis of **89**.

Entry	SM	Reagents		Catalyst	Solv.	temp (0°C)	time (h)	% yield of ester <b>89</b>	Ref.
	MHT (eq)	Phthalic acid (eq)	DCC (eq)	DMAP (%)					
1	1	0.4	1	0.05	DCM	rt	72	0	10, 28, 92
2	1	0.4	2	0.05	DCM	30	72	30	-
3	1	0.4	4	0.10	DCM	30	72	40.8	-

**Table 2.10:** Optimisation of the synthesis of Phthalate twin triphenylene **89**.

The NMR of the solid **89** is as expected. The proton on the phthalic acid is **e** and **f** and both are doublet doublet (2H each), the remaining four peaks at the aromatic region are for the triphenylene with (2H each) (Figure 2.30). The MALDI-TOF MS:  $m/z$   $C_{104}H_{146}O_{14}$  1619.45 ( $M^+$ , 100%) for the expected compound (Figure 2.31). Solid **89** melts directly to the isotropic liquid at 80°C much lower than the isophthalate isomer.

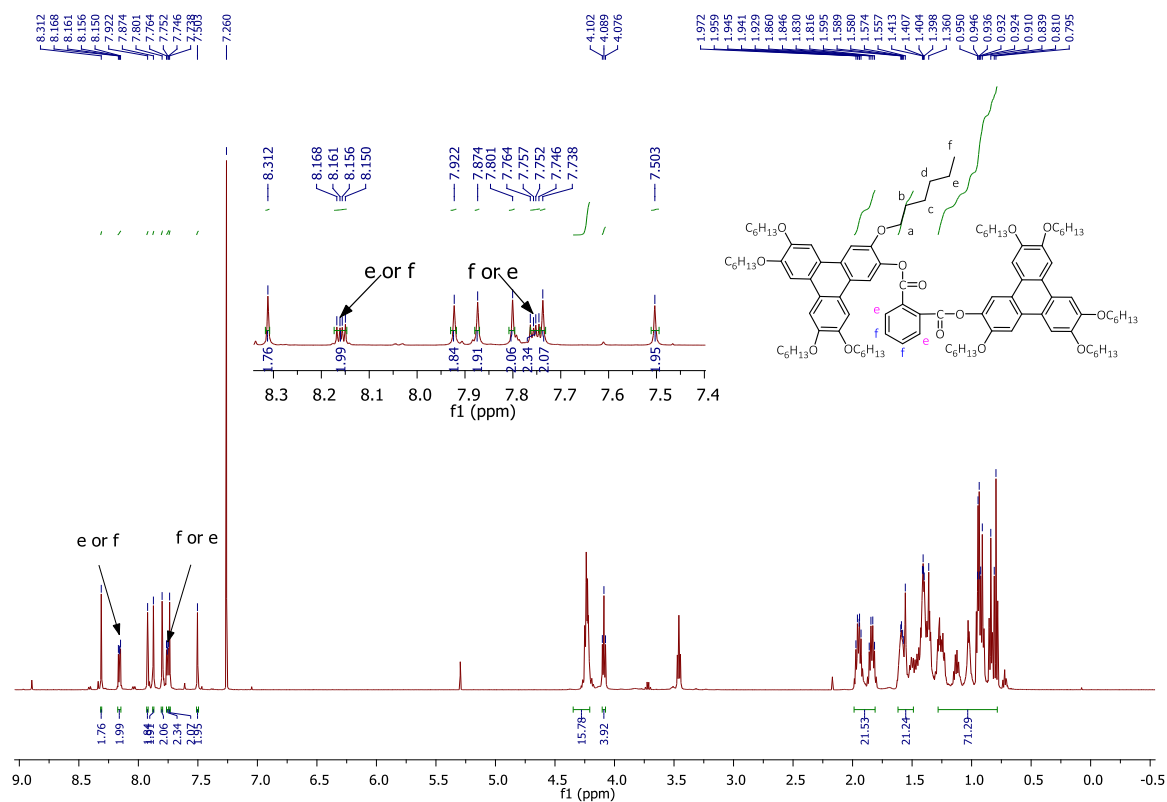
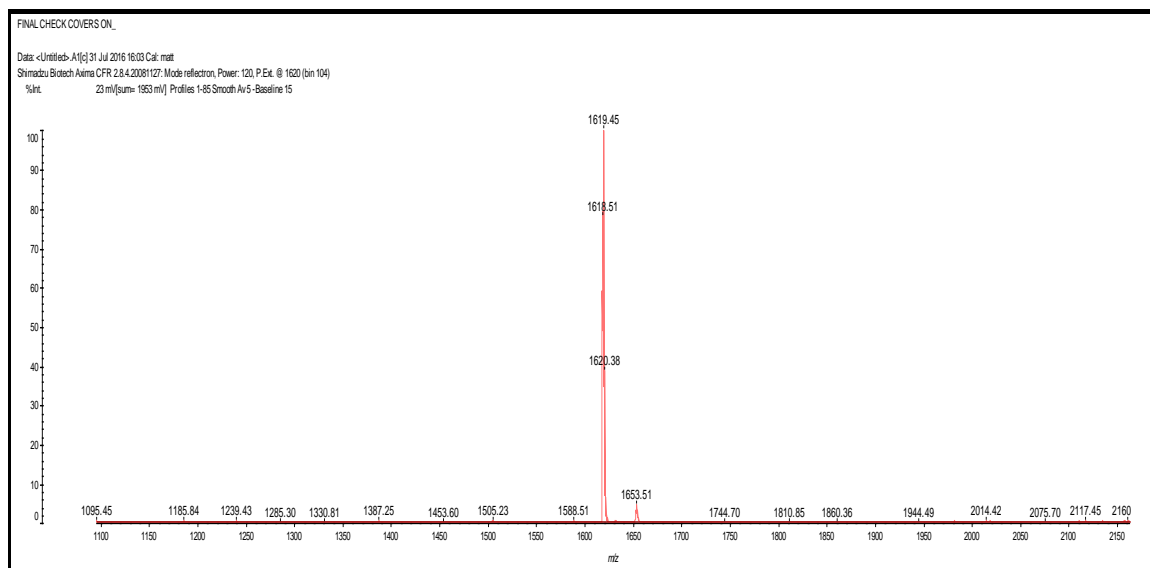
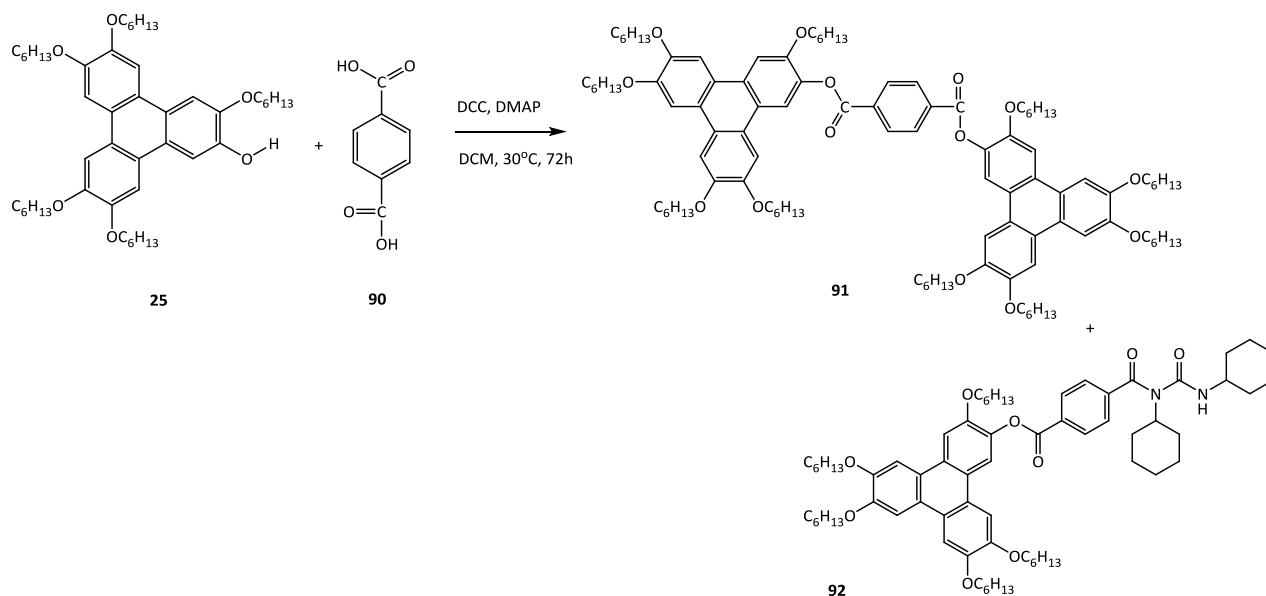


Figure 2.30:  $^1H$  NMR of phthalate twin triphenylene **89** in  $CDCl_3$ .



**Figure 2. 31:** MALDI-TOF MS of phthalate twin triphenylene **89**.

### 2.12.3.3. Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)terephthalate **91**



**Scheme 55:** Synthesis of Terephthalate twin triphenylene **91**

The terephthalate isomer was similarly synthesised. Resulting solid **91** was colourless and in 35% yield; also alongside was the by-product **92**, obtained as white (0.18g, 42%). Different



reaction was done to optimise the condition for **91** Table 2.11, entries 4 and 5 is the best for the synthesis of **89**, the increase in temperature do not affect the yield in the entries 4 and 5

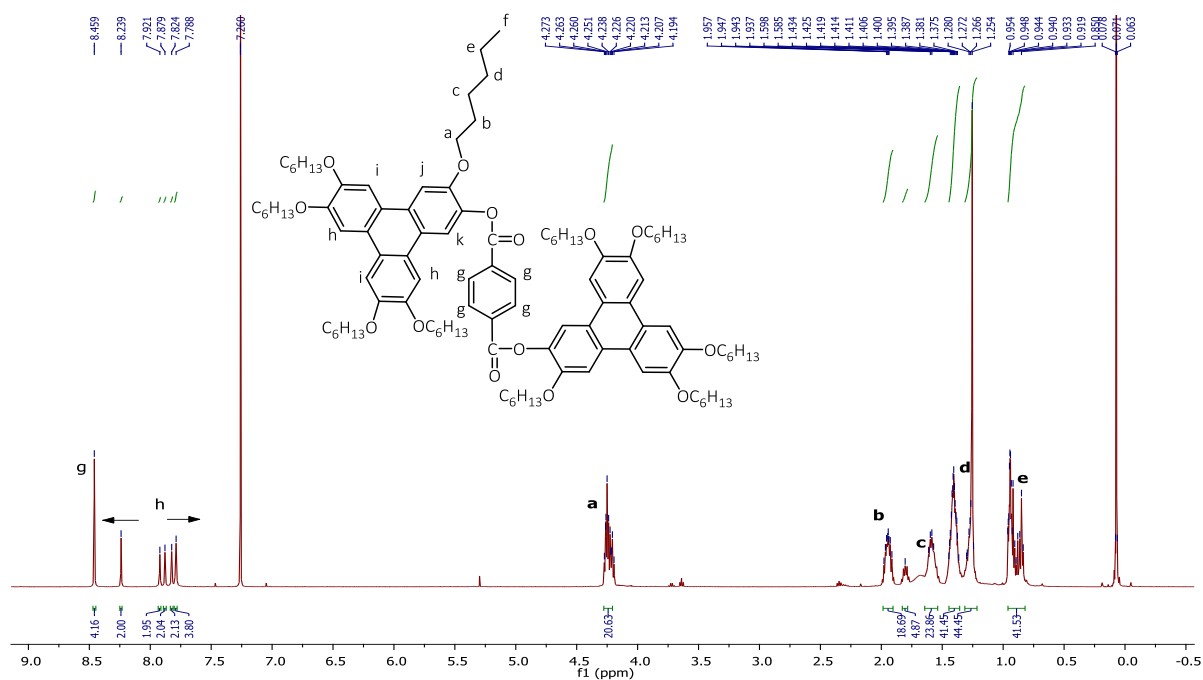
Entry	SM	Reagents		Catalyst	Solv.	temp (0°C)	time (h)	% yield of ester <b>91</b>	% yield of Urea <b>92</b>	Ref
	MHT (eq)	Terephthalic acid (eq)	DCC (eq)	DMAP (%)						
1	1	0.4	1	0.05	DCM	rt	72	0	-	10, 28, 92
2	1	0.4	2	0.05	DCM	25	48	12	20	-
3	1	0.4	4	0.10	DCM	30	72	20	33	-
4	1	0.4	4	0.20	DCM	30	48	34.6	42	-
5	1	0.4	4	0.20	DCM	40	72	35.3	42.3	-

**Table 2.11:** Optimisation of the synthesis of terphthalate twin triphenylene **91**.

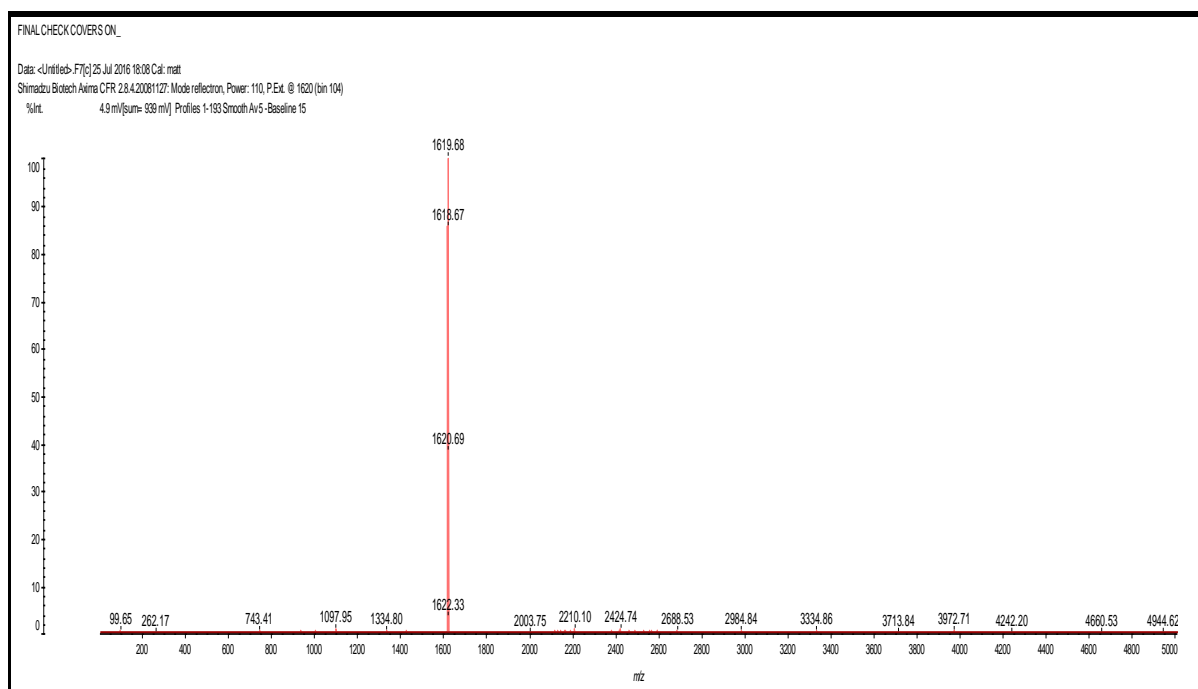
The NMR represented for **91** (g) peak is singlet (4H) from the bridging benzene ring. The proton h, l, j and k (2H each) of the aromatic region are clearly seen (Figure 2.32). MALDI-TOF MS:  $m/z$  C<sub>104</sub>H<sub>146</sub>O<sub>14</sub> 1619.68 (M<sup>+</sup>, 100%) for Compound **91** is as shown in Figure 2.33 and the by-product **92**, MALDI TOF MS:  $m/z$  C<sub>69</sub>H<sub>98</sub>N<sub>2</sub>O<sub>9</sub> 1098.84 (M<sup>+</sup>, 100%)

The compound melts directly to an isotropic liquid at 175°C. On cooling, however, a classic nematic texture is seen in part of the sample which overall appears to be a mixture of two immiscible materials. The sample was dissolved from the slide and examined by NMR spectroscopy. No evidence for decomposition was found. Further investigations on this

material are needed to understand the origin of the observations (likely a solvent residue impurity) and to finalise the mesophase behaviour.



**Figure 2.32:** <sup>1</sup>H NMR of Terephthalate twin triphenylene **91** in CDCl<sub>3</sub>



**Figure 2.33.** MALDI-TOF MS of Terephthalate twin triphenylene **91**.

### 2.12.4. N-Acyl Ureas (byproduct) from Isophthalate **86** and Terephthalate **91**

High yield of the side products (N-acyl ureas) occurred during the activation of carboxylic groups with DCC in the reaction of the isophthalate **86** and terephthalate **91** mixture respectively.

