University of East Anglia

Triphenylene as a Scaffold for New Molecular Materials

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy at the University of East Anglia, Norwich.

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Abstract

The work described in this thesis centres around our desire to use triphenylene as the scaffold for building new molecular materials. This has been approached in three different ways; firstly a twin linked by pyrrole units, secondly by twinning with triazoles, and finally *via* the formylation of triphenylene.

A tetra-hexyloxysubstituted dipyrrolyltriphenylene twin had previously been synthesised in the group, however characterisation was difficult and therefore a twin with improved solubility was designed. The synthesis of tetra-decyloxysubstituted dipyrrolyltriphenylene was completed successfully, but the twinning of the compound could not be achieved. One possible explanation was interference of the long alkyl chains in the neighbouring positions to the pyrrole units. A new target precursor was designed with just two alkyl chains on the triphenylene. Previous work in the group had shown difficulties in the synthesis of the di-hexyloxysubstituted triphenylene, however with careful manipulations the synthesis was successful. New complications were found with the solubility of the di-hexyloxysubstituted dipyrrolyltriphenylene that could not be overcome. At this point crystals of the tetra-hexyloxysubstituted dipyrrolyltriphenylene twin had been obtained and full characterisation achieved.

With the explosion of Click chemistry in the recent years, a twin linked by triazoles was targeted. The twin was designed from a tetra-hexyloxysubstituted diazidetriphenylene, coupled with di-hexyloxysubstituted diacetylenetriphenylene. The diacetylene triphenylene was synthesised successfully following on from the work achieved in the first project. Two routes were explored for the synthesis of the diazide. The first, a direct conversion of the dibromide to the diazide, gave no reaction. The second route was a series of manipulations starting from the dinitrotriphenylene. Some difficulties were found with the reduction of the dinitro compound to the diamine, however these were overcome using carefully controlled conditions. The corresponding diamide was synthesised to allow for full characterisation, as the diamine was found to decompose rapidly. Crystals were grown of the diamide and the x-ray structure was obtained, this showed an unexpected structure. The expected 3,6-substitution pattern had not been formed, in fact we had synthesised the 1,8-bisimide-2,7,10,11-tetrakis(hexyloxy) triphenylene. As the triazole linked triphenylene twin was not accessible, the diacetylenetriphenylene was twinned with itself. High dilution conditions were followed and the twin was successfully isolated. The twin showed no mesophase behaviour and remained stable beyond 300 ^{o}C.

The third part of the thesis is based on the formylation of tetra-hexyloxysubstituted triphenylene. The formation of the triphenylene dialdehyde had previously eluded our group, however following a new protocol gave a successful synthesis. There were a number of potential compounds to investigate from this versatile precursor. We chose to target BODIPY-triphenylene hybrid compounds. Two compounds were designed, one from the dialdehyde where the BODIPY fragment would be attached *via* the central *meso*-carbon, and one from the dipyrrole where the BODIPY would be attached *via* the alpha positions of the pyrrole. Kryptopyrrole was used in the synthesis from the dipyrrole, to attempt to discourage potential polymer formation, however the reactions were not successful. The bis-BODIPYtriphenylene *via* the dialdehyde was successfully synthesised and the compound was observed for potential mesophase behaviour; it was seen to melt with decomposition at 150-160 ^{o}C. Finally, the triphenylene dialdehyde was used to synthesise a twin linked by diamines. The novel twinned structure has a central "void" region that we know to disfavour columnar organisation. The compound was observed for potential mesophase behaviour, and the twin was seen to exhibit only a stable nematic discotic mesophase up to 300 ^{o}C.

Contents

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.

Rebecca Jane Turner
May 2015

Acknowledgements

First of all I would like to thank my supervisor Prof. Andy Cammidge, his constant support and guidance kept me focussed and helped me get through to this completed thesis. Also Dr. Lydia Sosa who was always there for me through the good and difficult times, both in and out of the lab, and for encouraging me to pursue a PhD in the first place! Dr Maria 'Paz' Munoz-Herranz thank you for welcoming me into your lab, I learnt a lot from you and had great times working alongside your group.

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Finally, I want to thank my parents and sisters for their support and love which has kept me going, and for always believing in me.

Abbreviations

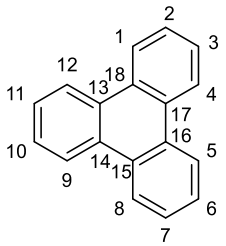
abs - absorption
aq. - aqueous
Ar - aryl
Atm - atmosphere
Boc - *tert*-butyloxycarbonyl
BODIPY - 4,4-difluoro-4-boro-3a,4a-diaza-*s*-indacenes
b.p. - boiling point
Bu - butyl
col - columnar
conc. - concentrated
d - doublet
δ - chemical shift in parts per million (ppm)
DDQ - 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
D_L - discotic lamellar
DLC - discotic liquid crystal
DIPEA - *N*,*N*-diisopropylethylamine
DMF - *N*,*N*-dimethylformamide
DMSO - dimethylsulphoxide
emiss - emission
eq. - equivalent
FET - field effect transistor
h - hour
HOMO - highest occupied molecular orbital
I - isoptropic liquid
IR - infra-red
λ - wavelength
LC - liquid crystal
LCD - liquid crystal display
LUMO - lowest unoccupied molecule orbital
m - multiplet
MALDI - Matrix-assisted laser desorption/ionisation
MOF - metal-organic framework
mol - mole
mmol - millimole
m.p. - melting point
MS - mass spectrometry
m/z - mass to charge ratio
N_C - nematic columnar
N_D - nematic discotic
N_L - nematic lateral
NMR- nuclear magnetic resonance
OFET - organic field effect transistor
OLED - organic light emitting diode
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 - 2,4,6-trinitrophenol
TP - triphenylene
UV/Vis - ultraviolet/visible spectroscopy

Chapter 1

Introduction

1.1 History and Structure of Triphenylene

The compound triphenylene (**1**) was first discovered by Schultz when isolated from the pryolytic products of benzene,[1] and has been studied in the literature for over a century. It is a symmetrical, planar, aromatic hydrocarbon consisting of four fused benzene rings (Figure 1.1). Triphenylene, **1**, has twelve possible sites for substitution, with the peripheral sites 2, 3, 6, 7, 10 and 11 being most commonly used.



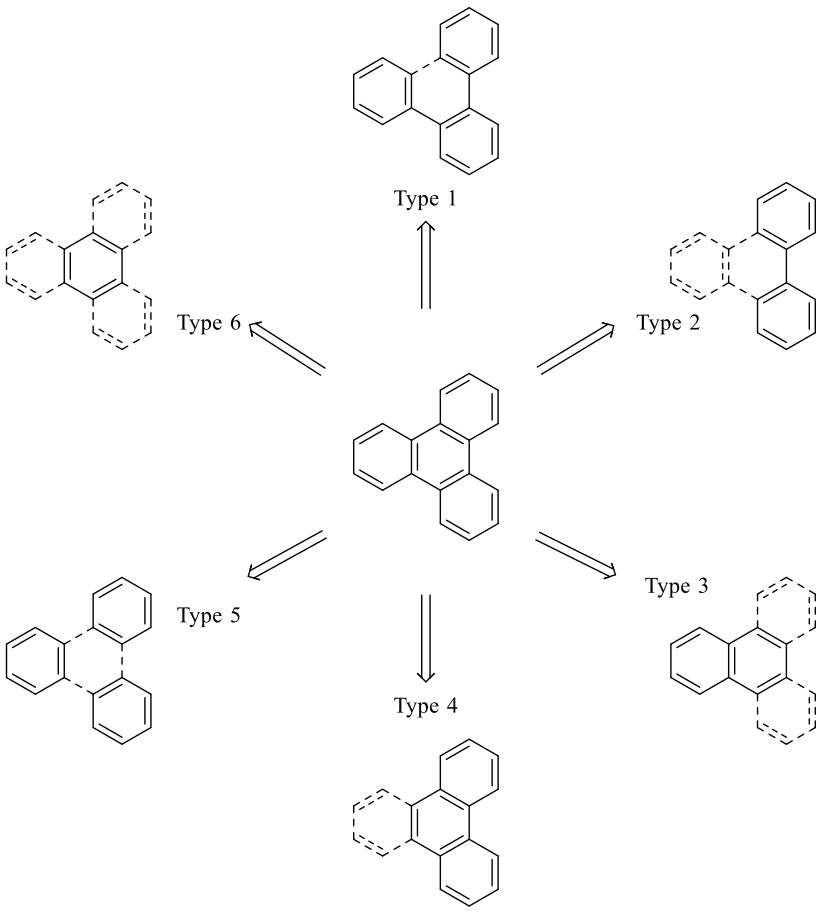
1

Figure 1.1: Structure of triphenylene, **1**, and numbering system.