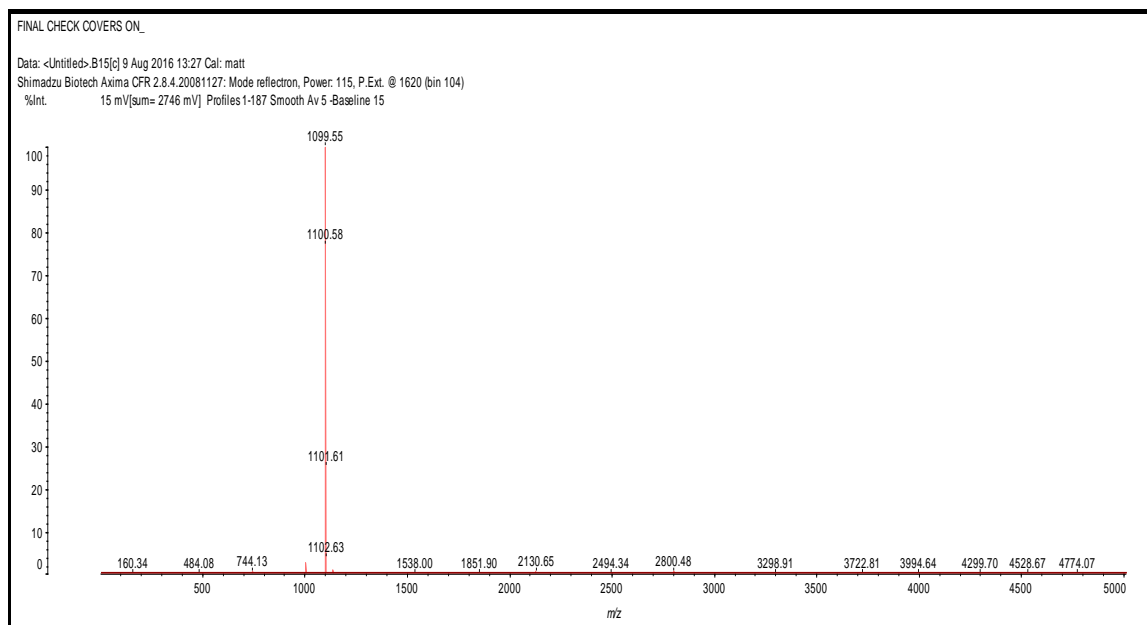


Figure 2.34: MALDI-TOF MS of N-acyl urea **87** of isophthalate **86**

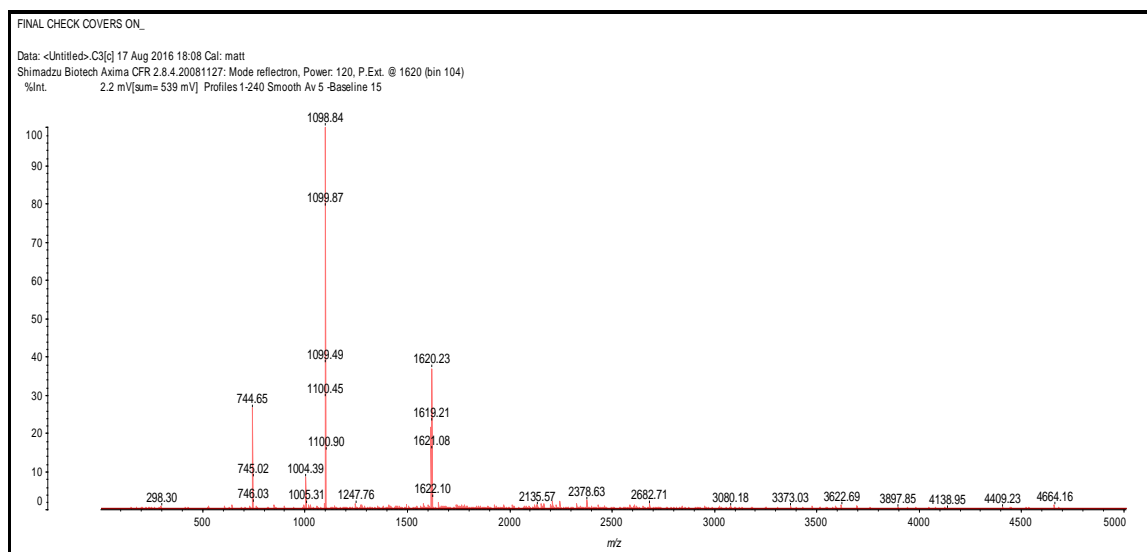


Figure 2.35. MALDI-TOF MS of N-acyl urea **92** in crude of terephthalate **91**

The reaction of isophthalate **86** and terephthalate **91** respectively yielded the byproducts **87** and **92** (Scheme 53 and 55) also as seen on the MALDI-TOF MS (Figure 2.34 and 2.35). The NMR spectrum of **87**, aromatic region has nine peaks three peaks (h1/h2 (doublet), j and l (triplet) with 1H each) of which are from the benzoic acid ring and the remaining six (6 singlets of 1H each) are from the triphenylene benzene ring, the proton peak of (-OCH<sub>2</sub>) of the hexyloxy long chain is a multiplet with 10H, the remaining proton on the long chain is found at the aliphatic region as (multiplets with 10H, 10H, 20H and 15H respectively) and the cyclohexane chain k and l has 2 singlet with 10H each as seen on the NMR spectrum and MALDI-TOF MS is as shown below Figure **2.36** and **2.37** respectively. The melting point was 90°C; however, this compound does not show liquid crystal phase it melted completely at 90°C. Interestingly, this compound yield is more than the main product. The product is to be re-analysed for future research.

The NMR and MALDI-TOF MS data confirms the structure of the by-product **87** as seen in Figure 2.36 and 2.37. *N*-acyl urea **92** in crude of terephthalate **91** was identified with MALDI-TOF MS as seen in Figure **2.35**.

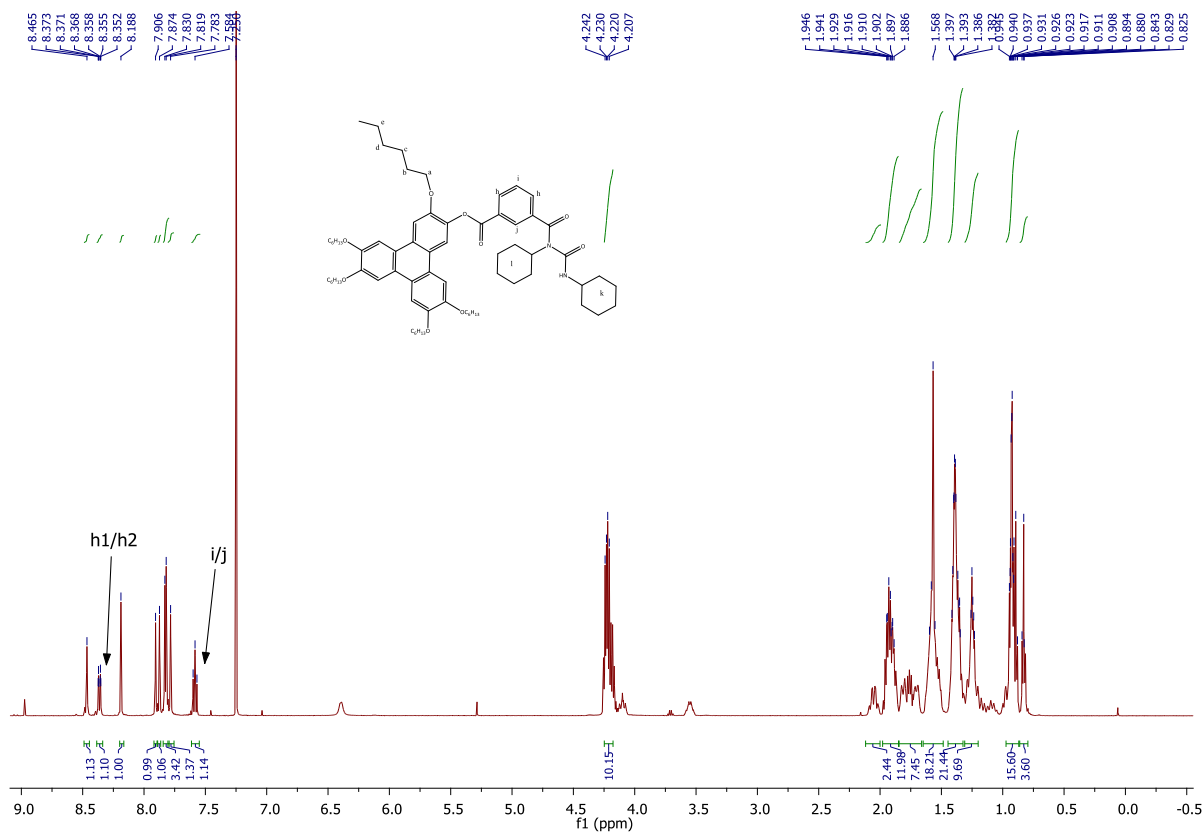


Figure 2.36. <sup>1</sup>H NMR of *N*-acyl urea **87** of Isophthalate **86** in CDCl<sub>3</sub>

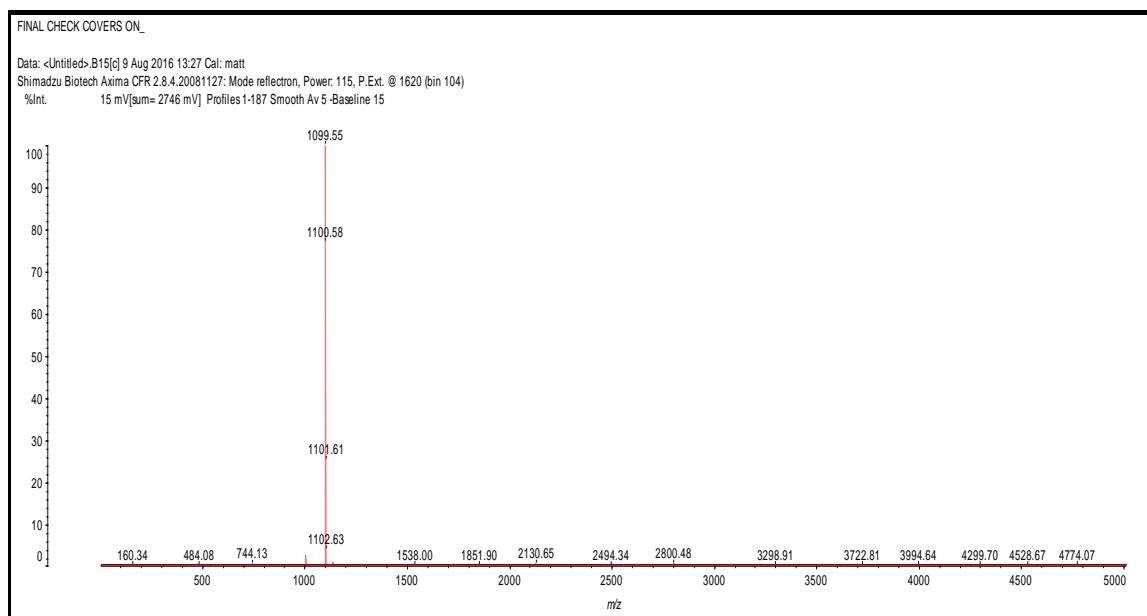
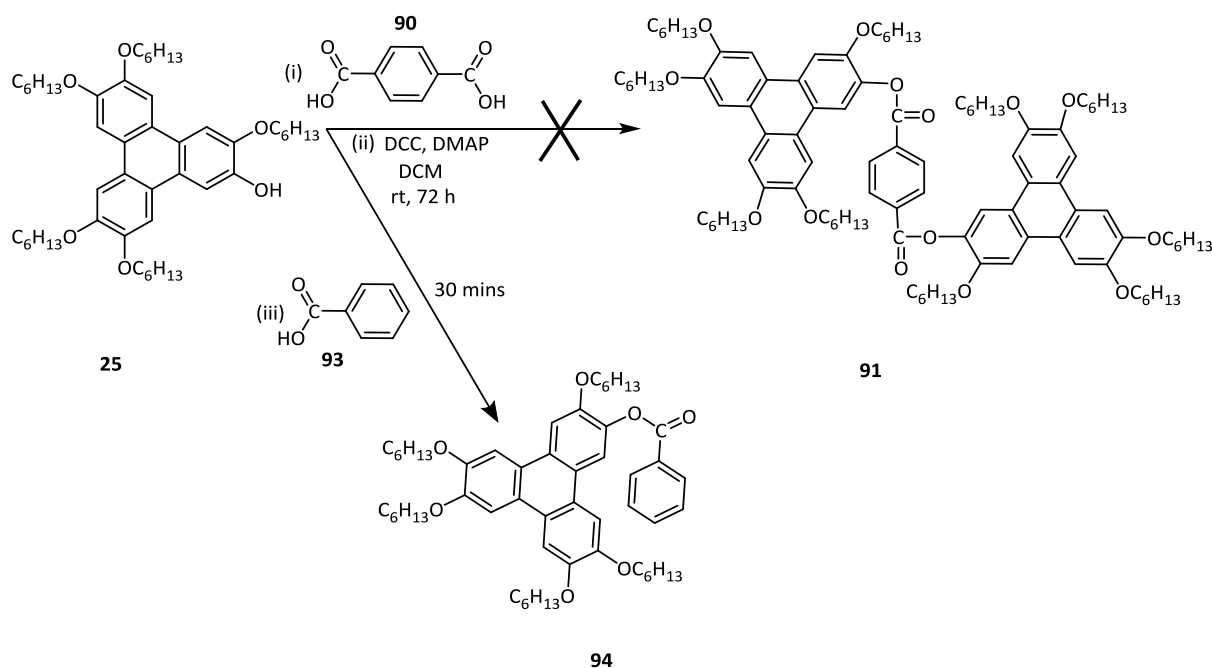


Figure 2.37. MALDI-TOF MS for *N*-acyl urea **87** of Isophthalate .

### 2.12.5 Synthesis of triphenylene benzoate **94**



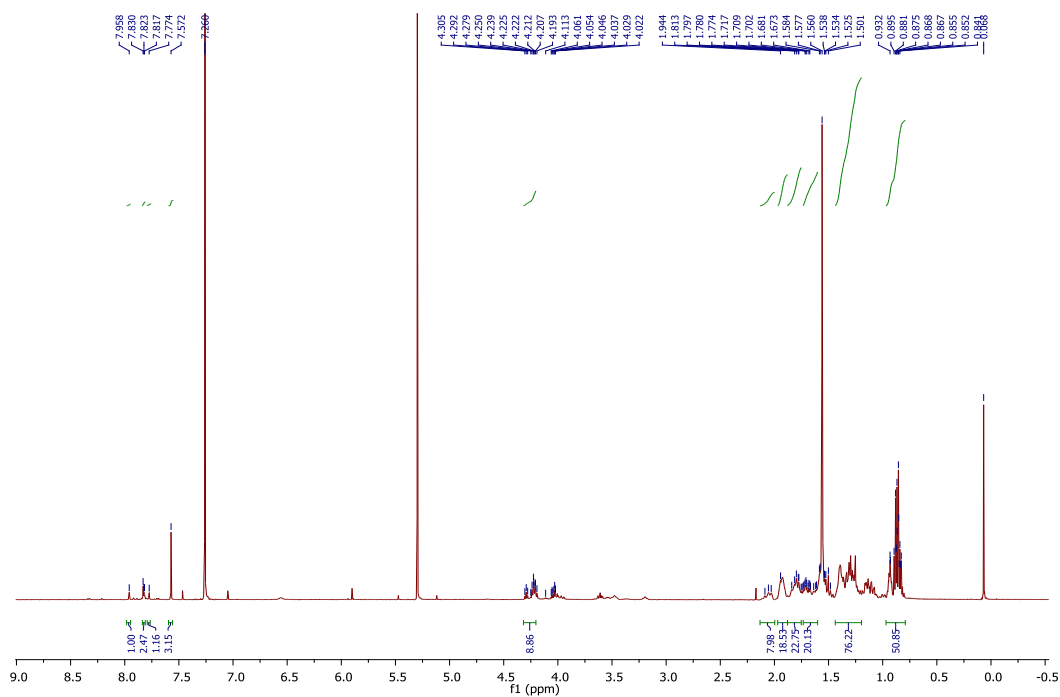
**Scheme 56:** Attempted synthesis of Terephthalate twin triphenylene **91** at room temperature.