1.2 Synthesis of Triphenylene

Since its discovery, there have been many methods developed to synthesise triphenylene. The early syntheses focussed on triphenylene itself and recently the focus has shifted onto the facile synthesis of substituted triphenylene. The synthesis of such substituted triphenylenes will herein be reviewed.

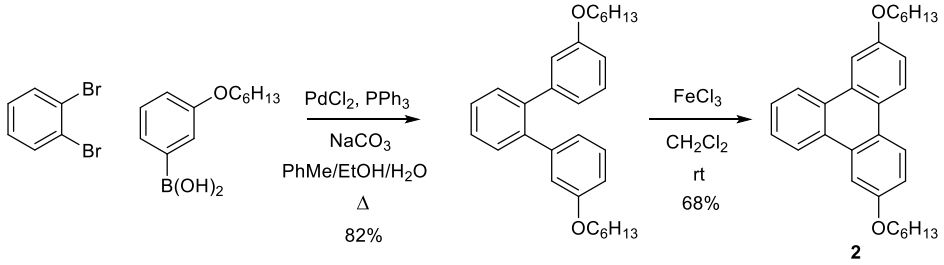
Scheme 1.1 shows the six most commonly utilised syntheses of triphenylene, the solid lines showing the isolated intermediates, and the dotted lines showing the key step in the formation of the final triphenylene.[2]



Scheme 1.1: Different routes of triphenylene syntheses

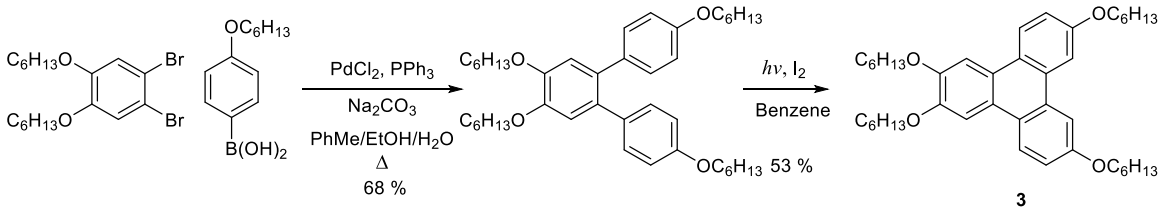
1.2.1 Type 1 Syntheses

The key step in type 1 syntheses is the cyclisation of an *ortho*-terphenyl. There are many examples of this being used in the synthesis of triphenylenes; with terphenyls most commonly synthesised by palladium-catalysed cross coupling reactions, this synthesis can produce both symmetrically and unsymmetrically substituted triphenylenes. Oxidative cyclisation was initially developed for the synthesis of phenols and is now a classic step in the formation of biaryl bonds. There are many oxidising agents that have been used in this coupling reaction, for example $VOCl_3$, $MoCl_5$, VOF_3, $K_3Fe(CN)_6$ and $FeCl_3$ (Scheme 1.2).



Scheme 1.2: Synthesis of 2,7-bis(hexyloxy)triphenylene **2**[3]

Photocyclisation is also utilised in type 1 syntheses, irradiation of the terphenyl with UV light in the presence of iodine yields the desired triphenylene (Scheme 1.3).

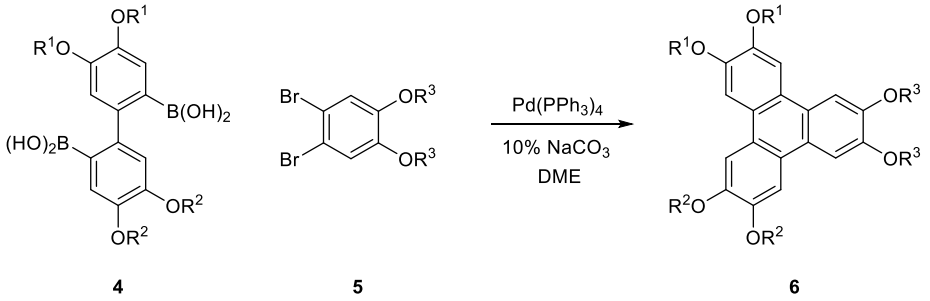


Scheme 1.3: Synthesis of 2,3,7,10-tetrakis(hexyloxy)triphenylene **3**[3]

1.2.2 Type 2 Syntheses

The formation of triphenylene from a biphenyl is the characteristic step in type 2 syntheses. There are three ways in which this can be done; palladium-catalysed coupling, Diels-Alder cycloaddition and oxidative cyclisation.

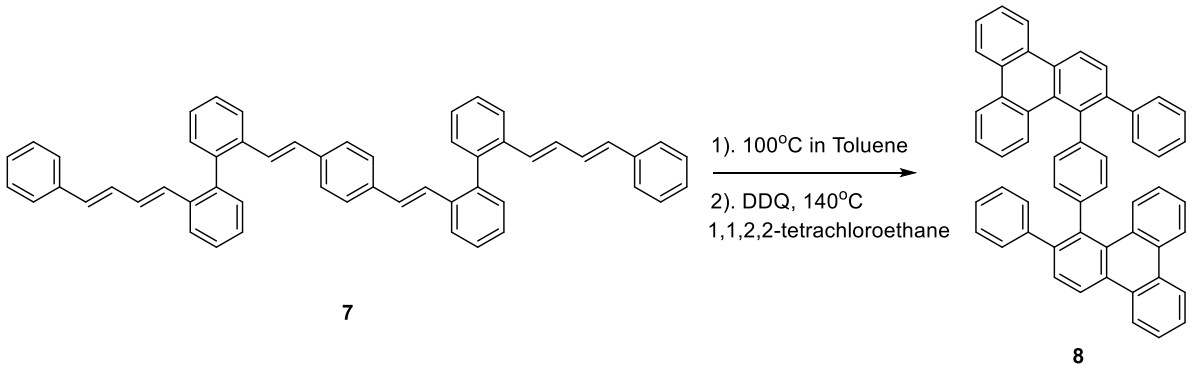
In Scheme 1.4, unsymmetrically substituted triphenylenes are synthesised by a double Suzuki coupling reaction between the diboronic acid **4** and dibromide **5**.[4] This is an efficient way to form unsymmetrically substituted triphenylenes with many different R-groups reported to work with this synthesis.



4 **5** **6**

Scheme 1.4: Palladium-catalysed synthesis of unsymmetrical triphenylene **6**[4]

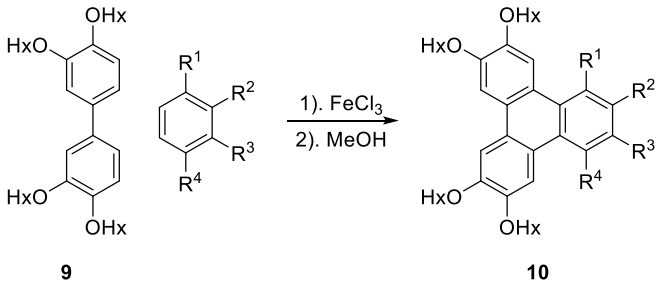
An interesting synthesis of triphenylene *via* intramolecular Diels-Alder reaction was published in 1996.[5] A double Diels-Alder reaction of **7** followed by rearomatisation with DDQ gave compound **8** containing two triphenylene units.



7 **8**

Scheme 1.5: Diels-Alder Synthesis of compound **8**[5]

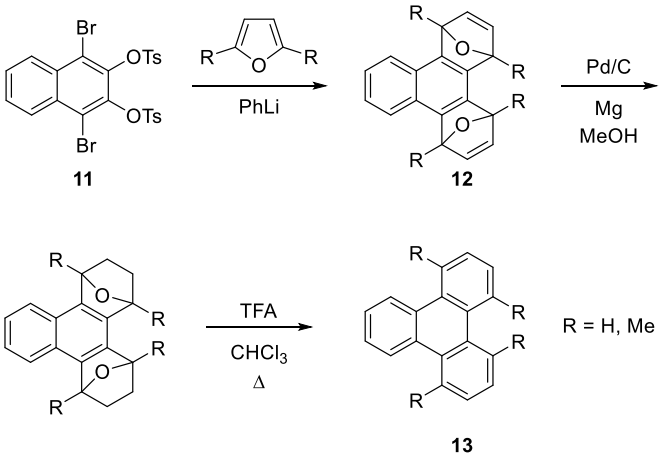
Oxidative cyclisation follows the same conditions as in type 1, many different oxidants can be utilised, and an example is shown in Scheme 1.6. The paper by Boden *et al*. shows that this route tolerates substituents in the sterically hindered α-position, which were previously difficult to obtain.[6]



Scheme 1.6: Oxidative coupling of triphenylene **10** from biphenyl **9**[6]

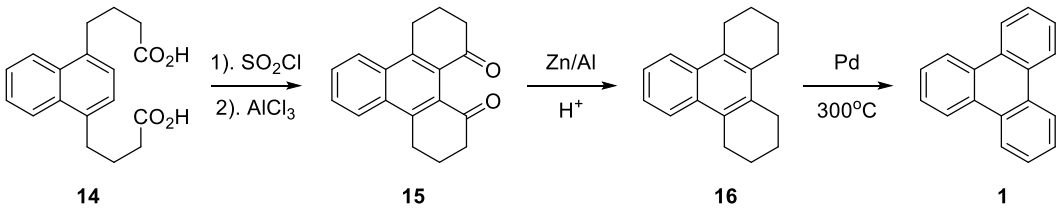
1.2.3 Type 3 Syntheses

Type 3 methods focus on the synthesis of triphenylene from a naphthalene core. Most syntheses through this route go *via* a Diels-Alder reaction. One such example is shown in Scheme 1.7, reaction of **11** with phenyllithium creates an *in situ* tetradehydronaphthalene that reacts with furan to give **12**, which is reacted further to yield triphenylene **13**.[7]



Scheme 1.7: Synthesis of triphenylene **13** *via* Diels-Alder[7]

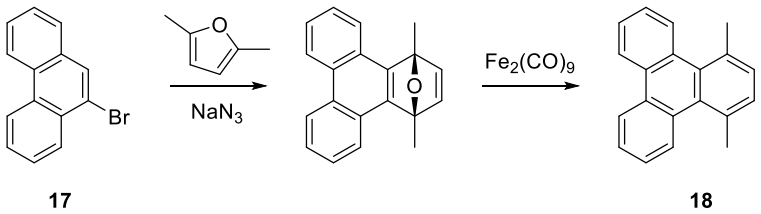
Type 3 synthesis of triphenylene have also utilised the Friedel-Crafts reaction. Functionalised naphthalene **14** is cyclised to give **15**, a Clemmensen reduction yields **16**, then dehydrogenation with palladium gives the triphenylene **1**.[8]



Scheme 1.8: Synthesis of triphenylene **1** *via* Friedel-Crafts reaction[8]

1.2.4 Type 4 Syntheses

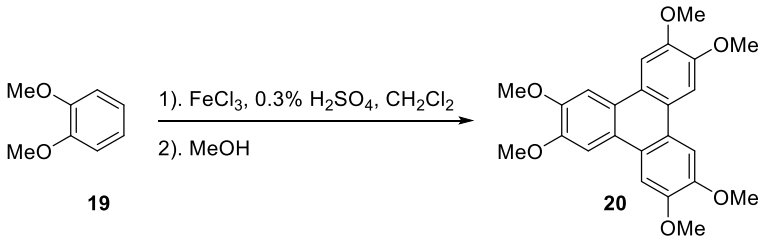
Type 4 syntheses are characterised by the formation of the triphenylene ring from a phenanthrene moiety. Diels-Alder reactions are again a common route for these types of syntheses, one interesting example is shown in Scheme 1.9 where the phenanthrene, **17**, acts as the dienophile in a reverse Diels-Alder reaction.[9] Formation of the triphenylene by photocyclisation[10] has also been used.



Scheme 1.9: Synthesis of 1,4-dimethyloxytriphenylene **18**[9]

1.2.5 Type 5 Syntheses

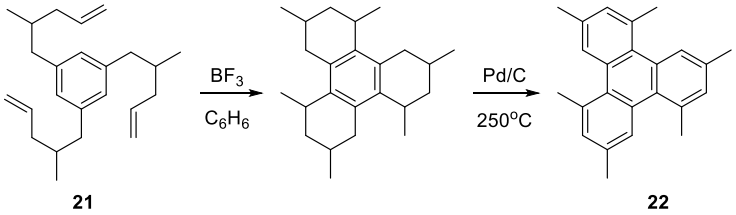
Syntheses of type 5 see the final triphenylene made by the trimerisation of three benzene rings. There are many examples of this synthesis being used in the literature; oxidative trimerisation is one of the classic syntheses of triphenylene (Scheme 1.10).[11]



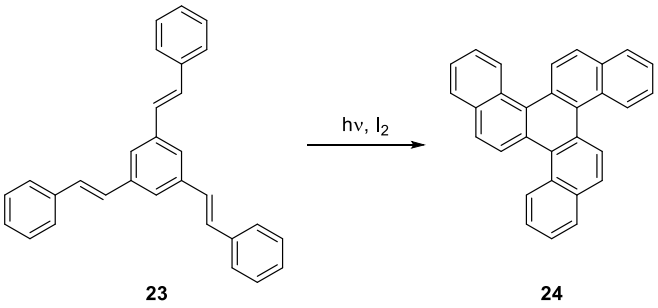
Scheme 1.10: Oxidative trimerisation of **19** to yield **20**[11]

1.2.6 Type 6 Syntheses

In type 6 syntheses, the peripheral rings of the triphenylene are formed in the final step. There are few examples of this type in the literature, two examples are shown in Schemes 1.11 and 1.12.



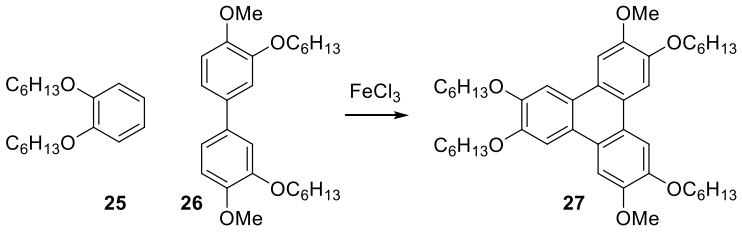
Scheme 1.11: Acid catalysed cyclisation of **21** to yield **22**[12]



Scheme 1.12: Photocyclisation of **23** to yield triphenylene **24**[13]

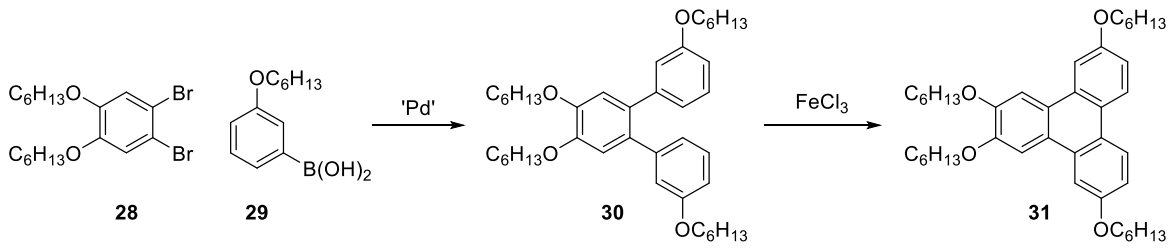
1.2.7 Unsymmetrically Substituted Syntheses

Unsymmetrically substituted triphenylene systems are of great interest due to the possibility of further functionalization. The most common route to such compounds is *via* a type 2 biphenyl-phenyl coupling. One example of this is shown in Scheme 1.13,[14] oxidative coupling of 1,2-dihexoxybenzene **25** with biphenyl **26** with ferric chloride gave unsymmetrically substituted triphenylene **27**.



Scheme 1.13: Biphenyl-phenyl coupling to unsymmetrically substituted triphenylene **27**

The desire for more freedom around functionalising the triphenylene ring led to development of more versatile syntheses of unsymmetrically substituted triphenylenes. One such synthesis came from recent advancement in our group that gave 2,3,6,11-substitued triphenylenes, allowing for further functionalisation in positions -7 and -10 (Scheme 1.14). A Suzuki-Miyaura cross-coupling reaction between 1,2-dibromo-4,5-dihexyloxybenzene **28** and 3-hexyloxybenzene boronic acid **29** yields the corresponding terphenyl **30**. Oxidative coupling with ferric chloride yields 2,3,6,11-tetra(hexyloxy)triphenylene **31**.



Scheme 1.14: Synthesis of 2,3,6,11--tetra(hexyloxy)triphenylene **31**

The success of this procedure led to the synthesis of a range of functionalised triphenylenes[15] (Figure 1.2). These structures show that a range of functional groups can be introduced, including electron donating methoxy groups, electron withdrawing aldehyde and nitrile groups, also electron deficient pyridines and electron rich thiophenes and furans.