In our early investigations of these esterification reactions, a number of problems were encountered. Specifically the reactions did not proceed at room temperature and we suspected the issue was the phthalic acids themselves. A control experiment was therefore performed. 3,6,7,10,11-Pentakis(hexyloxy)triphenylene-2-ol **25**, benzene-1,4-dicarboxylic acid **90**, (*N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP) were stirred in dry DCM at room temperature for 72 h. The reaction did not give the expected product **91**. Other reactions were performed as seen in entries 2-4 varying the amount of DCC and DMAP, however there was no difference in the yield of the product. More DCC and benzoic acid were added to the above mixture (Scheme **56**) and it was further stirred for 1 h. Work up and recrystallisation gave **94** as a colourless solid in 86% yield as seen in entry 4 Table 2.12

Entry	SM	Reagents			Cat.	Solv.	temp (0°C)	time	% yield <b>91</b>	% yield <b>94</b>	Ref
		Tere-phthal-ic acid (eq)	Ben-zoic acid	DCC (eq)							
1	1	0.4	_____	1	0.05	DCM	rt	72 h	0	-----	10, 28, 92
2	1	0.4	_____	2	0.10	DCM	rt	48 h	0	-----	10, 28, 92
3	1	0.4	_____	4	0.20	DCM	rt	48 h	0	-----	10, 28, 92
4	1	0.4	2	4	0.20	DCM	rt	1 h	-----	86%	----

**Table 2.12:** Control experiment for the terephthalate reaction.

The NMR spectrum Figure **2.38** clearly shows the starting material MHT **25** see Figure 2.13. No new product is observed. To confirm if it is the insolubility of the dibenzoic acid **90**, a compound with good solubility (benzoic acid **91**) was added and new product was formed.



**Figure 2.38.** NMR spectrum of the product before adding Benzoic acid (**Scheme 56**)

The MALDI-TOF MS:  $m/z$  calculated for  $C_{55}H_{77}O_7$  ( $M+H$ )<sup>+</sup> 849.57 found 849.36.

The NMR and MALDI-TOF MS of New product triphenylene benzoate **94** clearly confirms the formation of new product (Figure 2.39 and 2.40). Further analysis of **94** shows it is a liquid crystal (from 120 °C) with characteristic hexagonal columnar phase and it shows a transition at temperature 168°C into the isotropic liquid.



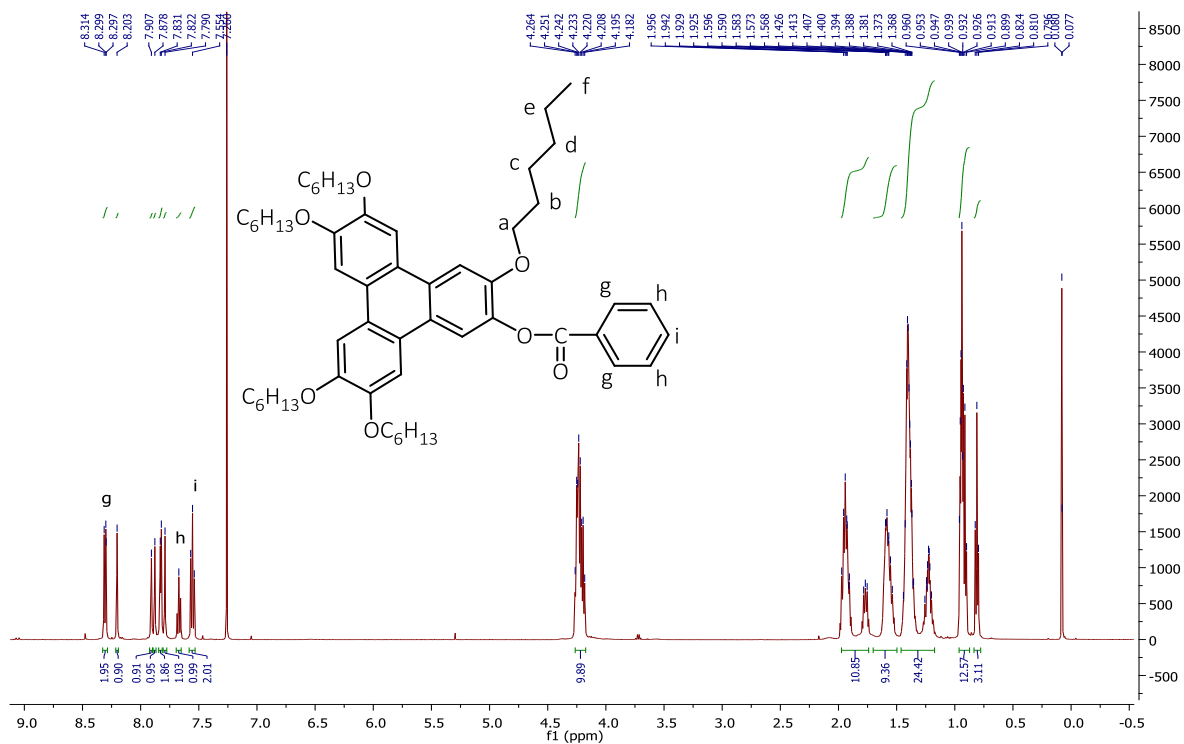


Figure 2.39: <sup>1</sup>H NMR of triphenylene benzoate **94** in CDCl<sub>3</sub>

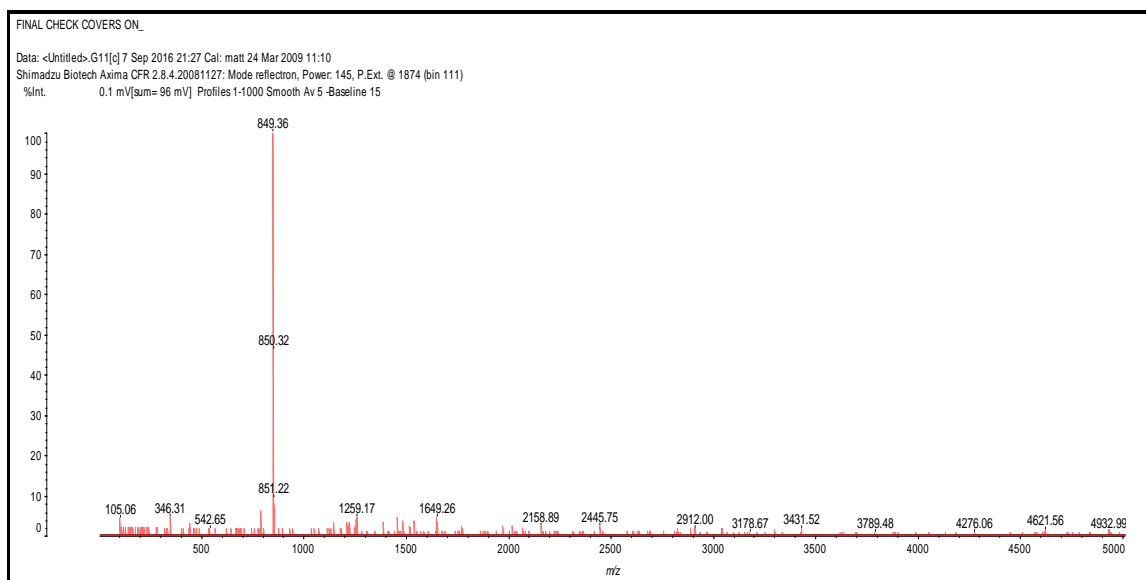


Figure 2.40. MALDI-TOF MS for triphenylene benzoate **94**.

### 2.13 Conclusion:

This research aimed at the synthesis of twinned triphenylenes with staggered bridges because the products may have unusual liquid crystal properties because the bridging mode gives a unique architecture. In the work, a new synthesis was optimised for important unsymmetrically substituted triphenylene intermediates. The synthesis of the staggered ferrocene-triphenylene twins was not successful owing to the inefficiency of the coupling steps.

The synthesis of the model Ferrocenyl-triphenylene **69** from the hexyloxytriphenylene **68** through direct linking with excess Ferroceneboronic acid was successful. The Ferrocenyl triphenylene **69** is a new compound, but it is not a liquid crystal. An attempt was made to synthesise the twin through a diacetylene precursor. The synthesis of the triphenylene diacetylene **71** was successful but the Ferrocenyl-acetylene triphenylene was not formed in the subsequent cross-coupling reaction, instead acetylene dimer was formed (Scheme **40**).

Another route was devised to give different twins from mono-hydroxy-triphenylene (MHT) **25**. The synthesis of the MHT and the monoacetylene triphenylene derivative was successful but to synthesise the model monoferrocenyl triphenylene and the twin compound was not successful, instead dimer was formed (Scheme **44**). Another attempt was done using ferrocene acetylene but still the Ferrocenyl acetylene twin triphenylene did not form but 4% of the monoferrocenyl acetylene **78** was realised. There was high yield of the ferrocene dimer **82** obtained. The acetylene links do not seem to be suitable for the twin linking. Nevertheless, twinned Ferrocenyl ester **84** (Scheme **46**) and other benzoyl twin triphenylene esters Isophthalate ester **86**, Phthalate ester **89** and Terephthalate ester **91** were synthesised. Triphenylene benzoate **94** was synthesised in a model reaction at room temperature (Scheme **50**), and is a liquid crystal. Also, high yield of byproduct **87** and **92** was realised during the synthesis of **86** and **91** (Scheme **47** and **49**). Further analysis needs to be carried out to confirm the detailed liquid crystal properties for compound **84**, **86** and **91** because they appear promising.

## CHAPTER 3 EXPERIMENTAL

### 3.1 General methods and Instruments

Compounds synthesised were characterised by 500 MHz  $^1\text{H}$  NMR and 126 MHz for  $^{13}\text{C}$  on A Bruker Avance III 500 MHz spectrometer. The signals were reported in ppm with  $^1\text{H}$  signals referenced to the residual proton of deuterated chloroform ( $\text{CDCl}_3$ ) at 7.26 ppm;  $^{13}\text{C}$  signals were referenced to the solvent signal at 77.16 ppm.

High Resolution Mass Spectrometry (HRMS) analysis was carried out at the EPSRC National mass spectrometry service centre Swansea University. MALDI-mass spectrometry was performed by direct sample disposition on Shimadzu Axima-CFR Instrument.

UV-Vis spectra were recorded on Perkin-Elmer UV-VIS spectrometer LAMBDA XLS.

Infrared (IR) spectra were recorded on a Perkin-Elmer spectrum fourier transform Interferometer, FT-IR Spectrometer UATR two to check the IR machine name again. The prominent peaks on the IR spectrum are the only ones reported.

Thin layer Chromatography (TLC) was carried out on Merck Silica Gel 60  $\text{F}_{254}$  aluminium backed sheets, Compounds were observed under UV light at 254nm or 366nm.

Column chromatography was performed using Silica gel Davisil LC 60A 40-63 micron of 70-230 mesh (Grace GM BH& Co) at room temperature applying low air pressure.

Melting points were recorded using Reichert thermovar microscope with thermopar based temperature control and Kofler hot stage melting point apparatus with a digiton model 2751-K display.

Transition temperatures were observed by optical polarising microscope with TMS 92 thermal analyser and Linkham THM 600 cell.

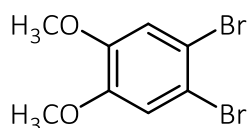
### 3.2 Reagents and solvents

All reagents and solvents used were obtained commercially and used without purification unless stated. Solvents used in most reactions were dry solvents, dried with their respective drying agents and distilled under nitrogen or argon gas. Dichloromethane (DCM) was dried in calcium hydride ( $\text{CaH}_2$ ), tetrahydrofuran (THF) with sodium and benzophenone, toluene with calcium chloride ( $\text{CaCl}_2$ ) and triethylamine (TEA) with calcium hydride. Petroleum ether used

was 40-60°C boiling point range. Diethylether, acetone, ethylacetate, hexane, ethanol, methanol used were not dry. Solvents used were all solvent grades. Water used was distilled and the drying agent used to dry organic layer after extraction is anhydrous Magnesium sulphate (MgSO<sub>4</sub>). Organic extracts were evaporated on a rotary evaporator.

### 3.3 Synthesis of Triphenylene core 2,7-dibromo-3,6,10,11-tetrakis(methoxy)triphenylene

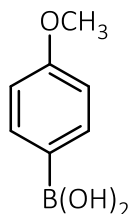
#### 3.3.1. Synthesis of 1,2-dibromo-4,5-dimethoxybenzene **56**<sup>72</sup>



According to the procedure of Fanta,<sup>58</sup> veratrole (30.0 g, 0.217 mol) was stirred in dichloromethane (70 ml) at 0°C. Bromine (76.3 g, 0.478 mol) was added dropwise while stirring for 2 h. The mixture was further allowed to stir 1 h at room temperature. The reaction mixture was washed with sodium thiosulphate brine and water. The aqueous layer was extracted with DCM (3x100 ml). The organic extract was dried with magnesium sulphate (MgSO<sub>4</sub>) and the solvent was evaporated. The residue was recrystallized from Isopropanol giving a needle-like colourless crystals **56** (58 g, 90%).

Mp 90°C (lit. 90-92°C)<sup>75</sup>; IR (thin film, cm<sup>-1</sup>) 3012, 2841, 2931, 1682, 1585, 1495; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS 500 MHz): δ 7.06(s, 2H) 3.85(s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz): δ 149.10, 116.0, 114.9, 56.4 ppm. MS (MALDI): *m/z* calculated for C<sub>8</sub>H<sub>9</sub>Br<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 295.89 found 295.10. The data is consistent with values in lit.<sup>75</sup>

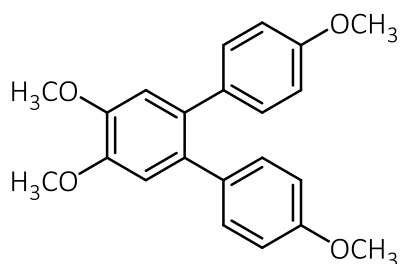
### 3.3.2. Synthesis of 4-methoxyphenylboronic acid **57**<sup>48</sup>



Magnesium turnings (1.92 g, 0.079 mol) and a few crystals of iodine were stirred and heated together under a stream of nitrogen for 10 minutes. Dry THF (100 ml) was added to the mixture, followed by 1,2-dibromoethane and the resulting mixture was stirred for 10 min. 4-bromoanisole (10.0 g, 0.054 mol) was then added to the mixture and it was refluxed. After 1 h the mixture was allowed to cool to room temperature. The cooled mixture was then added gently to trimethyl borate (11.1 g, 0.107 mol) in dry THF (100 ml) at  $-78^{\circ}\text{C}$ . The mixture was allowed to warm up overnight to room temperature. 2M HCl (100 ml) was added until the precipitate dissolved. The mixture was extracted with diethylether (3x100 ml) and the organic layer was dried with  $\text{MgSO}_4$ . The organic layer was evaporated and the solid was washed thoroughly with petroleum ether. The solid was recrystallized from hot water giving the product as colourless crystals **57** (5.6 g, 68%).

Mp (no melting point it degrades on heating): IR (thin film,  $\text{cm}^{-1}$ ) 3194, 2261, 1352, 1193, 882, 705,  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , TMS, 500 MHz);  $\delta$  7.64 (d,  $J = 8.5$  Hz, 2H), 6.89 (d,  $J = 8.5$  Hz, 2H), 4.86 (s, 2H), 3.79 (s, 3H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ , 126 MHz):  $\delta$  153.2, 136.8, 114.3, 99.6, 55.6 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_7\text{H}_9\text{BO}_3$  ( $\text{M}^+$ , 100%): 152.06 found 152.10. The data is consistent with values in lit.<sup>48</sup>

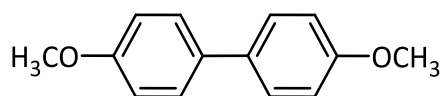
### 3.3.3. Synthesis of 4,4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl **58**<sup>67</sup>



According to the procedure used by Cammidge and Gopee.<sup>18</sup> 1,2-Dibromo-4,5-dimethoxybenzene **56** (2.47 g, 8.330 mmol), 4-methoxyphenylboronic acid **57** (18.7 g, 90.9 mmol), palladium (II)chloride (0.10 g, 0.533 mmol), triphenylphosphine (0.28 g, 1.052 mmol) and sodium carbonate (3.60 g, 0.031 mmol) were stirred in a mixture of toluene, ethanol and water (3:3:1). The resulting mixture was then refluxed under nitrogen and monitored with TLC until completion for 192 h. 2M HCl and water (200 ml) was added then extracted with DCM (3x150 ml). The organic layer was evaporated and the brown oily compound obtained was slowly recrystallized in dichloromethane and ethanol (1:1). It was further purified by column chromatography eluting with DCM and petroleum ether (7:3) giving the product as colourless solid **58** (2.2 g, 75%).

Mp 146<sup>0</sup>C; (lit. 144 °C)<sup>67</sup> IR (thin film, cm<sup>-1</sup>), 3059, 3001, 2886, 2838, 1607, 1496, 1233; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.05 (d, *J* = 8.5 Hz, 4H), 6.89 (s, 2H), 6.77 (d, *J* = 8.5 Hz, 4H), 3.92 (s, 6H), 3.77 (s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz): δ 158.2, 148.1, 134.2, 132.7, 131.1, 113.8, 113.5, 56.2, 55.3 ppm. MS (MALDI): *m/z* 350.4 (M<sup>+</sup>, 100%). HRMS, (ESI) [C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>] [M+H]<sup>+</sup>: Calculated: 349.1434; Found: 349.1431. The data are consistent with the values in lit<sup>67</sup>.