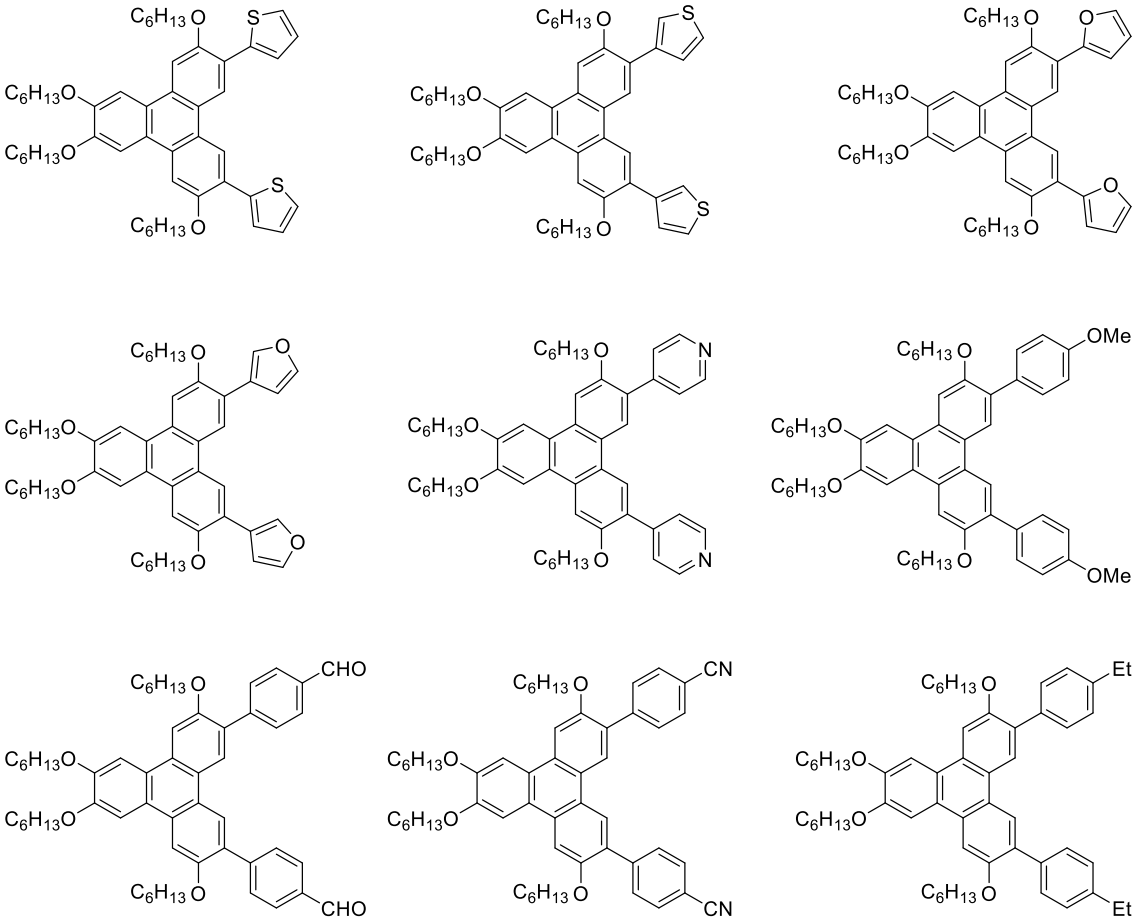


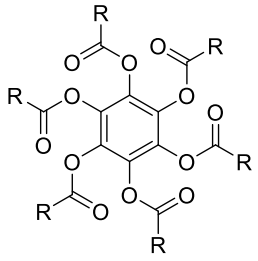
Figure 1.2: Range of unsymmetrically substituted functionalised triphenylenes

1.3 Properties of Triphenylene

Triphenylene compounds have a range of properties that make them such interesting compounds to investigate. One of the major reasons that triphenylene compounds are so widely studied is due to the fact that they form liquid crystalline mesophases. Triphenylene derivatives are also thermally and chemically stable and as shown earlier there are many syntheses available that give rise to different functionalisation. They have interesting one-dimensional charge transfer, and energy migration which lend themselves to a variety of potential applications.

1.3.1 Triphenylene as Liquid Crystal

Triphenylene derivatives were first shown to form mesophases in 1978,[16] just after disc-shaped molecules were first shown to form liquid crystals in 1977 by Chandrashekar.[17] Chandrashekar synthesised a range of benzene-hexa-n-alkanoates **32** (Figure 1.3), and through thermal, optical and x-ray studies, liquid crystalline properties were observed.



32

Figure 1.3: Structure of benzene-hexa-n-alkanoate, **32**, where R= n-C_4H_9 to n-C_9H_{19}

Discotic liquid crystals (DLCs); formed by disc-shaped molecules, are thermotropic liquid crystals, meaning they form as a function of temperature. On observations of many DLC mesophases, they have been further classified by the arrangement of the molecules and amount of order they contain. The types observed are columnar, nematic, smectic and cubic, these are then further subcatagorised. Columnar mesophases are by far the most common mesophases of discotics observed, followed by the nematic mesophase. Cubic and smectic

mesophases are far more rare. Many different cores have been shown to form discotic mesophases, such as phthalocyanine, triphenylene, coronene, truxene, porphyrin, napthalene, anthracene and perylene (Figure 1.4).

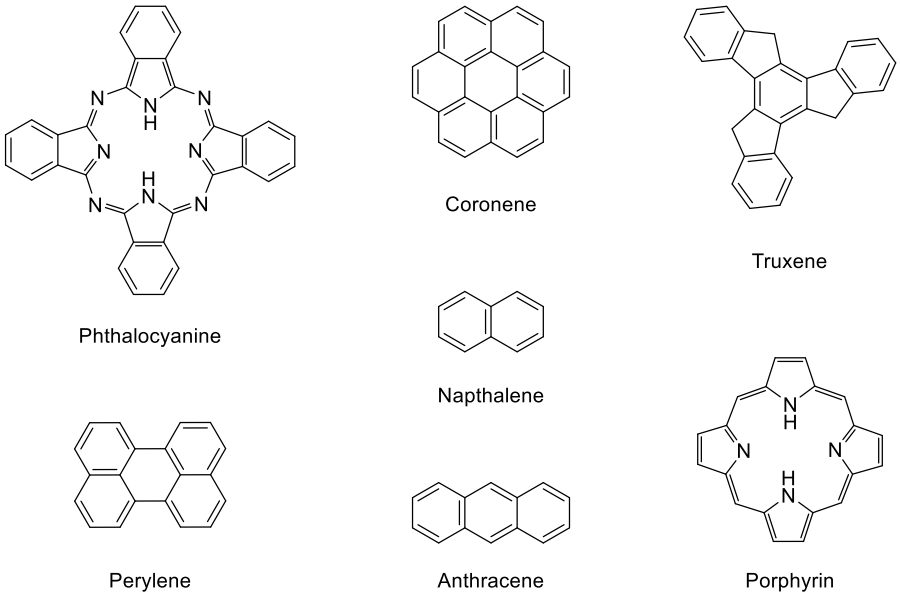


Figure 1.4: Other cores that exhibit DLC mesophases

1.3.1.1 Nematic Phase

Nematic discotic liquid crystals have very little order, the mesogens are arranged parallel to one another, with orientational order but no long-range positional order. The short axis of the molecules defines the director as shown in Figure 1.5.

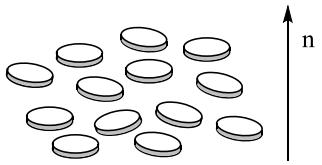


Figure 1.5: Arrangement of molecules in nematic discotic mesophase

In 1981 it was reported that triphenylen-2,3,6,7,10,11-hexayl hexakis(4-n-alkoxybenzoates) (Figure 1.6) form nematic discotic mesophases. [18]

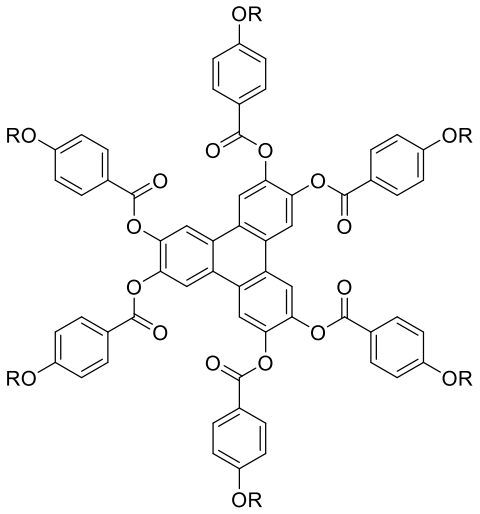


Figure 1.6: Structure of triphenylen-2,3,6,7,10,11-hexayl hexakis(4-*n*-alkoxybenzoate)

Subsequent work in the triphenylene-hexabenzoate series of compounds has shown that introducing methyl groups *ortho* to the ester linkage supresses columnar mesophase formation and only N_D mesophases are observed (Figure 1.7).[19] While methyl groups *meta* to the ester link group also supress the columnar mesophase, they also exhibit the hexagonal disordered columnar mesophase. Where the methyl groups point towards the triphenylene core, the steric interactions force the phenyl rings out of the plane of the triphenylene core, this decreases the face-to-face interaction that promotes columnar phases, meaning only nematic discotic phases are observed.

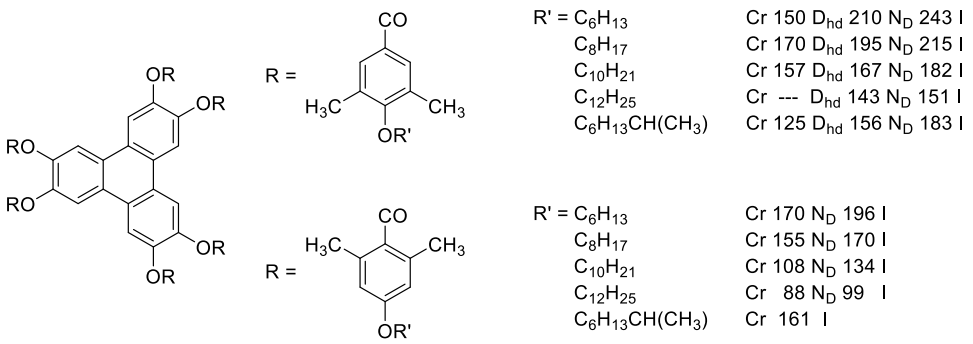
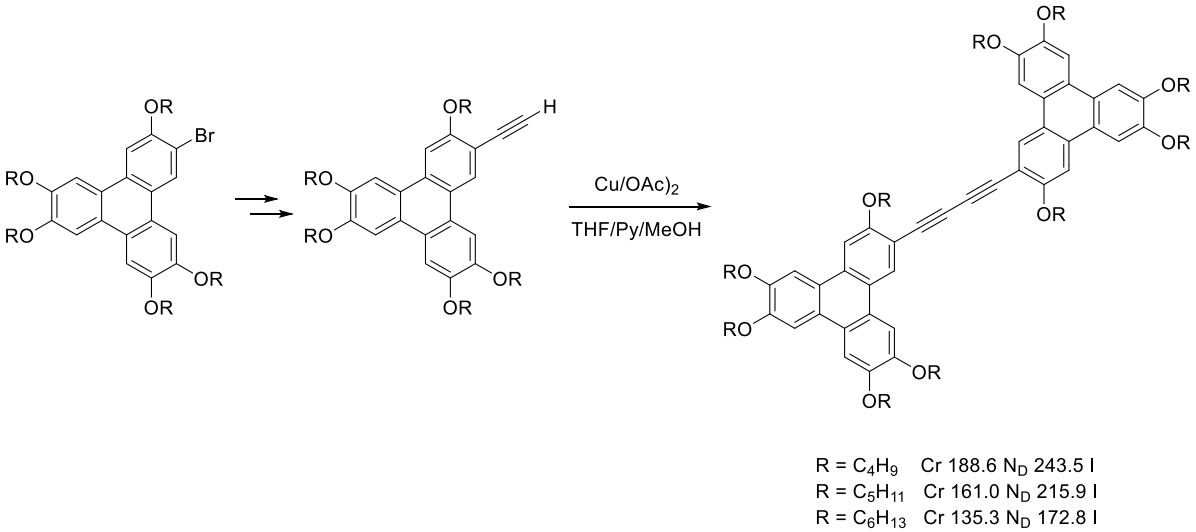


Figure 1.7: Effect of methyl position on mesophase behaviour

Due to the difficulties in designing discotic mesogens to form nematic discotic phases, there are few that have been reported. Since the work on the triphenylene-hexabenzoate series, the focus has shifted to synthesising triphenylene dimers. To form nematic discotic phases, the π-π interactions need to be dimished, in 2002 Kumar showed that linking two triphenylene units *via* a rigid conjugated spacer yielded nematic material[20] (Scheme 1.15).



Scheme 1.15: Synthesis of triphenylene dimer showing nematic mesophases

The dimers were linked by a diacetylene bridge and they showed nematic mesophases over a wide temperature range. Interestingly, the monomers showed only ordered columnar mesophases.

1.3.1.2 Nematic Columnar Mesophase

The nematic columnar mesophase (N_C) is induced by the charge-transfer interactions that arise between a donor molecule and an acceptor. The molecules are stacked in columns with short-range orientational order, but the assembled columns do not form a 2D lattice; due to the difference in length of side chains.

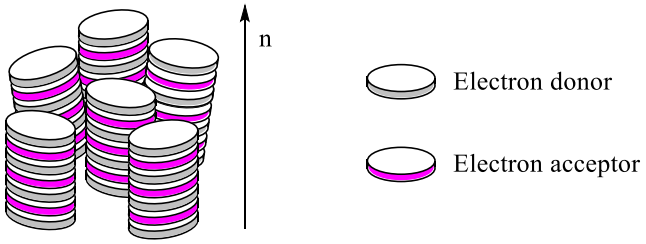


Figure 1.8: Arrangement of molecules in the N_C phase.

1.3.1.3 Nematic Lateral Mesophase

In 2001 a novel discotic mesophase was discovered, the nematic lateral (N_L) phase[21]. They showed that a charge-transfer complex between an electron acceptor and an electron donor form the N_L mesophase. The molecules are arranged into disk-shaped superstructure which exhibit the nematic arrangement (Figure 1.9).

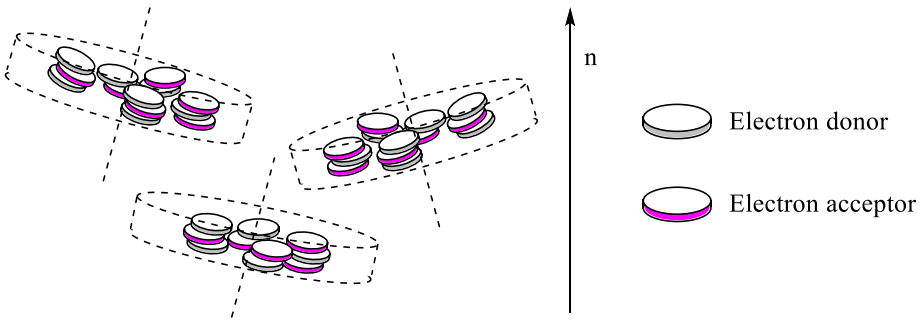


Figure 1.9: Arrangement of molecules in the N_L phase.

1.3.1.4 Columnar Phases

Columnar mesophases have been known since disk-shaped molecules were first shown to form liquid crystal phases in 1977.[17] The mesogens stack on top of each other into columns due to the large π-π interactions between the aromatic cores; as a result of this, the majority of discotic liquid crystals formed are columnar DLCs. The columns formed form part of a larger 2D lattice. There are a number of symmetries known, some of these are shown in Figure 1.10.