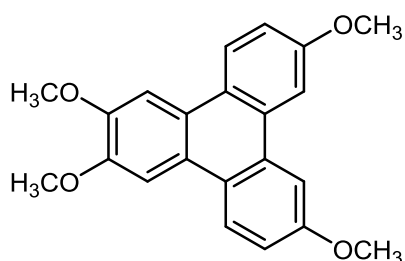
### 3.3.3.1 Dimethoxybiphenyl (terphenyl byproduct) **59**<sup>72</sup>



The organic layer of **58** was evaporated and the brown oily compound obtained was slowly recrystallized in dichloromethane and ethanol (1:1). It was further purified by column chromatography eluting with DCM and petroleum ether (7:3) giving the product **58** as colourless solid (2.2 g, 75%) and by product **59** of 20% yield.

IR (thin film,  $\text{cm}^{-1}$ ) 3039, 2884, 2838, 1603, 1492, 1274, 1241.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz): 7.46-7.50 (m, 4H), 6.94-6.98 (m, 4H), 3.85 (s, 6H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 126 MHz): 158.6, 133.4, 127.6, 114.1, 155.2 ppm.

### 3.3.4. Synthesis of 2, 3, 7, 10-tetramethoxytriphenylene **60**<sup>67</sup>

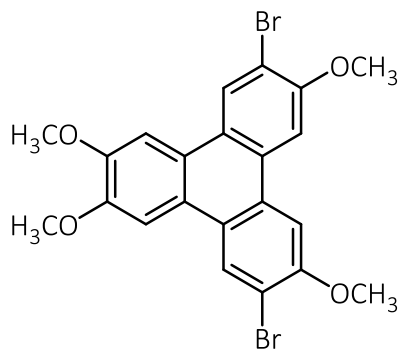


Cyclisation of compound **58** was achieved using Artal *et al.* procedure.<sup>68</sup> Tetramethoxyterphenyl **58** (1.92 g, 0.006 mol) was stirred in dichloromethane (70 ml) and nitromethane (4 ml) at room temperature. Iron(III) chloride (2.72 g, 0.016 mol) was added in portions over 2 h and was further stirred for 2 h, cold methanol was then added slowly and stirring the mixture, the mixture was washed several times with water and the aqueous layer was further extracted with DCM (3x150 ml). The organic layer was dried in  $\text{MgSO}_4$  and was evaporated. The solid

obtained was slowly recrystallized from dichloromethane and methanol (2:1), without column chromatography and a colourless solid **60** was obtained (0.99 g, 52%).

Mp 170°C (lit.175°C)<sup>67</sup>; IR (thin film, cm<sup>-1</sup>) 2884, 2830, 1739, 1593, 1417, 1202; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 8.42 (d, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 2.5 Hz, 2H), 7.89 (s, 2H), 7.30 (dd, *J*=9.0 Hz, 2.5, 2H), 4.11 (s, 6H), 4.03 (s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 158.2, 148.9, 130.3, 125.9, 124.6, 124.2, 123.3, 106.2, 104.3, 56.1, 55.7 ppm. MS (MALDI): *m/z* calculated for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> (M<sup>+</sup>, 100%): 348.14 found 348.10. The data are consistent with the values in lit<sup>67</sup>

### 3.3.5. Synthesis of 2,7-dibromo-3,6,10,11-tetramethoxytriphenylene **61**<sup>67</sup>



According to the procedure of Cammidge and Gopee<sup>48</sup> 2,3,7,10-tetramethoxytriphenylene **60** (0.50 g, 1.44 mmol) was stirred in dichloromethane (20 ml) and cooled at 0°C. Bromine (0.507 g, 3.17 mmol) was added dropwise and the mixture was stirred. The reaction was monitored by TLC to completion. The mixture was washed with sodium metabisulfite (20%) and was extracted with dichloromethane (3x150 ml). The organic layer was dried with MgSO<sub>4</sub> and solvent was evaporated. The crude product was purified by column chromatography eluting with dichloromethane and petroleum ether (7:3) and the solid obtained was recrystallized from dichloromethane and isopropanol (1:1) to give pure product **61** as a colourless solid (0.44 g, 61%).

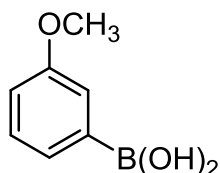
IR (thin film, cm<sup>-1</sup>) 2995, 2884, 1587, 1458, 1408, 1241, 1206; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 8.61 (s, 2H), 7.85 (s, 2H), 7.75 (s, 2H), 4.15 (s, 6H), 4.13 (s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 154.1, 149.3, 128.7, 128.0, 122.1, 113.2, 104.5, 103.8, 56.5, 56.2 ppm. MS (MALDI): *m/z*



calculated for  $C_{22}H_{18}Br_2O_4$  ( $M^+$ , 100%): 505.96 found 505.96. The data are consistent with the values in lit<sup>73</sup>

### 3.4 Synthesis of triphenylene core 2,11-dibromo-3,6,7,10-tetramethoxytriphenylene.

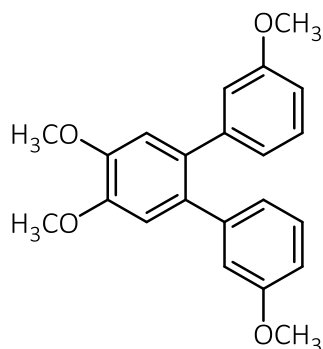
#### 3.4.1. Synthesis of 3-methoxyphenylboronic acid **62**<sup>94</sup>



Magnesium turnings (5.85 g, 0.241 mol) and a few crystals of iodine were stirred and heated together under a stream of nitrogen for 10 mins. Dry THF (150 ml) was added to the mixture, followed by 1,2-dibromoethane and the mixture was stirred for 10 mins. 3-Bromoanisole (30.0 g, 0.160 mol) was then added to the mixture which was refluxed for 1 hour and allowed to cool. The cold mixture was then added slowly to trimethyl borate (33.3 g, 0.321 mol) in cold dry THF (200 ml). The mixture was allowed to warm overnight to room temperature. 2M HCl (150 ml) was added until the precipitate dissolved, the mixture was extracted with diethylether (3x100 ml) and the organic layer was dried with  $MgSO_4$ . The organic layer was evaporated and the solid was washed thoroughly with petroleum ether. The solid was recrystallized from hot water giving the product **62** as colourless crystals (18.4 g, 75%).

Mp (no melting point it degrades on heating); IR (thin film,  $cm^{-1}$ ) 3194, 2261, 1352, 1193, 882, 705;  $^1H$ -NMR (500 MHz, TMS,  $CD_3OD$ )  $\delta$  7.27 (t,  $J = 7.5$  Hz, 1H), 7.15 (d,  $J = 7.5$  Hz, 1H), 7.11 (d,  $J = 2.5$ , 1H), 6.94 (dd,  $J = 7.5, 2.5$  Hz, 1H), 3.78 (s, 3H) ppm;  $^{13}C$ -NMR ( $CD_3OD$ , 126 MHz) 160.5, 129.7, 127.3, 119.7, 117.2, 55.5 ppm. MS (MALDI):  $m/z$  calculated for  $C_7H_9BO_3$  ( $M^+$ , 100%): 151.07 found 151.90. The data are consistent with values in lit.<sup>94</sup>

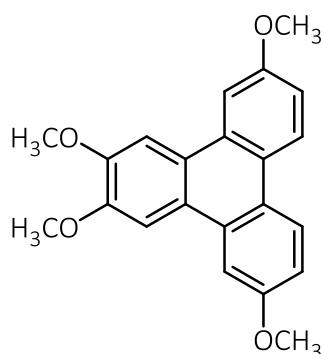
### 3.4.2. Synthesis of 3,3'',4',5'-tetramethoxy-1,1':2',1''-terphenyl **63**



1,2-Dibromo-4,5-dimethoxybenzene **56** (0.500 g, 1.69 mmol), 3-methoxyphenylboronic acid **62** (1.28 g, 8.45 mmol), triphenylphosphine (0.160 g, 0.608 mmol) and potassium carbonate (1.17 g, 8.45 mmol) were stirred in toluene then bis(triphenylphosphine)palladium(II) chloride (0.0827 g, 0.101 mmol) was added to the mixture and refluxed under nitrogen atmosphere. The reaction was monitored by TLC and NMR. The reaction was completed after 24 h and water was added and was extracted with DCM (3x100 ml). The organic layer was dried with MgSO<sub>4</sub> and evaporated. The solid was recrystallized in DCM and ethanol (6:4), giving the product **63** as a light brown solid (0.55 g, 92%).

Mp 133°C; IR (thin film, cm<sup>-1</sup>) 3002, 2952, 2842, 2157, 1575, 1519, 1485; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 500MHz): δ 7.14 (t, *J* = 8.0 Hz, 2H), 6.95 (s, 2H), 6.77 (dd, *J* = 8.0, 2.5 Hz, 2H), 6.74 (dd, *J* = 8.0, 2.5 Hz, 2H), 94 (s, 6H), 3.63 (s, 6H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 159.5, 148.6, 143.2, 133.3, 129.3, 122.7, 115.8, 113.9, 112.7, 56.5, 55.5 ppm. MS (MALDI): *m/z* calculated for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub> (M<sup>+</sup>, 100%): 350.15 found 350.20.

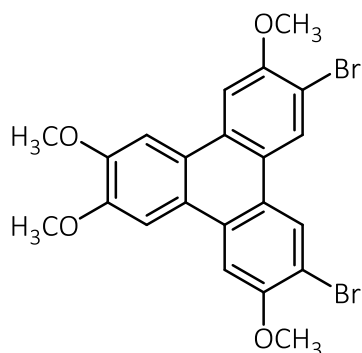
### 3.4.3. Synthesis of tetramethoxytriphenylene **64**



Terphenyl **63** (4.00 g, 11.4 mmol) was stirred in dichloromethane (70 ml) and nitromethane (2 ml) at room temperature. Iron(III) chloride (7.55 g, 45.7 mmol) was added slowly over 2 h and further stirred for 2 h. The reaction was monitored with TLC until completion. Solids in the Mixture were filtered off and washed several times with methanol and dried under vacuo. Resulting solid **64** was colourless (3.87 g, 98%).

Mp 206°C; IR (thin film,  $\text{cm}^{-1}$ ) 2832, 2157, 1609, 1545, 1518, 1498, 1241, 1203;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS, 500MHz)  $\delta$  8.48 (d,  $J = 9.0$  Hz, 2H), 7.88(s, 2H), 7.87 (d,  $J = 2.5$  Hz, 2H), 7.23 (dd,  $J = 9.0, 2.5$  Hz, 2H), 4.12 (s, 6H), 4.02 (s, 6H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 126 MHz) 158.5, 149.8, 130.3, 129.0, 124.9, 121.2, 114.6, 106.5, 105.1, 56.4, 56.1 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{22}\text{H}_{20}\text{O}_4$  ( $\text{M}^+$ , 100%): 348.14 found 348.20.

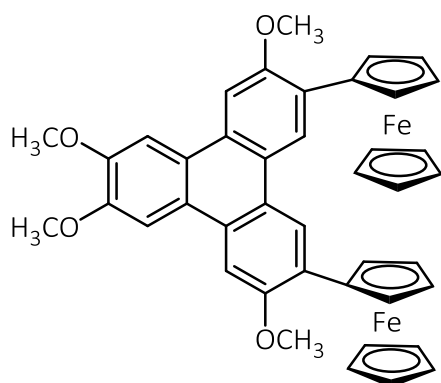
### 3. 4. 4. Synthesis of 3,6-dibromo-2,7,10,11-tetramethoxytriphenylene **65**



Tetramethoxytriphenylene **64** (0.504 g, 1.44 mmol) was stirred in dichloromethane (30 ml) and cooled at 0°C. Bromine (0.505 g, 3.17 mmol) was added drop wise and stirred 2 h. The mixture was washed with sodium metabisulfite (20%). The resulting compound was seen as precipitate and was filtered and washed several times with ethanol and dried. Resulting compound **65** was off white solid (0.69 g, 93%).

Mp >300°C (decomp); IR (thin film, cm<sup>-1</sup>) 2935, 2834, 1740, 1602, 1537, 1507, 1489, 1472, 1263, 1258, 1202; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 500 MHz) δ 8.61 (s, 2H), 7.85 (s, 2H), 7.75 (s, 2H), 4.15 (s, 6H), 4.13 (s, 6H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 154.0, 150.0, 129.2, 127.6, 124.0, 123.1, 112.6, 107.3, 105.4, 56.1, 55.1 ppm: MS (MALDI): *m/z* calculated For C<sub>22</sub>H<sub>19</sub>Br<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup>: HRMS 506.9615 found: 506.9626 (Isotope pattern Figure 2.8).

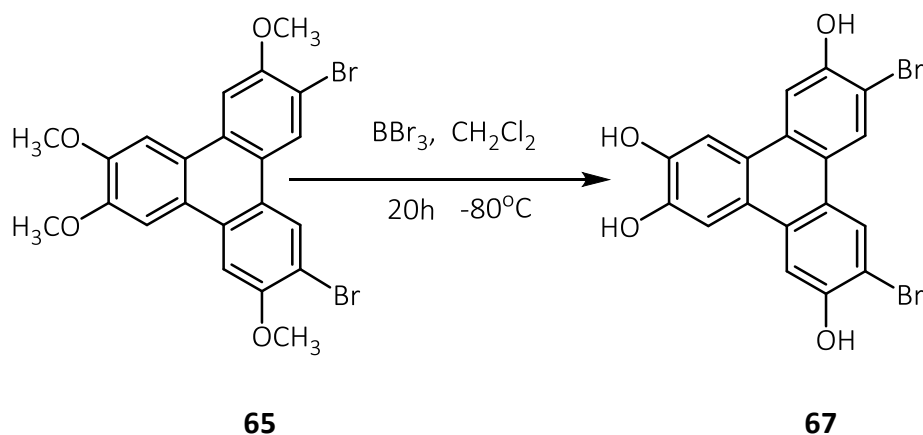
### 3.4.5 Attempted Synthesis of 3,6-Diferrocenyl-2,7,10,11-tetramethoxy triphenylene **66**



3,6-Dibromo-2,7,10,11-tetramethoxytriphenylene **65** (0.27 g, 0.530 mmol), ferrocene monoboronic (0.61 g, 2.65 mmol), 12% mol triphenylphosphine (0.050 g, 0.191 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.37 g, 2.65 mmol) stirred in degassed toluene for 20 minutes then 3% mol bis(triphenylphosphine)palladium(II)dichloride (0.022 g, 0.0318 mmol) was added. The reaction was allowed to reflux under N<sub>2</sub> atmosphere for 72 h. After work up, TLC and NMR analysis showed no evidence for formation of the desired product **66** the compound is not in the solution for reaction to occur because it was noted that the starting materials did not dissolve in the toluene solvent. However, other solvents were also tried but no evidence for the formation of the product.

### 3.6 Conversion of 3,6-Dibromo-2,7,10,11-tetramethoxy-triphenylene **65** into 3,6-Dibromo-2,7,10,11-hexyloxytriphenylene

#### 3.6.1. Demethylation of 3,6-dibromo-2,7,10,11-tetramethoxytriphenylene **65**

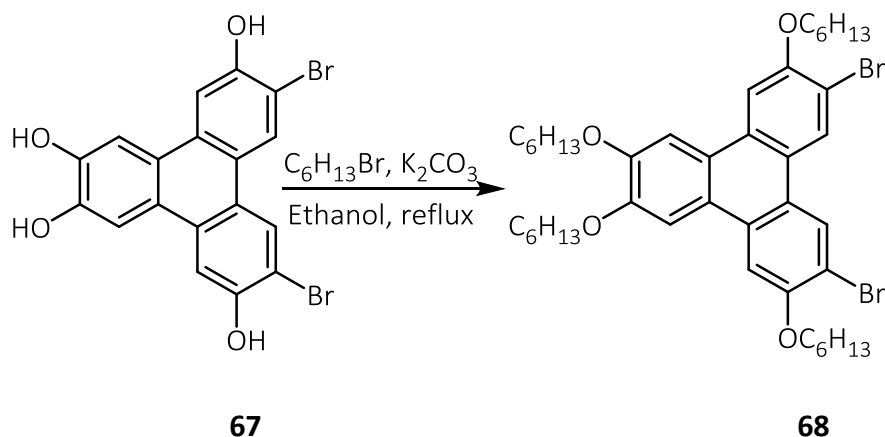


3,6-Dibromo-2,7,10,11-tetramethoxytriphenylene **65** (4.00 g, 7.94 mmol) was stirred in dichloromethane (30 ml) at  $-80^{\circ}\text{C}$  and borontribromide (11.9 g, 0.05 mmol) was added to the mixture slowly. Reaction was allowed to stir and warmed up overnight to room temperature. Reaction was stopped after 20 h and placed in ice, ethanol was added to mixture dropwise and then evaporated to dryness in vacuo. The titled compound **67** (white solid) 3.42 g, 96%, was used without further purification.

Mp (No melting point it degrades) IR (thin film,  $\text{cm}^{-1}$ ) 3368, 1610, 1420;  $^1\text{H-NMR}$  (500 MHz, TMS,  $\text{d}_6$ -acetone)  $\delta$  8.70 (s, 2H), 8.16 (s, 2H), 8.02 (s, 2H) ppm;  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 126 MHz) 153.5, 147.5, 130.7, 128.2, 124.0, 123.4, 110.8, 109.5, 109.4 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{18}\text{H}_{10}\text{Br}_2\text{O}_4$  ( $\text{M}^+$ , 100%) 449.90 found 449.90.