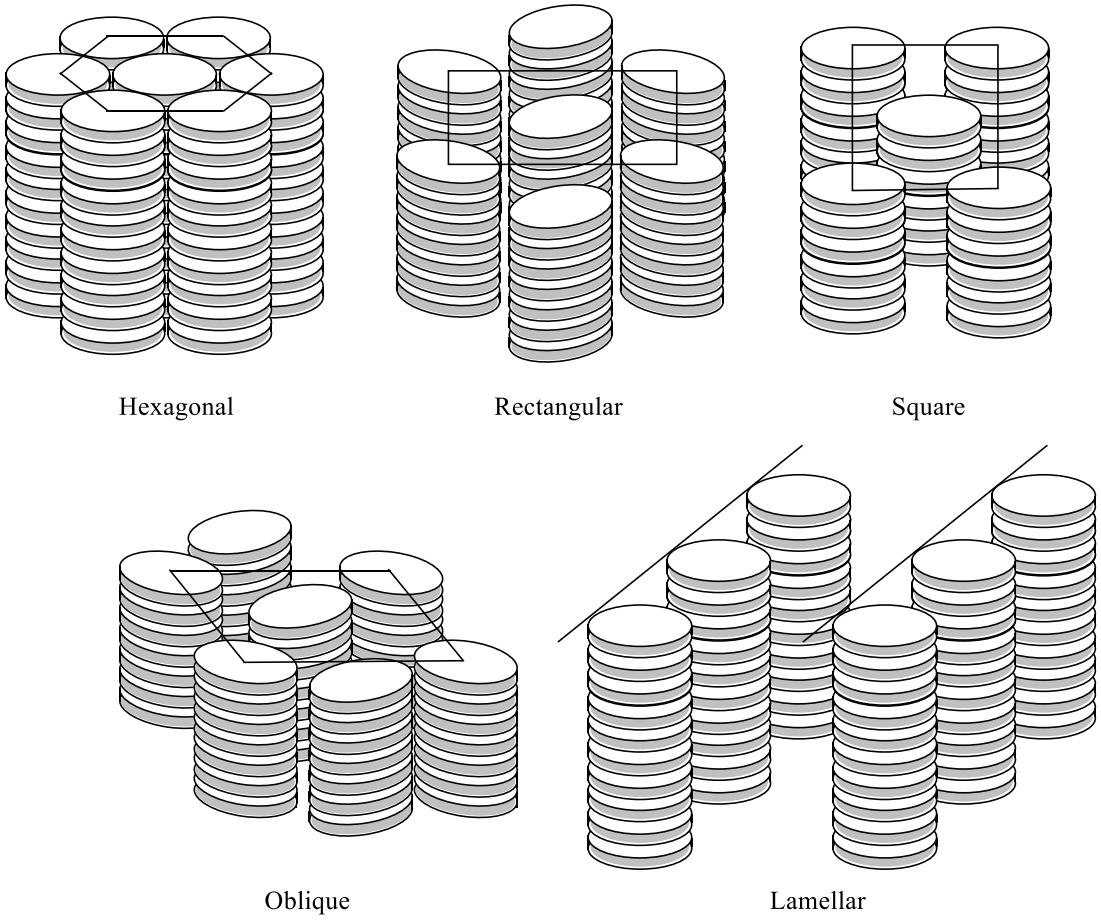


Figure 1.10: Symmetries of columnar DLC 2D lattices

Within the columns the mesogens can be in a regularly ordered pattern or disordered (Figure 1.11)

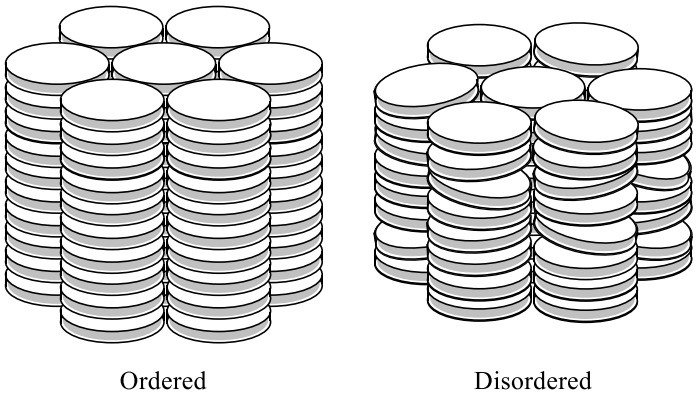


Figure 1.11: Ordering of mesogens within columnar phase

A number of triphenylene derivatives have been shown to form columnar mesophases, some examples are shown Figure 1.12.

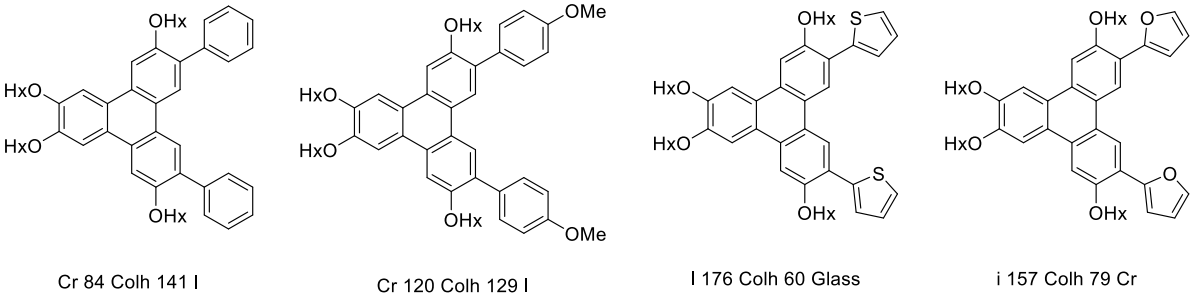


Figure 1.12: Triphenylene derivatives showing columnar mesophases

1.3.1.5 Smectic Phase

As mentioned before, the smectic mesophase is rarely observed in discotic mesogens, however it has been shown that where there is either a reduced number of peripheral chains, or an uneven distibution of said chains, a smectic mesophase is observed.[22,23] The smectic phase is also known as the discotic lamellar phase, denoted D_L.

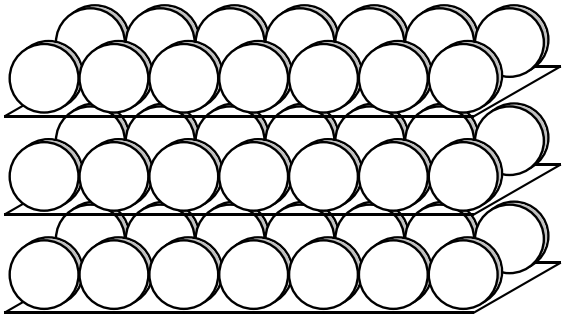


Figure 1.13: Arrangement of molecules in the D_L phase.

1.3.1.6 Cubic Phase

The cubic phase is commonly observed in lytropic liquid crystals (meaning they form as a function of solvent), although in discotic mesogens it is very rare, having only been recorded being formed by phthalocyanine derivatives.[24] The structure is made of linked, branched columns that form a cubic lattice.

1.4 Applications

Triphenylene derivatives have a wide range of applications, many due to the liquid crystalline properties many derivatives possess. These applications will be discussed herein.

1.4.1 Organic Light Emitting Diodes

In 2001 Hanack *et al*. reported conjugated bridged triphenylene derivatives showing electroluminescent properties. These compounds were able to 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.[25] They have two main benefits over liquid crystal displays (LCD), first they do not require a backlight so are much thinner and lighter, secondly they can be viewed from a range of angles. 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 π-conjugation in the molecule.[26] Wendorff *et al*. showed in 1997 that triphenylene derivatives **33** can be used in single layer OLED. Then in 2001 Hanack *et al*. reported conjugated bridged triphenylene derivatives **34** showing eletroluminescent properties that could be used as the emissive layer in an OLED. They showed that their triphenylene derivatives could be used in single and double layer displays.

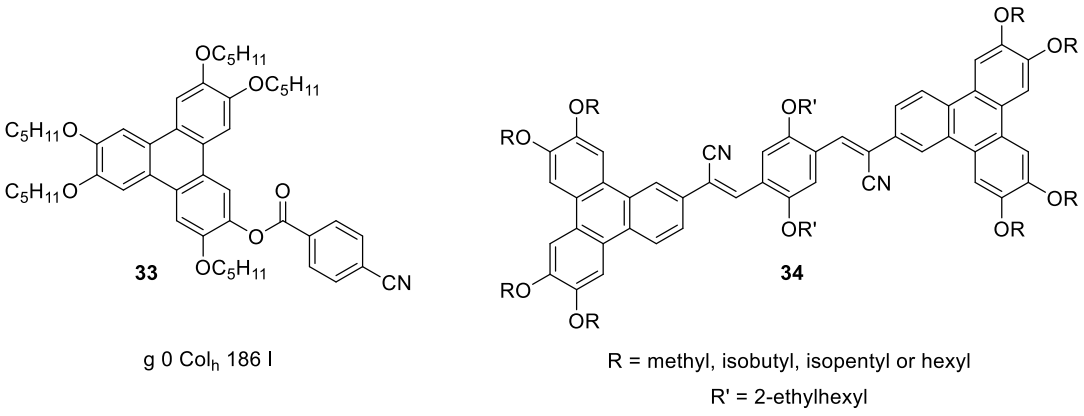


Figure 1.14: Triphenylene derivatives utilised in OLED devices

1.4.2 Optical Compensation Films for LCDs

Liquid crystal display (LCD) devices have been dominated by calamitic LCs since they were invented.[27] A 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.[28]

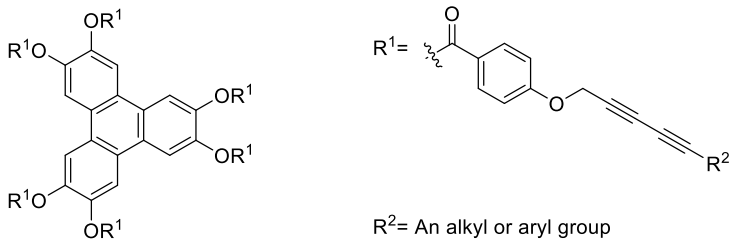


Figure 1.15: Example of TP based DLC patented by Fuji Photo Film Company

This negative birefringence optical compensation film was used to overcome the issues of the narrow viewing angle of the compounds utilised in the LCDs, and the slow optical speed. 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.[29]

1.4.3 One-dimensional Energy Migration

Columnar liquid crystals have been reported as one-dimensional systems for electronic excitation transport since 1987.[30] 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.