### 3.6.2. Alkylation 3,6-Dibromo-2,7,10,11-tetrahexyloxytetraol triphenylene **67**

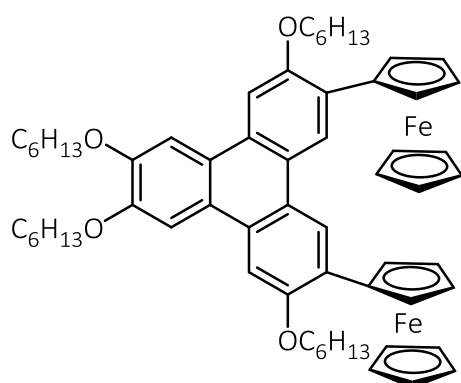
#### 3.6.2.1. Synthesis of 3,6-Dibromo-2,7,10,11-tetrahexyloxytriphenylene **68**



3,6-Dibromo-2,7,10,11-tetrahexyloxytetraol triphenylene **67** (2.23 g, 5.00 mmol) was stirred in degassed ethanol (30 ml), bromohexane (4.95 g, 0.03 mol) and  $K_2CO_3$  (4.15 g, 0.03 mol). Mixture was refluxed under nitrogen atmosphere for 24 h. Filtered and solvent evaporated. Dilute  $H_2SO_4$  was added to neutralise the remaining  $K_2CO_3$ . Mixture was extracted with dichloromethane (3x100 ml). The organic layer was dried with  $MgSO_4$  and evaporated. The solid obtained was recrystallized in dichloromethane: ethanol (2:1) to give the title compound **68** as a colourless solid (3.70 g, 94%).

IR (thin film,  $cm^{-1}$ ) 2925, 2857, 1598, 1468, 1423, 1387, 1248, 1177.  $^1H$ -NMR ( $CDCl_3$ , TMS, 500 MHz)  $\delta$  8.33 (s, 2H), 7.75 (s, 2H), 7.59 (s, 2H), 4.25 (t,  $J = 6.7$  Hz, 8H), 4.20 (t,  $J = 6.7$ , 8H), 1.90-2.00 (m, 8H), 1.56-1.66 (m, 16H), 1.35-1.47(m, 8H), 0.94 (t,  $J = 6.7$  Hz, 12H) ppm;  $^{13}C$ -NMR ( $CDCl_3$ , 126 MHz) 154.0, 150.1, 129.2, 127.6, 124.0, 123.1, 112.6, 107.3, 105.4, 69.7, 69.5, 31.9, 29.5, 26.0, 22.8, 14.2 ppm. MS (MALDI):  $m/z$  calculated for  $C_{42}H_{58}Br_2O_4$  ( $M^+$ , 100%): 786.73 found 786.40. The data are consistent with values in lit<sup>48</sup>

### 3.7 Synthesis of Ferrocenyl triphenylene **69**



**69**

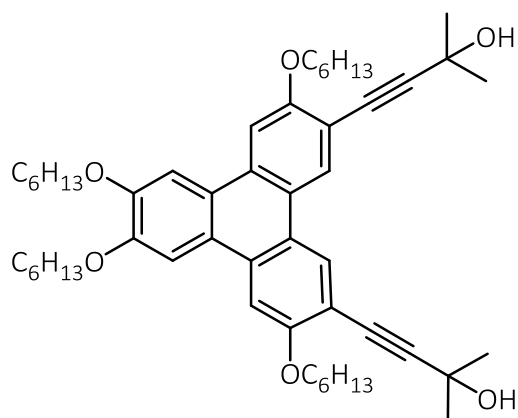
3,6-Dibromo-2,7,10,11-tetrahexyloxytriphenylene **68** (0.500 g, 0.64 mmol), ferrocene monoboronic acid (1.17 g, 5.10 mmol), 12% mol triphenylphosphine (0.120 g, 0.46 mmol) and  $K_2CO_3$  (0.71 g, 5.10 mmol) were stirred in degassed toluene for 20 mins. Bis (triphenylphosphine)palladium(II) chloride (0.054 g, 0.076 mmol) 3% was added and the reaction was allowed to reflux under  $N_2$  atmosphere for 1 hour. Reaction was stopped, washed with sodium hydroxide and the mixture extracted with dichloromethane (3x100ml). The organic layer was dried with  $MgSO_4$  and then evaporated. The resulting Solid was recrystallised from DCM: ethanol (2: 3) to give orange product **69** (0.40 g, 56%).

Mp 202°C; IR (thin film,  $cm^{-1}$ ) 3089, 2938, 2884, 2930, 2857, 1725, 1425, 1260, 1173;  $^1H$ -NMR ( $CDCl_3$ , TMS, 500 MHz)  $\delta$  8.75 (s, 2H), 7.92 (s, 2H), 7.79 (s, 2H), 5.00-5.04 (m, 4H), 4.38-4.42 (m, 4H), 4.28(t,  $J=7.0$  Hz, 4H), 4.30 (t,  $J=7.0$  Hz, 4H), 2.05 (q,  $J=7.0$  Hz, 4H), 1.97(q,  $J=7.0$  Hz, 4H), 1.67(q,  $J=7.0$  Hz, 4H), 1.61(q,  $J=7.0$  Hz, 4H), 1.35-1.52(m, 16H), 0.98(t,  $J=7.0$  Hz, 6H), 0.95(t,  $J=7.0$  Hz, 6H) ppm;  $^{13}C$ -NMR ( $CDCl_3$ , 126 MHz)  $\delta$  155.7, 149.9, 128.4, 127.8, 123.8, 123.2, 108.1, 104.6, 83.6, 77.2, 70.2, 70.0, 69.4, 69.0, 68.9, 32.1, 29.9, 26.3, 23.1, 14.5 ppm. HRMS:  $m/z$  calculated For  $C_{62}H_{77}Fe_2O_4$  ( $M+H$ ) $^+$ : 997.4519 found: 997.4516 (Isotope pattern Figure 2.11)



### 3.8 Attempted Synthesis of Ferrocenyl triphenylene from diacetylene triphenylene

#### 3.8.1 Synthesis of 4,4'-(2,7,10,11-tetrakis(hexyloxy)triphenylene-3,6-diylbis(2-methylbut-3-yn-2-ol) **70**<sup>48</sup>



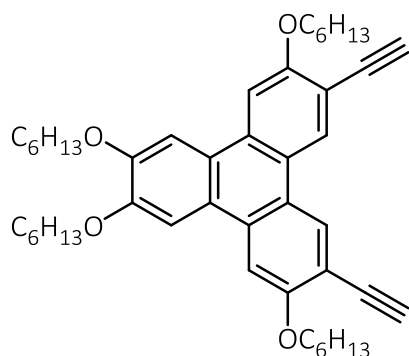
**70**

3,6-Dibromo-2,7,10,11-tetrahexyloxy triphenylene **68** (0.900 g, 1.15 mmol) was stirred in dry toluene with copper(I) iodide (0.284 g, 0.15 mmol) and triphenylphosphine (0.072 g, 0.28 mmol) was added. The mixture was stirred in dry triethylamine (30 ml) under nitrogen atmosphere for 10 mins, then bis(triphenylphosphine)palladium(II) chloride (0.05 g, 0.69 mmol) was added and refluxed for 15 mins. Heat was then removed from the reaction and 2-methyl-but-3-yn-2-ol (0.482 g, 5.74 mmol) was added dropwise using dropping funnel. Mixture was then returned on heat and left to reflux under nitrogen atmosphere for 48 h. Reaction was stopped and mixture was cooled to room temperature. Water was added and extracted with dichloromethane, the organic layer was dried with magnesium sulphate and evaporated under vacuo. The brown solid obtained was recrystallized from DCM: Petroleum ether (2:1), giving a yellow solid **70** (0.56 g, 93%).

Cryst 189, Col<sub>h</sub> 90 Iso (°C); IR (thin film, cm<sup>-1</sup>) 3367, 2980, 2931, 2903, 2846, 2227, 1610, 1499, 1431; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, 500 MHz) δ 8.43 (s, 2H), 7.73 (s, 2H), 7.60 (s, 2H), 4.16 (m, 8H), 2.25 (s, 2H), 1.91-1.96 (m, 8H), 1.71 (s, 12H) 1.58-1.66 (m, 8H), 1.34-1.45 (m, 16H), 0.92-0.96

(m, 12H) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  158.0, 150.1, 130.0, 128.7, 124.8, 122.6, 112.7, 107.7, 104.5, 98.8, 76.9, 69.8, 69.1, 31.8, 31.6, 29.5, 26.0, 25.8, 22.8, 14.2 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{52}\text{H}_{72}\text{O}_6$  ( $\text{M}^+$ , 100%): 793.14 found 792.50. The data is consistent with the literature values.<sup>48</sup>

### 3. 8. 2 Synthesis of 3,6-diethynyl-2,7,10,11-tetrakis (hexyloxy) triphenylene **71**<sup>48</sup>

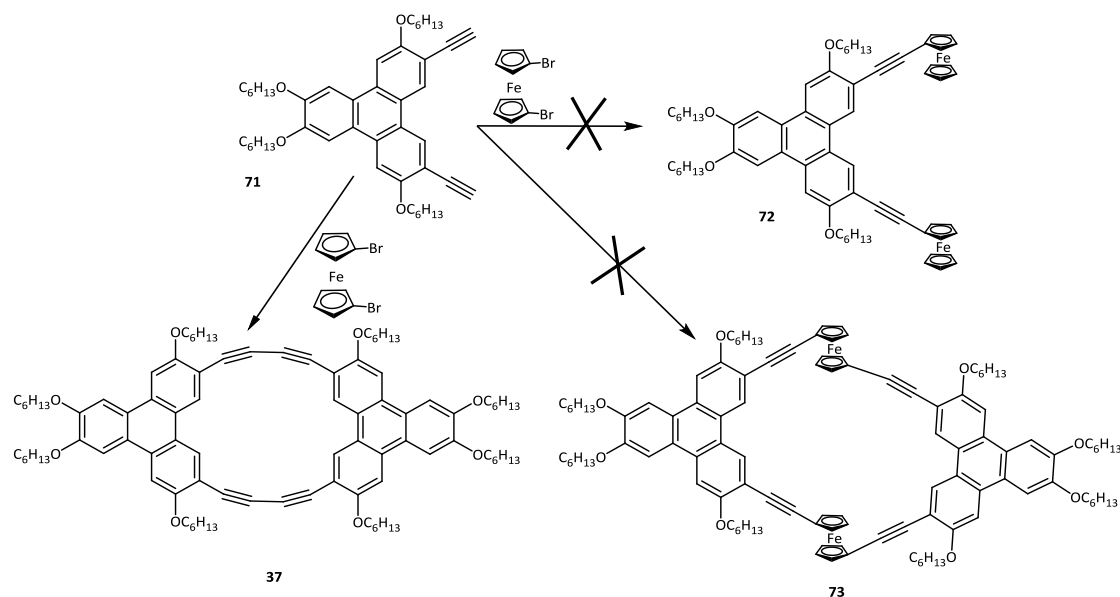


**71**

4,4'-(2,7,10,11-Tetrakis (hexyloxy) triphenylene-3,6-diylbis(2-methylbut-3-yn-2-ol) **70** (1.00 g, 1.26 mmol) was stirred in dry toluene under nitrogen atmosphere. Sodium hydride (60% dispersion in oil) (0.234 g, 6.31 mmol) was added in portions and the mixture was heated at reflux for 2 h. The mixture was poured into ice-cold distilled water and the organic layer was extracted with dichloromethane (3x50 ml), dried with  $\text{MgSO}_4$  and evaporated in vacuo leaving a dark brown oily substance, which was recrystallised in DCM and ethanol. The resulting solid **71** was pale orange colour (0.82 g, 92%).

Mp 140°C, lit 140°C<sup>52</sup>; IR (thin film,  $\text{cm}^{-1}$ ) 3315, 3291, 2877, 2106, 1608, 1539, 1499, 1431;  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s, 2H), 7.80 (s, 2H), 7.68 (s, 2H), 4.25 (m, 8H), 3.37 (s, 2H), 1.91-2.01 (m, 8H), 1.55-1.64 (m, 16H), 1.35-1.46 (m, 16H), 0.92-0.97 (m, 12H) ppm.  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 150.4, 130.7, 129.7, 124.9, 122.9, 112.1, 107.9, 104.9, 81.8, 80.8, 69.6, 69.2, 32.1, 31.9, 29.8, 29.6, 26.2, 25.9, 23.0, 22.8, 14.4 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{46}\text{H}_{60}\text{O}_4$  ( $\text{M}^+$ , 100%): 676.98 found 676.50. The data is consistent with the literature values.<sup>48</sup>

### 3.8.3 Attempted Synthesis of 2,3,6,11-tetrakis (hexyloxy)-7,10 bis(ferrocenylethynyl)triphenylene **72**



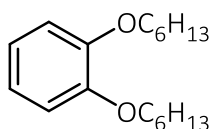
A mixture of 1,1'-dibromoferrocene (0.30 g, 0.89 mmol), copper (I) iodide (0.004 g, 0.021 mmol) and bis(triphenylphosphine)palladium(II)chloride (0.012 g, 0.014 mmol) stirred and refluxed in TEA (10 ml)/THF (5 ml) under nitrogen atmosphere for 15 mins. 3,6-Diethynyl-2,7,10,11-tetrakis(hexyloxy)triphenylene **71** (0.100 g,  $0.148 \times 10^{-4}$  mol) dissolved in THF (5 ml) and was added slowly with syringe pump 5ml/h to the mixture and allowed to reflux for 72 h. Reaction was stopped and organic layer extracted with dichloromethane (3x100 ml) dried with  $\text{MgSO}_4$  and evaporated in vacuo, resulting yellowish crude solid of was columned in DCM: PE (1: 9). Resulting solid **37** was obtained as pale yellow (0.030, 16%) instead of **72**.

Furthermore, a mixture of 1,1'-dibromoferrocene (0.10 g, 0.30 mmol), Copper (I) iodide (0.05 g, 0.27 mmol) and bis(triphenylphosphine)palladium(II)dichloride (0.06 g, 0.09 mmol) stirred and refluxed in TEA (20 ml)/ THF (10 ml) under nitrogen atmosphere for 20 mins. 3, 6-Diethynyl- 2, 7,10,11-tetrakis(hexyloxy)triphenylene **71** (0.600 g, 0.89 mol) dissolved in THF (30 ml) and was added slowly with syringe pump to the mixture and allowed to reflux for 48 h. Resulting solid **37** was obtained as yellow (0.045, 16%).

Mp 280°C (decomposed); IR (thin film,  $\text{cm}^{-1}$ ) 2948, 2922, 2853, 2184, 2125, 1416, 1387, 1369;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.32 (s, 4H), 7.81 (s, 4H), 7.67 (s, 4H), 4.28 (t,  $J=6.4$  Hz, 8H), 4.24 (t,  $J=6.4$  Hz, 8H), 1.99-1.89 (m, 16H), 1.60-1.56 (m, 16H), 1.45-1.40 (m, 32H), 0.99-0.93 (m, 24H) ppm; UV-Vis (DCM) max (log  $\epsilon$ ) 336 (4.71), 355 (4.55), 375 (4.77), 400 (4.29), 424(4.54); MS (MALDI):  $m/z$  calculated for  $\text{C}_{92}\text{H}_{116}\text{O}_8$  ( $\text{M}^+$  + 100%):1349.93 found 1349.86 The data is consistent with the literature values.<sup>48</sup>

### 3.9. Synthesis of monohydroxypenta(hexyloxy)triphenylene and derivatives

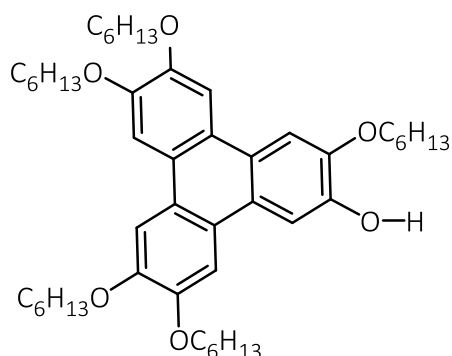
#### 3.9. 1. Synthesis of 1,2-dihexyloxybenzene **74**<sup>22</sup>



1,2-dihexyloxybenzene (DHB) **74** was synthesised according to conditions used by Cammidge group.<sup>22</sup> Pyrocatechol (20 g, 0.18 mol), 1-bromohexane (89.4 g, 0.54 mol) and potassium carbonate (74.6 g, 0.54 mol) were stirred in ethanol (300 ml) at 80°C for 2 days. The mixture was allowed to cool to room temperature, filtered, washed with distilled water and extracted with dichloromethane (3x50 ml). The organic layer was evaporated in vacuo giving orange oily compound, which was distilled. The pure product was collected at 185°C as a colourless oil (48.7 g, 97 %).

IR (thin film) 2931, 2860, 1591  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (s, 4H), 4.02 (t,  $J = 7.0$  Hz, 4H), 1.79-1.88 (m, 4H), 1.47-1.55 (m, 4H), 1.32-1.42 (m, 8H), 0.91-0.97 (m, 6H) ppm;  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 121.2, 114.2, 69.4, 31.7, 29.5, 26.0, 22.7, 14.2 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{18}\text{H}_{30}\text{O}_2$  ( $\text{M}^+$ , 100%): 278.22 found 278.44.

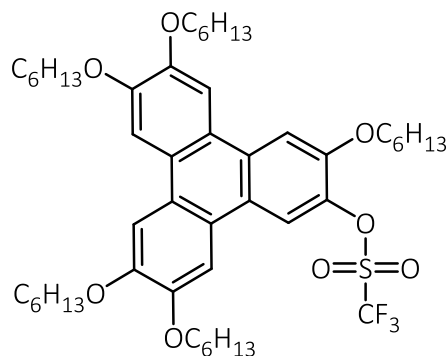
### 3.9.2. Synthesis of 3,6,7,10,11- pentakis(hexyloxy)triphenylen-2-ol **25**<sup>30</sup>



3,6,7,10,11- Pentakis(hexyloxy)triphenylen-2-ol **25** was synthesised by a two-step procedure used at Cammidge group.<sup>30</sup> 1,2-Dihexyloxybenzene **74** (10.0 g, 0.036 mol) was stirred in dry dichloromethane (200 ml) and nitromethane (1ml) added then stirred for 10 mins at 0°C. First portion of FeCl<sub>3</sub> (17.5 g, 0.108 mol) was added slowly and trifluoroacetic acid (TFA) (0.5 ml) was added to the mixture and stirred for further 45 minutes and the second portion of FeCl<sub>3</sub> was added. The mixture was stirred at 0°C for a further 45 minutes. Methanol (100 ml) and water (200ml) were added to stop the reaction, organic layer was extracted with DCM (3x50 ml), dried with MgSO<sub>4</sub> and evaporated in vacuo. The resulting solid was purified by column chromatography eluting with ethyl acetate and hexane (5: 95). To obtain the product as a grey solid **25** (8.90g, 67%).

Mp 70°C; IR (thin film, cm<sup>-1</sup>) 3555, 2924, 2856, 1618, 1514, 1437, 1257, 1168; <sup>1</sup>H- NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (s, 1H), 7.81 – 7.84 (m, 4H), 7.77 (s, 1H), 5.91 (s, 1H), 4.17 – 4.32 (m, 10H), 1.99 – 1.88 (m, 10H), 1.51 – 1.64 (m, 10H), 1.31-1.48(m, 20H), 0.98-0.88(m, 15H) ppm. <sup>13</sup>C- NMR (126 MHz, CDCl<sub>3</sub>) δ 149.0, 148.7, 145.7, 145.2, 123.8, 123.4, 107.6, 106.4, 104.3, 69.8, 69.5, 69.0, 31.7, 29.6, 29.4, 25.9, 22.5, 14.2 ppm. MS (MALDI): *m/z* Calculated for C<sub>48</sub>H<sub>72</sub>O<sub>6</sub> (M<sup>+</sup>, 100%): 744.53 found 744.46. The data are consistent with the literature values<sup>30</sup>

**3.9.3. Synthesis of 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl trifluoromethanesulfonate **75**<sup>30</sup>**



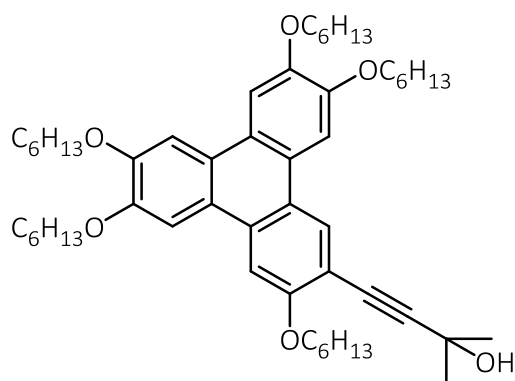
3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-ol **25** (1.50 g, 0.002 mol) and stirred in dry dichloromethane (50 ml) and was warmed for 10 mins, cooled and pyridine (0.79 g, 0.010 mol) was added at -20°C under nitrogen atmosphere. Trifluoromethanesulphonic acid anhydride (4.54 g, 0.016 mol) was added slowly to the mixture over 45 mins. The mixture was allowed to continue stirring and warmed at room temperature overnight. Dilute (2M) hydrochloric acid (100 ml) was added and the organic layer was extracted with dichloromethane (3x20 ml) and dried with magnesium sulphate and then evaporated in vacuo. Solid obtained was recrystallized in DCM: ethanol (2:1), resulting pure product **75** was a colourless solid (1.72 g, 98%).

Mp 172°C; IR (thin film, cm<sup>-1</sup>) 2962, 2876, 1618, 1518, 1436, 1398, 1206, 1102; <sup>1</sup>H- NMR (500 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 7.89 (s, 1H), 7.85 – 7.78 (m, 3H), 7.72 (s, 1H), 4.31 – 4.18 (m, 10H), 1.89 – 2.02 (m, 10H), 1.56 – 1.65 (m, 10H), 1.47 – 1.33 (m, 20H), 0.89-0.98 (m, 15H) ppm.

<sup>13</sup>C -NMR (126 MHz, CDCl<sub>3</sub>) δ 150.8, 149.9, 149.4, 138.7, 129.9, 125.6, 123.9, 123.3, 122.7, 117.1(q, J = 10), 108.5, 107.6, 107.1, 69.7, 31.9 29.7, 25.9, 22.9, 14.5 ppm. MS (MALDI): *m/z* calculated for C<sub>49</sub>H<sub>72</sub>F<sub>3</sub>O<sub>8</sub>S (M+H)<sup>+</sup>; 877.49; found 877.92. The data are consistent with the literature values of <sup>30</sup>

### 3.10. Synthesis of ferrocenyl triphenylene from triphenylene monoacetylene

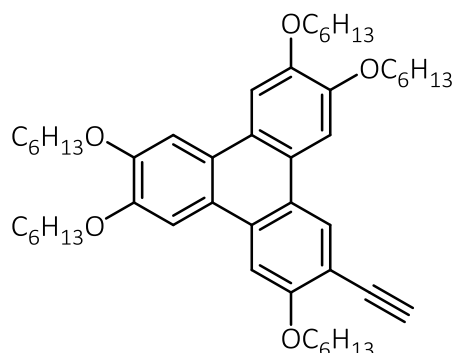
#### 3.10.1. Synthesis of 2-Methyl-4-(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)but-3-yn-2-ol **76**



A mixture of 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl trifluoromethanesulfonate **75** (0.400 g,  $4.56 \times 10^{-4}$  mol), bis(triphenylphosphine)palladium(II)chloride (0.016 g,  $2.28 \times 10^{-5}$  mol), pyrrolidine and triethylamine (TEA) (0.4 / 0.6) respectively was stirred for 10 mins under argon atmosphere. Triethylamine (4 ml) was added to 2-methyl-but-3-yn-2-ol (0.192 g,  $2.28 \times 10^{-3}$  mol), then dropped slowly by dropping pipette into the mixture. The reaction was allowed to reflux for 15 h, washed with water and extracted with dichloromethane (3x10 ml). The organic layer was dried with magnesium sulphate and evaporated in vacuo. Solid obtained was recrystallised in dichloromethane: ethanol. The resulting solid **76** obtained was pale yellow (0.32 g, 89%).

Mp 151°C; IR (thin film,  $\text{cm}^{-1}$ ) 3243, 2962, 2933, 2876, 28, 1618, 1518, 1436;  $^1\text{H}$ - NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (s, 1H), 7.88 (s, 1H), 7.86 (s, 1H), 7.81 (s, 1H), 7.75 (s, 1H), 4.20-4.27 (m, 10H), 1.89 – 2.00 (m, 10H), 1.72 (s, 6H), 1.52-1.67 (m, 10H), 1.34-1.48 (m, 20H), 0.92-0.96 (m, 15H) ppm.  $^{13}\text{C}$ - NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.9, 150.4, 130.6, 128.7, 125.6, 123.7, 123.2, 112.1, 108.3, 107.7, 106.7, 104.7, 98.2, 70.1, 69.6, 66.2, 32.0, 31.8, 29.7, 26.1, 22.9, 14.3 ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{53}\text{H}_{79}\text{O}_6$  ( $\text{M}+\text{H}$ ) $^+$ ; 811.59; found 811.20.

### 3.10. 2. Synthesis of Ethynyl-3,6,7,10,11-pentakis(hexyloxy)triphenylene **77**

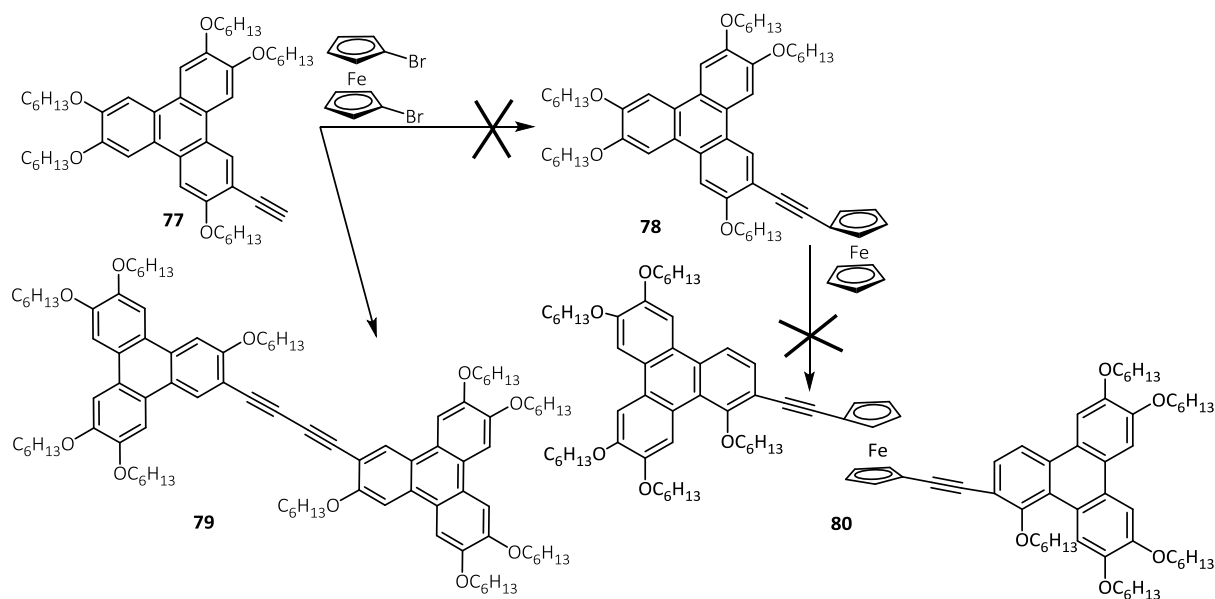


2-methyl-4-(3,6,7,10,11-pentakis(hexyloxy)triphenylene-2-yl)but-3-yn-2-ol **76** (0.140g,  $1.73 \times 10^{-4}$  mol) and sodium hydride (60% dispersion in oil) (0.025 g,  $1.04 \times 10^{-3}$  mol) were stirred in dry toluene for 2 h. Mixture was poured onto ice cold water and extracted with dichloromethane (3x20 ml), evaporated in vacuo. The resulting compound was yellow oil. Crystallization from cold ethanol gave pale yellow solid **77** (0.13 g, 97%).

Mp 150°C; IR (thin film,  $\text{cm}^{-1}$ ) 3316, 2951, 2922, 2850, 2105, 1612, 1512, 1479, 1433;  $^1\text{H}$ - NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (s, 1H), 7.88 (s, 1H), 7.82 (s, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 4.21 – 4.31 (m, 10H), 3.42 (s, 1H), 1.91-2.01 (m, 10H), 1.52 – 1.67 (m, 10H), 1.35 – 1.50 (m, 20H), 0.93-0.97(m, 15H) ppm.  $^{13}\text{C}$ - NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 148.8, 129.7, 124.8, 122.5, 112.1, 107.9, 104.9, 81.8, 80.8, 69.9, 69.7, 32.1, 31.3, 29.7, 29.6, 26.2, 23.0, 14.4ppm. MS (MALDI):  $m/z$  calculated for  $\text{C}_{50}\text{H}_{73}\text{O}_5$  ( $\text{M}+\text{H}$ ) $^+$ ; 753.55 found 753.12.



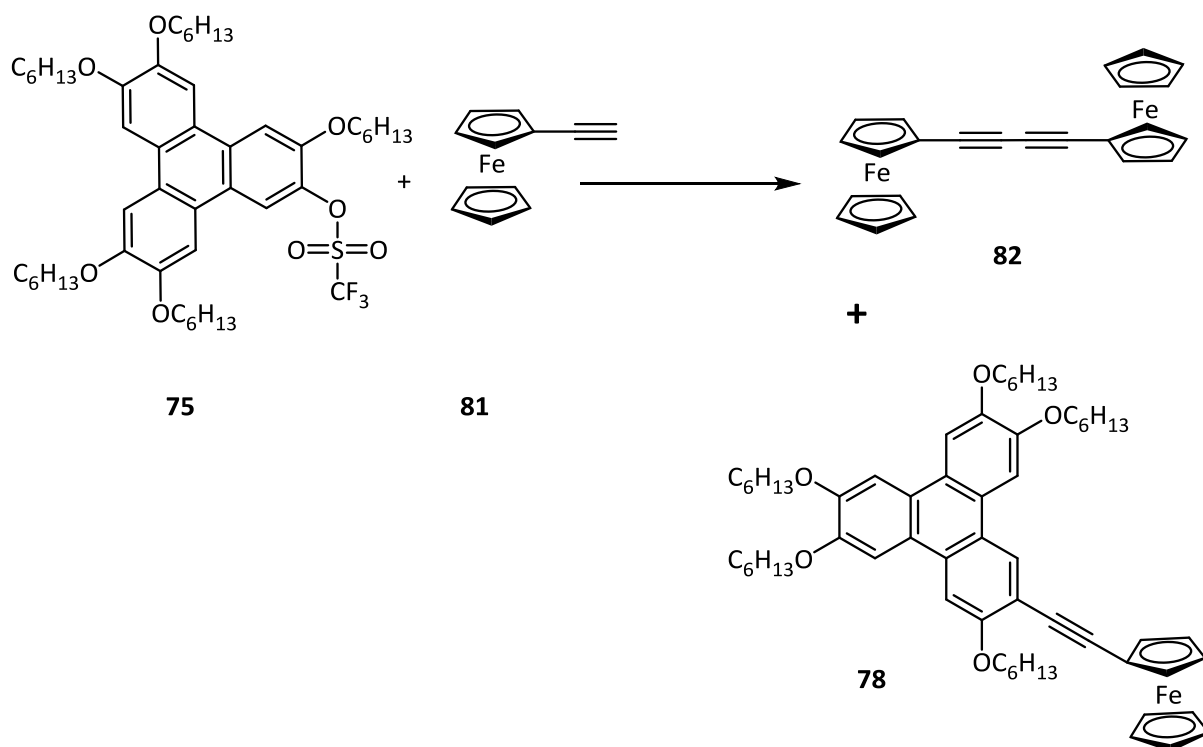
### 3.10.3. Attempted Synthesis of 2,3,6,7,10-pentakis(hexyloxy)-11-(ferrocenylethynyl)-triphenylene **80**.



1,1'-Dibromoferrocene (0.204 g,  $5.97 \times 10^{-4}$  mol) and bis(triphenylphosphine) palladium(II) chloride ( $0.007$  g,  $9.95 \times 10^{-6}$  mol) were stirred in a mixture of freshly distilled triethylamine (5 ml) and THF (3 ml) under nitrogen atmosphere at room temperature for 30 mins, Copper(I)iodide ( $0.005$  g,  $2.83 \times 10^{-5}$  mol) was then added. THF (2 ml) was also added to 2-ethynyl-3,6,7,10,11-pentakis(hexyloxy)triphenylene **77** ( $0.150$  g,  $1.99 \times 10^{-4}$  mol) which was then added slowly by syringe pump to the mixture, then heated at  $50^\circ\text{C}$  for 48 h. Organic layer was extracted with dichloromethane (3x 15 ml), evaporated to dryness in vacuo. The crude solid was columned with (ethylacetate/Hexane 1:9) isolating only **79** as yellow solid ( $0.076$ g, 47%). No yield for the desired Compound **80**.

Mp  $120^\circ\text{C}$ ; IR (thin film,  $\text{cm}^{-1}$ ) 2955, 2926, 2857, 1736, 1608, 1517, 1467, 1430, 1260.  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (s, 2H), 7.89 (s, 2H), 7.87 (s, 2H), 7.81 (s, 2H), 7.79 (s, 2H), 4.20-4.33 (m, 20H), 1.90-2.04 (m, 20H), 1.34-1.47 (m, 40H), 0.85-0.99 (m, 30) ppm. MS (MALDI):  $m/z$  1504.10 ( $\text{M}^+$ , 100) $^+$ ; HRMS; calculated For  $\text{C}_{100}\text{H}_{142}\text{O}_{10}$ : found 1504.23 (Isotope pattern Figure 2.19).