1.4.4 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.[31] These TP systems were highly sensitive to the prescence of volatile substances, including non-polar molecules such as alkane hydrocarbons, and also alcohols, ester 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 CO_2 over CH_4 and N_2.[32] 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.

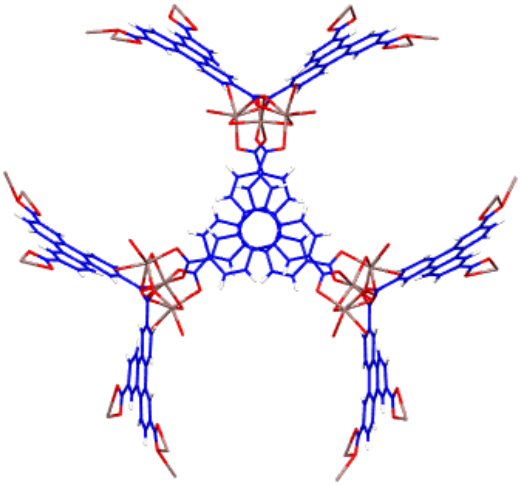


Figure 1.16: Crystal structure of TP-MOF {crystal data used from SI of paper}[32]

1.4.5 Organic Field-Effect Transistors

The concept of a field-effect transistor (FET) was first realised by Lilienfield in 1930, however the first metal oxide semiconductor FET was not fabricated until 1960. Since then, the first organic field-effect transistor (OFET) was designed that used polythiophene as the active semiconducting material. The OFET had two major advantages, the cost of materials

and manufactoring were reduced and the device became more environmentally friendly. Triphenylene derivatives had not been widely reported in the area of OFETs due to their high bandgap energy which results in poor semi-conducting properties. However in 2005 a paper from Hoang *et al*. described the design and synthesis of new semi-conducting materials based on the triphenylene core that are applicable to OFETs. The compounds synthesised are thiophene-based π-extended triphenylenes (Figure 1.17). They were shown to have good film forming properties, a high degree of crystallinity and lower optical bandgap energies (with repect to other reported triphenylene derivatives). The mobilities of the compounds were not very high but further work into the synthesis of new triphenylene derivatives for future OFET fabrication is ongoing.

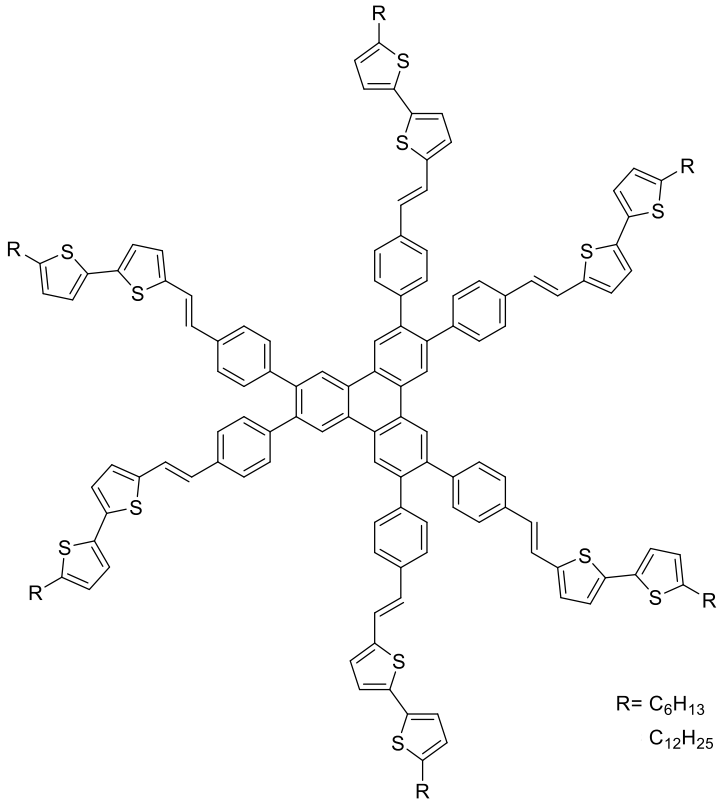


Figure 1.17: Structure of thiophene based π-extended triphenlyene for OFET fabrication

1.4.6 Photovoltaic Solar Cells

Triphenylene moieties have also been utilised in photovoltaic solar cells, Chen *et al*. modified zinc oxide nanoparticles to introduce dithiol-functionalised triphenylene ligands (Figure

1.18).[33] They found that the modified nanoparticles enhanced the charge separation and transfer efficiency.

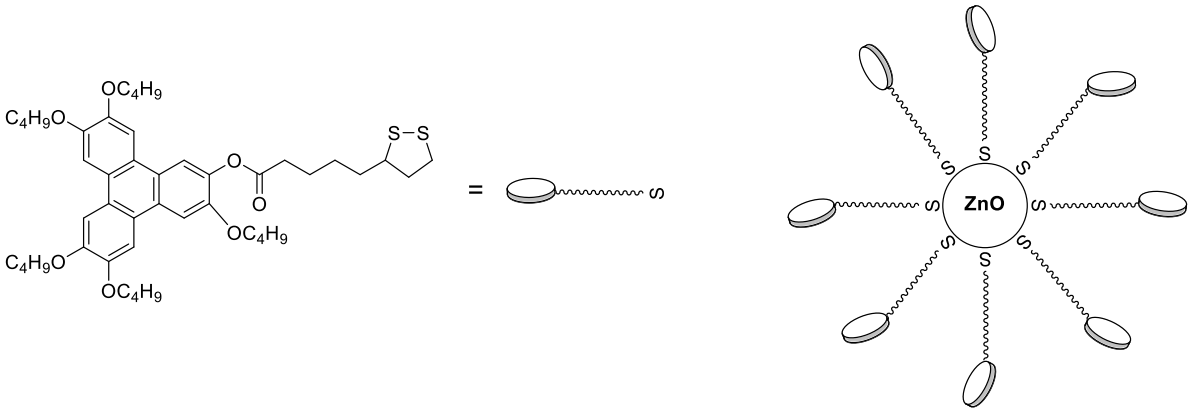


Figure 1.18: Structure of dithiol-triphenylene ligand, structure of ZnO nanoparticle modified with triphenylene ligands

After the modification of the nanoparticles, the power conversion efficiency of the solar cells increased from 0.45% to 0.95%, this efficiency is still considered low for practical applications, however it is a step in the right direction and further improvements are being investigated.

1.4.7 Other Applications

Measurements of conductivity and photoconductivity show that triphenylene mesophases behave as one-dimensional semiconductors.[34, 35, 36]

1.5 Dimers

Recently the focus in synthesis of triphenylene derivatives has shifted to the formation of dimer or twinned compounds. A definition of dimer in relation to liquid crystals means two mesogenic groups that are linked by either a flexible or rigid spacer.[37] The term ‘diad’ will be used to describe two triphenylene units linked by one spacer, while the term ‘twin’ will be used to describe two triphenylene units linked by two spacers (Figure 1.19). There are many examples of diads in the literature, however only a few examples exist of twinned triphenylene compounds.