### 3.10. 4. Synthesis of 2,3,6,7,10-pentakis(hexyloxy)-11-(ferrocenylethynyl)triphenylene **78**.



Ethynylferrocene (0.144 g, 0.686 mmol), 3,6,7,10,11-pentakis(hexyloxy)triphenylene-2-yl trifluoromethanesulfonate **75** (0.318 g, 0.342 mmol), bis(triphenylphosphine)palladium(II) chloride (0.024g, 0.034 mmol) and copper (I) oxide (0.072 g, 0.376 mmol) were all mixed in a two necked flask with dry triethylamine (40 ml) and stirred under nitrogen atmosphere at 50°C after which dilute hydrochloric acid was added and the mixture was extracted with (3x20 ml), dried with MgSO<sub>4</sub> and evaporated to dryness in vacuo. Solid obtained was recrystallized in DCM/EtOH giving **78** as an orange solid (0.013g, 4%) and dimer **82**.

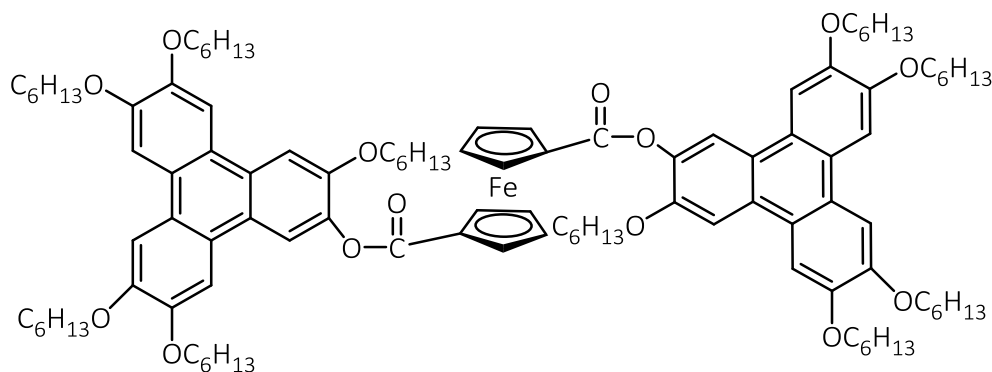
Mp 152°C; IR (thin film, cm<sup>-1</sup>) 2955, 2929, 2858, 1737, 1615, 1516, 1468, 1435, 1391, 1263.

MS (MALDI); *m/z* calculated for C<sub>60</sub>H<sub>81</sub>FeO<sub>5</sub> (M +H)<sup>+</sup> 937.57; found 937.57.

### 3.11 Synthesis of twin triphenylene ester

#### 3.11.1 Synthesis of ferrocenyl ester

##### 3.11.1.1. Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)ferrocenylate **84**



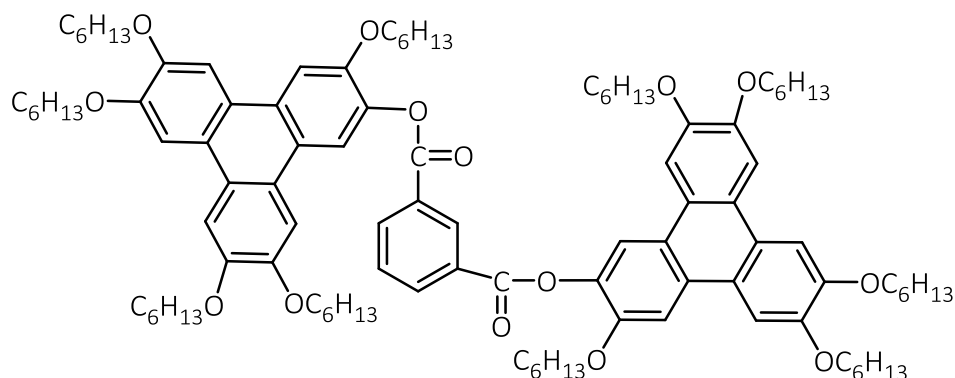
3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-ol **25** (0.500 g,  $6.71 \times 10^{-4}$  mol), 1, 1'-ferrocenedicarboxylic acid (0.075 g,  $2.68 \times 10^{-4}$  mol), *N,N'*-dicyclohexyl carbodiimide (DCC) (0.278 g,  $1.342 \times 10^{-3}$  mol), 4-(dimethylamino)pyridine (DMAP) (0.004 g,  $3.35 \times 10^{-5}$  mol) were stirred in dry DCM (50 ml) at 25°C for 48 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50ml), dried with MgSO<sub>4</sub> and evaporated to dryness in vacuo. The crude solid was purified by column chromatography eluting with ethylacetate/hexane (1: 20) and recrystallised in ethanol and DCM giving orange solid **84** (0.19 g, 41%).

Mp 125°C; IR (thin film, cm<sup>-1</sup>) 2929, 2856, 1727, 1705, 1616, 1514, 1453, 1431, 1259.

MS (MALDI): *m/z* calculated for C<sub>108</sub>H<sub>151</sub>FeO<sub>14</sub> (M+H)<sup>+</sup>; 1729.05; found 1729.05.

### 3.11.2 Synthesis of benzoyl ester

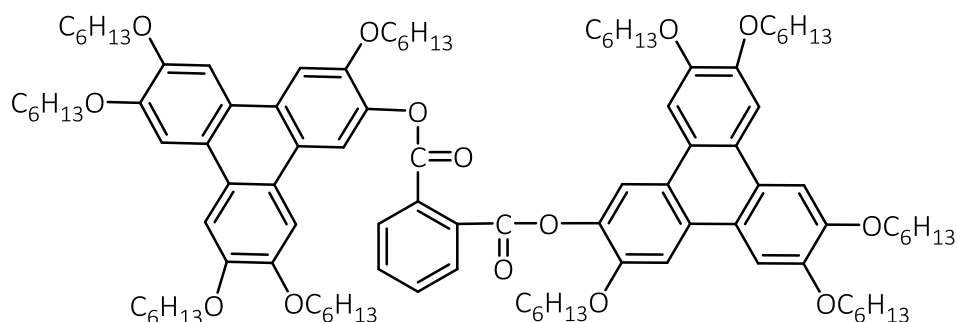
#### 3.11.2.1 Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)isophthalate **86**



3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-ol **25** (0.500 g,  $6.71 \times 10^{-4}$  mol), benzene-1,3-dicarboxylic acid (0.046 g,  $2.74 \times 10^{-4}$  mol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.420 g,  $2.04 \times 10^{-3}$  mol) 4-(dimethylamino)pyridine (DMAP) (0.016 g,  $1.31 \times 10^{-4}$  mol) were stirred in dry DCM (50ml) at 30°C for 72 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50ml), dried with MgSO<sub>4</sub> and evaporated to dryness in vacuo. The crude solid was purified by column chromatography eluting with ethylacetate/hexane (1: 20) and recrystallised in ethanol and DCM isolating the product as light purple solid **86** (0.13 g, 29%).

Mp 176°C; IR (thin film, cm<sup>-1</sup>) 2954, 2858, 2928, 1741, 1616, 1511, 1432, 1260, 1225; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 9.16(s, 1H), 8.51 (dd, *J* = 7.7, 1.5 Hz, 2H), 8.18 (s, 2H), 7.87 (s, 2H), 7.82 (s, 2H), 7.77 (s, 2H), 7.76 (s, 2H), 7.74 (s, 2H), 7.69 (t, *J*=7.7, 1H), , 4.10-4.20 (m, 20H), 1.80-1.92 (m, 16H), 1.69-1.76 (m, 4H), 1.25-1.41 (m, 20H), 1.12-1.24 (m, 10H) 0.70-0.92 (M, 30H) ppm. <sup>13</sup>C-NMR (126 MHz); δ 164.2, 149.8, 148.9, 139.9, 128.2, 124.7, 123.5, 123.3, 123.2, 116.8, 108.0, 107.0, 106.4, 69.9, 69.8, 69.2, 69.0, 31.7, 31.5, 29.6, 29.0, 25.8, 22.7, 22.6, 22.3, 14.1 ppm. MS (MALDI): *m/z* calculated for C<sub>104</sub>H<sub>146</sub>O<sub>14</sub> (M<sup>+</sup>, 100%): 1620.07 found 1620.38

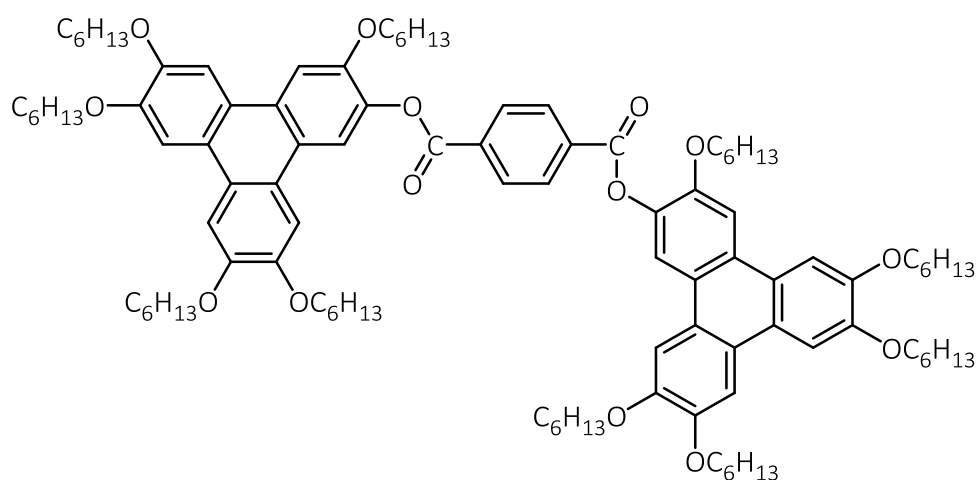
### 3. 11. 2. 2. Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)phthalate **89**



3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-ol **25** (0.530 g,  $7.11 \times 10^{-4}$  mol), benzene-1,2-dicarboxylic acid (0.046 g,  $2.74 \times 10^{-4}$  mol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.280 g,  $1.36 \times 10^{-3}$  mol), 4-(dimethylamino)pyridine (DMAP) (0.004 g,  $3.36 \times 10^{-5}$  mol) were stirred in dry DCM (50 ml) at 30°C for 72 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50 ml), dried with  $\text{MgSO}_4$  and evaporated to dryness in vacuo. The crude product was loaded onto a silica column and eluted with a 1:20 mixture of ethylacetate/hexane. The solid was recrystallized from dichloromethane and ethanol giving the desired product **89** (0.18g, 41%).

Mp 82°C; IR (thin film,  $\text{cm}^{-1}$ ) 2929, 2858, 1738, 1616, 1509, 1432, 1259;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (s, 1H), 8.08 (dd,  $J = 6.0, 3.5\text{Hz}$ , 2H), 7.85 (s, 1H), 7.85 (s, 1H), 7.80 (s, 1H), 7.72 (s, 1H), 7.68 (dd,  $J = 6.0, 3.5\text{ Hz}$ , 2H), 7.66 (s, 1H), 4.09-4.22 (m, 16H), 4.01 (t,  $J = 6.5$ , 4H) 1.81-1.92 (m, 10H), 1.71-1.81 (m, 10H), 1.51-1.60 (m, 20H), 1.08-1.30 (m, 20H), 0.89-1.05 (m, 20H), 0.76-0.88 (m, 30H) ppm.  $^{13}\text{C-NMR}$  (126 MHz);  $\delta$  166.0, 150.0, 149.8, , 139.9, 132.2, 131.7, 129.9, 128.4, 125.0, 123.7, 123.5, 123.0, 117.2, 108.1, 107.8, 69.6, 68.5, 31.9, 29.6, 25.8, 22.7, 14.2 ppm. MS (MALDI):  $m/z$  Calculated for  $\text{C}_{104}\text{H}_{146}\text{O}_{14}$  ( $\text{M}^+$ , 100%): 1620.07 found 1619. 45.

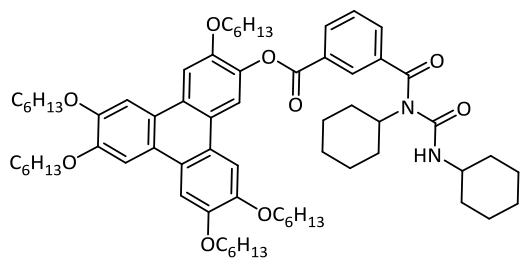
### 3. 11. 2. 3 Synthesis of bis(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)terephthalate **91**



3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-ol **25** (0.530 g,  $7.11 \times 10^{-4}$  mol), benzene-1,4-dicarboxylic acid (0.046 g,  $2.74 \times 10^{-4}$  mol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.280 g,  $1.36 \times 10^{-3}$  mol) 4-(dimethylamino)pyridine (DMAP) (0.0041 g,  $3.36 \times 10^{-5}$  mol) were stirred in dry DCM (50 ml) at 30°C for 72 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50ml), dried with MgSO<sub>4</sub> and evaporated to dryness in vacuo. The crude solid was purified by column chromatography eluting with ethylacetate/hexane (1: 20) the solid **91** was obtained as off white (0.15g, 35%).

Mp 175°C; IR (thin film, cm<sup>-1</sup>) 2918, 2850, 1731, 1515, 1435, 1261; <sup>1</sup>H- NMR (500 MHz, CDCl<sub>3</sub>) δ 8.46 (s, 4H), 8.24 (s, 2H), 7.92 (s, 2H), 7.88 (s, 2H), 7.82 (s, 2H), 7.79 (s, 4H), 4.19- 4.28 (m, 20H), 1.99- 1.89 (m, 16H), 1.76 - 1.84 (m, 4H), 1.52- 1.65 (m, 20H), 1.35- 1.48 (m, 40H), 0.87 - 0.98 (m, 30H) ppm. <sup>13</sup>C- NMR (126 MHz); δ 164.5, 149.8, 149.5, 148.9, 140.0, 133.8, 130.3, 128.4, 124.9, 123.4, 123.1, 116.9, 108.2, 106.5, 69.4, 69.2, 31.9, 29.6, 25.8, , 22.8, 14.1 ppm. MS (MALDI): *m/z* calculated for C<sub>104</sub>H<sub>146</sub>O<sub>14</sub> (M<sup>+</sup>, 100%): 1620.07 found 1619.68.

### 3.12. *N*-Acyl Urea **87** (byproduct) of Isophthalate **86**

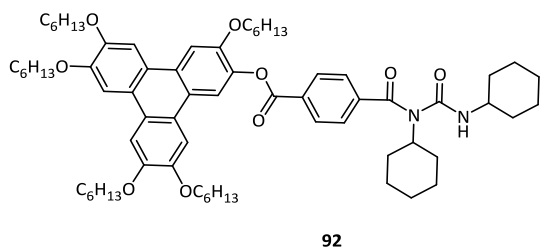


**87**

3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-ol **25** (0.500 g,  $6.71 \times 10^{-4}$  mol), benzene-1,3-dicarboxylic acid (0.046 g,  $2.74 \times 10^{-4}$  mol), *N,N'*-dicyclohexyl carbodiimide (DCC) (0.420 g,  $2.04 \times 10^{-3}$  mol) 4-(dimethylamino)pyridine (DMAP) (0.016 g,  $1.31 \times 10^{-4}$  mol) were stirred in dry DCM (50ml) at 30°C for 72 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50ml), dried with  $\text{MgSO}_4$  and evaporated to dryness in vacuo. The crude solid was purified by column chromatography eluting with ethylacetate/hexane (1: 20) isolating the product as light purple solid **86** (0.13 g, 29%) and the by-product **87** was obtained as white solid (0.22g, 51%).

Mp 95°C; IR (thin film,  $\text{cm}^{-1}$ ) 2930, 2857, 1738, 1651, 1514, 1437, 1258.  $^1\text{H}$ - NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.37(d,  $J=8.0$ , 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.88 (s, 1H), 7.84 (s, 1H), 7.79 (s, 1H), 7.60 (t,  $J = 8.0$  Hz, 1H), 4.15 – 4.27 (m, 10H), 1.85 – 2.00 (m, 10H), 1.48 – 1.66 (m, 20H), 1.33 – 1.47 (m, 20H), 1.20– 1.31 (m, 10H), 0.88 – 0.98 (m, 12H), 0.81 – 0.86 (m, 3H) ppm.  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 164.3, 154.1, 149.5, 149.1, 149.0, 140.0, 137.7, 132.4, 132.0, 130.2, 129.0, 128.8, 128.3, 123.6, 123.1, 116.9, 108.2, 107.5, 107.1, 106.6, 106.5, 70.1, 69.9, 69.7, 69.7, 58.0, 49.9, 31.8, 29.6, 26.4, 26.0, 22.8, 22.7, 14.2, 14.1 ppm. MS (MALDI):  $m/z$   $\text{C}_{69}\text{H}_{99}\text{N}_2\text{O}_9$  ( $\text{M} + \text{H}$ ) $^+$ : 1099.74 found 1099.55

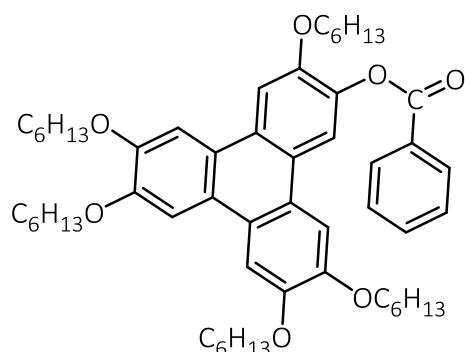
### 3.13. *N*-Acyl Urea **92** (byproduct) of Terephthalate **91**



3,6,7,10,11-Pentakis(hexyloxy)triphenylene-2-ol **25** (0.500 g,  $6.71 \times 10^{-4}$  mol), benzene-1,4-dicarboxylic acid (0.046 g,  $2.74 \times 10^{-4}$  mol), *N,N'*-dicyclohexyl carbodiimide (DCC) (0.420 g,  $2.04 \times 10^{-3}$  mol) 4-(Dimethylamino) pyridine (DMAP) (0.016 g,  $1.31 \times 10^{-4}$  mol) were stirred in dry DCM (50 ml) at 30°C for 72 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50 ml), dried with MgSO<sub>4</sub> and evaporated to dryness in vacuo. The crude solid mixture was purified by chromatography eluting with ethyl acetate/hexane (1:20) and the by-product solid **92** was obtained as white solid (0.18 g, 42%). MS (MALDI): *m/z* C<sub>69</sub>H<sub>98</sub>N<sub>2</sub>O<sub>9</sub> (M<sup>+</sup>, 100%): 1098.73 found 1098.84.



### 3.14. Synthesis of triphenylenebenzoate **94**



3,6,7,10,11-Pentakis(hexyloxy)triphenylene-2-ol **25** (0.100 g, 0.134 mmol), benzene-1,2-dicarboxylic acid (0.022 g, 0.134 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.05 g, 0.242 mmol) 4-(dimethylamino)pyridine (DMAP) (0.002 g, 0.013 mol) were stirred in dry DCM (50 ml) at 30°C for 72 h. Benzoic acid **93** (0.033 g, 0.268 mmol) was added and the mixture was further stirred for 1 h. The mixture was filtered, washed with dilute 2M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally washed with distilled water and extracted with DCM (3x50 ml), dried with MgSO<sub>4</sub> and evaporated to dryness in vacuo, then recrystallised from DCM/ EtOH and the resulting solid **94** was white (0.098 g, 86%)

Cryst 168, Col<sub>n</sub> 120 Iso (°C); IR (thin film, cm<sup>-1</sup>) 3298, 2955, 2930, 2857, 1733, 1618, 1516, 1435, 1259. <sup>1</sup>H- NMR (500 MHz, CDCl<sub>3</sub>); δ 8.23 (d, *J* = 7.5, 2H), 8.12 (s, 1H), 7.83 (s, 1H), 7.83 (s, 1H), 7.80 (s, 1H), 7.75 (s, 1H), 7.74 (s, 1H), 7.71 (s, 1H) 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H) 4.09-4.20 (m, 10H), 1.80-1.92 (m, 8H), 1.65-1.74 (m, 2H), 1.42-1.56 (m, 10H), 1.21-1.38 (m, 20H), 0.79 – 0.90 (m, 22H), 0.73 (t, *J* = 7.0 Hz, 3H) ppm. <sup>13</sup>C- NMR (126 MHz); δ 165.3, 150.0, 149.0, 140.3, 133.6, 130.4, 129.8, 128.7, 128.2, 124.8, 123.4, 117.0, 108.2, 107.5, 106.6, 69.3, 68.7, 31.8, 29.6, 25.7, 22.8, 14.2 ppm: MS (MALDI): *m/z* calculated for C<sub>55</sub>H<sub>77</sub>O<sub>7</sub> (M+H)<sup>+</sup>: 849.57 found 849.36.

## REFERENCES:

- (1) Lawson, D.; Buess, C. M. *Rev. Lit. Arts Am.* **1960**, 60, 313.
- (2) Cammidge, A. N.; Beddall, A. R.; Gopee, H. *Tetrahedron Lett.* **2007**, 48, 6700-6703.
- (3) Zhang, L.; Hughes, D. L.; Cammidge, A. N. *J. Org. Chem.* **2012**, 77, 4288-4297.
- (4) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, 36, 899-901.
- (5) Collings, P. J.; Hird, M. *Introduction to liquid crystals: chemistry and physics.* **2004**. CRC Press: London.
- (6) Kumar, S., *Chemistry of discotic liquid crystals: from monomers to polymers.* CRC press: **2016**. USA.
- (7) Kumar, S. *Liq. Cryst.* **2004**, 31, 1037–1059.
- (8) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, 9, 471–480.
- (9) Li, J.; He, Z.; Gopee, H.; Cammidge, A. N. *Org. Lett.* **2010**, 12, 472-475.
- (10) Cooke, G.; Hell, F.; Violini, S. *Synth. Commun.* **1997**, 27, 3745-3748.
- (11) Kaafarani, B. R.; Discotic Liquid Crystals for Opto-Electronic Applications. *Chemistry of Materials.* **2011**, 23, 378-396.
- (12) Vauchier, C.; Zann, A.; Le, B.P.; Dubois, J. C.; Billard, J. *Mol. Cryst. Liq. Cryst.* **1981**, 66, 103–114.
- (13) Hindmarsh, P.; Hird, M.; Styring, P.; Goodby, J. W. *J. Mater. Chem.* **1993**, 3, 169-182
- (14) Kumar, S.; Varshney, S. K. *Org. Lett.* **2002**, 4, 157–159.
- (15) Kouwer, P. H. J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *Macromolecules* **2001**, 34, 7582–7584.
- (16) Hatsusaka, K.; Ohta, K.; Yamamoto, I.; Shirai, H. *J. Mater. Chem.* **2001**, 11, 423–433.
- (17) Perez, D.; Guitian, E. *Chem. Soc. Rev.* **2004**, 33, 274–283.
- (18) Cammidge, A. N.; Gopee, H. *J. Mater. Chem.* **2001**, 11, 2773–2783.
- (19) Bushby R. J.; Hardy, C. *J. Chem. Soc., Perkin Trans. 1.* **1986**, 721.
- (20) Gribble, G. W.; Perni, R. B.; Onan, K. D. *J. Org. Chem.* **1985**, 50, 2934–2939.
- (21) Tombesi, O. L.; Rahman, A. U. *Chem. Ber.* **1966**, 1805–1809.
- (22) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Headdock, G. *Synthesis* **1995**, 31–32.
- (23) Manickam, M.; Smith A.; Belloni M.; Shelley E. J.; Ashton P. R.; Spencer N.; Preece J. A.; *Liq. Cryst.* **2002**, 29, 497.

- (24) A. Ulman, *Introduction to Ultrathin Films: From Langmuir-Blodgett Films to Self-Assembly*, Academic Press, Boston, **1991**.
- (25) Rego J. A.; Kumar S.; Ringsdorf H. *Chem. Mater.* **1996**, *8*, 1402.
- (26) Ellis.K.T; John, S. A. *Conducting Polymer Discotic Hybrid for Organic Semiconductor Applications. ICONN.* **2010**, 1-4.
- (27) Gopee, H.; Kong, X.; He, Z.; Chambrier, I.; Hughes, D. L.; Tizzard, G. J.; Coles, S. J.; Cammidge, A. N.; *Journal of Organic Chemistry* **2013**, *78*, 9505-9511.
- (28) Ban, J.; Chen, S., & Zhang, H. *RSC Advances.* **2014**, *4*, 54158-54167.
- (29) Kealy, T. J.; Pauson, P. L. *Nature*, **1951**, *168*, 1039.
- (30) Xiao, W.; He, Z.; Xu, M.; Wu, N.; Kong, X.; Jing, X. *Tetrahedron Lett.* **2015**, *56*, 700-705.
- (31) Imrie, C.; Engelbrecht, P.; Loubser, C.; McClelland, C. W. *Appl.Organomet. Chem.* **2001**, *1*, 15.
- (32) Lindsell, W. E.; Xinxin, L. *J. Chem. Res.* **1998**, *5*, 62.
- (33) Loubser, C.; Imrie, C. *J. Chem. Soc. Perkin Trans 2*, **1997**, *2*, 399.
- (34) Kim, S. Y.; Kadkin, O. N.; Kim, E. H.; Choi, M-G. *J. Organomet. Chem.* **2011**, *696*, 2429.
- (35) Rebiere, F.; Samuel O.; Kagan H. B. *Tetrahedron Lett.* **1990**, *31*, 3121–3124.
- (36) Alberg, D.; Unpublished lecture note, *Department of Chemistry, Carleton College, Northfield, MN.* <http://www.chm.uri.edu/bdeboef/chm292/Acetylferrocene.pdf> assessed 15/09/2016.
- (37) Deschenaux, R.; Goodby, J. W.: *Homogeneous Catalysis, Organic Synthesis, Materials Science* (Eds T Hayashi, A Togni), Wiley- VCH Verlag GmbH, Weinheim, **1995**.
- (38) Cooke, G.; Radhi, A.; Boden, N.; Bushby, R. J.; Lu. Z.; Brown. S, Heath. S. L. *Tetrahedron*, **2000**, *56*, 3385-3390.
- (39) Toniolo, T.; Valle, G.; Crisma, M.; Morretto, V.; Izbedski, J.; Pelka, J.; Schnieder, C. H. *Helv. Chim. Acta* **1990**, *73*, 626-633.
- (40) Imrie, C. T., Henderson, P. A. *Chem. Soc. Rev.* **2007**, *36*, 2096.
- (41) Murayama, K.; Sawada, Y.; Noguchi, K.; Tanaka, K., *J. Org. Chem.* **2013**, *78*, 6202-6210.

- (42) Kadkin, O. N.; Galyametdinov, Y. G. *Russ. Chem. Rev.* **2012**, *81*, 675.
- (43) Ji, H.; Zhao, K.; Yu, W.; Wang, B.; Hu, P. *Sci. China Ser. B Chem.* **2009**, *52*, 975–985.
- (44) Thevenet, D.; Neier, R. *Synthesis*. **2011**, *2011*, 3801–3806.
- (45) Deb, M, Kumar. D, Singh. J and Elias. A. J. *Organometallics*. **2016**, *35*, 1086-1091.
- (46) Liang, B., Dai, M., Chen, J.; Z. Yang; *J. Org. Chem.* **2005**, *70*, 391-393.
- (47) Gupta, S. K.; Raghunathan, V.; Lakshminarayanan, V.; Kumar, S. *J. Phys. Chem. B* **2009**, *113*, 12887–12895.
- (48) Zhang, L.; Gopee, H.; Hughes, D. L.; Cammidge, A. N. *Chem. Commun.* **2010**, *46*, 4255–4257.
- (49) Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1981**, *46*, 7740.
- (50) Okazaki, M.; *Macromolecules*. **1998**, *31*, 863-869
- (51) Lu, M.; Yang, K. H. *Japan J. Appl. Phys.* **2000**, *39*, L412–L415.
- (52) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887.
- (53) Wong, W.-Y.; Ho, C.-L. *J. Mater. Chem.* **2009**, *19*, 4457.
- (54) Clements, J.; Boden, N.; Gibson, T.; Chandler, R. .; Hulbert, J. .; Ruck-Keene, E. *Sensors Actuators B Chem.* **1998**, *47*, 37–42.
- (55) Gong, Y.; Huang, Y.; Jiang, L.; Lu, T. *Inorg. Chem.* **2014**, *53*, 9457–9459.
- (56) Blanzat, B.; Barthou, C.; Tercier, N.; Cedex, S.; Simon, J. *J. Am. Chem. Soc.* **1987**, *109*, 6193–6194.
- (57) Chen, X.; Chen, L.; Chen, Y. *RSC Adv.* **2014**, *4*, 3627–3632.
- (58) Fanta, P. *Synthesis* **1974**, *9*, 9-21.
- (59) Elschenbroic, C. *Organometallic Catalysis in Synthesis and Production*, **2006**. Wiley-VCH, Weinheim.
- (60) Chinchilla. R.; Nájera, C. *Chem. Soc. Rev.*, **2011**, *40*, 5084-5121.
- (61) Organic Chemistry portal reactions; *Named reactions* <http://www.organic-chemistry.org/namedreactions/Sonogashira-coupling>. Assessed 26/04/2013
- (62) Chinchilla. R and Nájera, C. *Chem. Rev.* **2007**, *107*, 874-922.
- (63) Organic Chemistry portal reactions; *Named reactions* <http://www.organic-chemistry.org/namedreactions/Suzuki-coupling>. Assessed 26/04/2013

- (64) Molander, G. A.; Bialatto, B. *J. Org. Chem.* **2003**, 68, 4302-4314;
- (65) Artal, M. C.; Toyne, K. J.; Goodby, J.; Barberá, W. J.; Photinos, D. J. *J. Mater. Chem.*, **2001**, 11, 2801-2807.
- (66) Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, 94, 4749.
- (67) Almutairi, T. *unpublished thesis*, **2015**. UEA.
- (68) Borner, R. C.; Bushby, R.; Cammidge, A. N. *Liq. Cryst.* **2006**, 33, 1439-1442.
- (69) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, 15, 851-858.
- (70) Leberre, V.; Angely, L.; Simonet-Geugeun, N.; Simonet, J. *J. Chem. Soc.* **1987**, 984.
- (71) Paliakov, E.; Strekowski, L. *Tetrahedron Lett.* **2004**, 45, 4093-4095
- (72) Ryan, S. *unpublished thesis*, **2011**. UEA.
- (73) Turner, J. R; *unpublished thesis*, **2015**. UEA.
- (74) Leerman, T.; Leroux, F. R.; Colobert, F. *Org. Lett.* **2011**, 13, 4479-4481
- (75) Zhang, L. *unpublished thesis*. **2011**. UEA.
- (76) Neises, B and Steglich, W. *Angew. Chem. Int. Ed. Engl.* **1978**, 17, 522.
- (77) Dengiz, C.; Breiten, B. J.; Gisseelbrelbrecht, J.P.; Boudon, C.; Trap, N.; Schweizer, W.B and Dielderich, F. *J. Org.Chem.* **2015**, 80, 882-896
- (78) Henderson, P.; Kumar, S.; Rego, J. A.; Ringsdorf, H and Schuhmacher, J. *Commu.* **1995**, 1059-1060.
- (79) Molander, G.; Maxwell, D. E. *J. Org. Chem.* **2006**, 71, 9198-9202.
- (80) Bai, L.; Wang, J-X.; Zhang, Y. *Green Chemistry.* **2003**, 5, 615-617.
- (81) Zuo, L.; Yao, S.; Wang, W.; Duan, W. *Tetrahedron Lett.* **2009**, 49, 4054-4056
- (82) Piatelli, M.; Fattorusso, E.; Nicolivillaus, R. A.; Magno, S. *Tetrahedron Lett.* **1965**, 21, 3229-3236.
- (83) Lee, S.K and Kim, K.D; Bullkorean. *Chem. Soc.* **2010**, 31, 3842-3843.
- (84) Li, G.; Patel, D.; Hiruby. *Tetrahedron Lett.* **1993**, 34, 5393-5396

- (85) Han. B.; Hu. P, wang. B.; Redshaw. C.; Zhao. Beilsten. *J. Org .Chem.* **2013**, 9, 2852-2881.
- (86) Xiao. W.; He. Z.; Remiro. S.; Turner, R.J.; Xu. M.; Yang. X.; Xiping. J.; Cammidge. A. *Org. Lett.* **2015**, 17, 3286-3289.
- (87) Alami, M.; Ferri. F.; Linstrumelle. G. *Tetrahedron. Lett.* **1993**, 34, 6403-6406.
- (88) Orgaonkar. S.; Verkade. J.G. *J. Org. Chem.* **2004**, 69, 5752-5755.
- (89) Liang. B.; Huang. M.; You. Z.; Xiong. Z.; Lu. K.; Fathi. R.; Chen. J.; Yang. Z. *J. Org. Chem.* **2005**, 70, 6097-6100.
- (90) Guan. J. T.; Weng. T. Q.; Yu. G.; Hua Liu. S. *Tetrahedron Lett.* **2007**, 48, 7129-7133.
- (91) Pu. X.; Li. H.; Colacot, T. J. *J. Org. Chem.* **2013**, 78, 568-581.
- (92) Schetter. B.; Speicer. B; *J. Org Chem.* **2004**, 689, 1472- 1480.
- (93) Wang. Z. *Comprehensive organic name reactions and reagents.* **2010**, John Wiley and Sons, Inc. 2651-2655. Chicago.
- (94) Cammidge, A. N.; Gopee, H. J. *Porphy. Phthalocyanines.* **2009**, 13, 235–246.