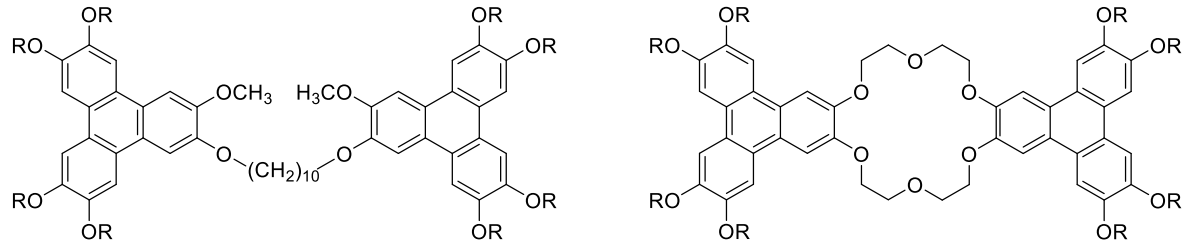


Figure 1.19: Structures to show meaning of terms ‘diad’[38] and twin’[39]

In 1995 the diad and triad in Figure 1.20 were reported,[38] they both formed glassy mesophases that slowly crystallised at room temperature. The formation of these ordered glassy films shows that triphenylene dimers display some properties of polymers.

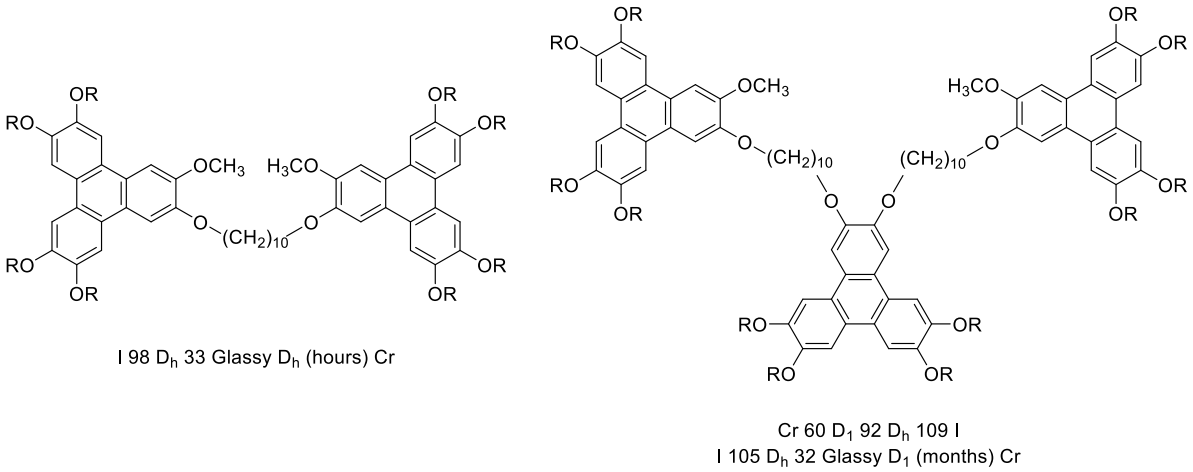
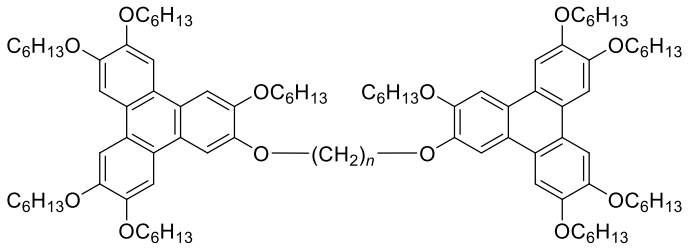


Figure 1.20: Structures of Diad and Triad synthesised by Boden *et al*.[38]

In 1999, Boden *et al*. did some further work on these diads and discovered more features of their liquid crystalline proprties.[40] They found that the length of the spacer greatly influences the behaviour of the diad, if the spacer is too short then the diad will not be liquid crystalline (Figure 1.21). The effect on the formation of a glassy phase was also seen, with the lifetime of the glassy state decreasing as the length of the spacer increases.



n =				
3	Cr 81	I		
5	Cr 98	I		
7	Cr 69	I		
8	Cr 58	Col_h 91	I	T_g 35 (*ca.* 18 hr)
9	Cr 72	Col_h 92	I	T_g 35 (*ca.* 15 hr)
10	Cr 50	Col_h 104	I	T_g 35 (*ca.* 11 hr)
12	Cr 68	Col_h 107	I	T_g 35 (*ca.* 12 hr)
16	Cr 41	Col_h 84	I	T_g 35 (*ca.* 3 hr)

Figure 1.21: DSC data for triphenylene diad above

A triphenylene diad linked by a phenylene dicarbamate unit was synthesised **35** (Figure 1.22), that also had good film forming properties, compared to the monomer.[41] This was thought to be due to the prescence of the flexible spacer and the hydrogen bonds forming between diads. This compound was found to have application in OLEDs due to the charge carrier mobility and good hole transporting properties of the diad.

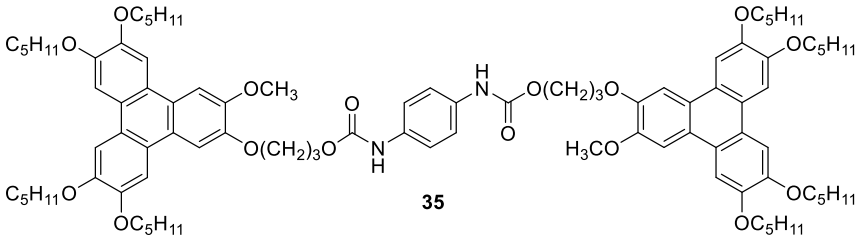


Figure 1.22: Triphenylene diad linked by a phenylene dicarbamate unit.[41]

In 2009 a range of diads linked by acetylene units were synthesised, the results showed that the dimers formed more stable, ordered columnar mesophases that the corresponing monomers and also improved semiconductive properties.[42] They also found that the high symmetry of **36** enhanced the π-π interaction between the triphenylene cores which also improved the formation of ordered columnar mesophases.

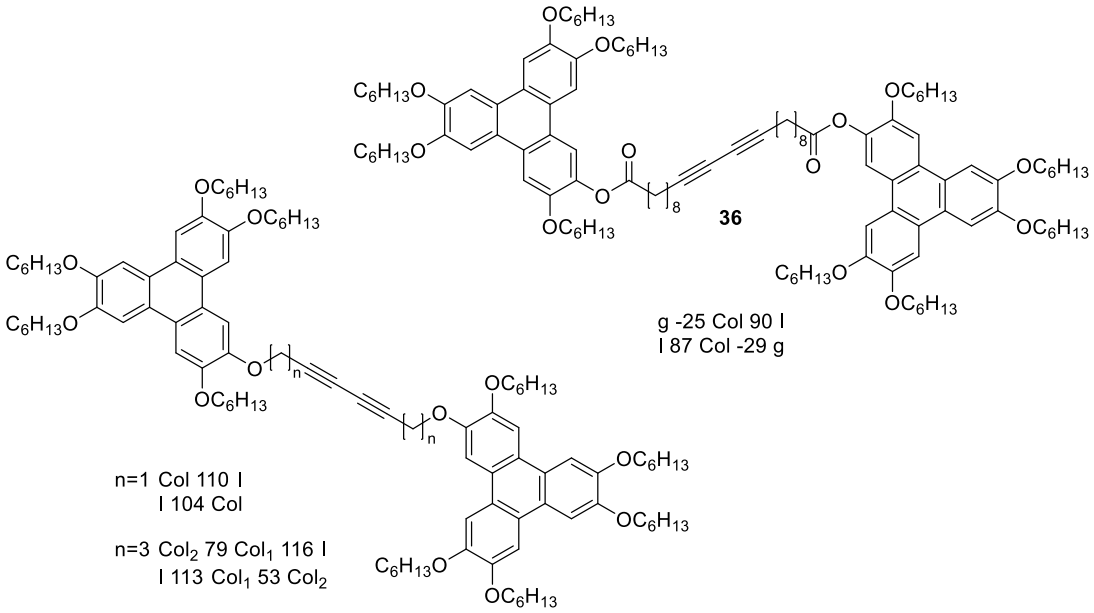


Figure 1.23: Acetylene linked triphenylene diads.[42]

More recently a triphenylene diad has been prepared by click chemistry, linking the triphenylene units *via* a triazole.[43] Neier *et al.* synthesised two diads, one linked by -CH_2- unit, and the other linked by a phenyl group; the idea being that the added aromatic group would aid the formation of columnar mesophases. However, on analysis of the diads they found that only the -CH_2- linked dimer showed mesophase behaviour. The group postulated

the reason stated by Kumar that the rigidity of the extra aromatic ring reduces the flexibilty the spacer provides, making the stacking of the triphenylene cores more difficult.[44]

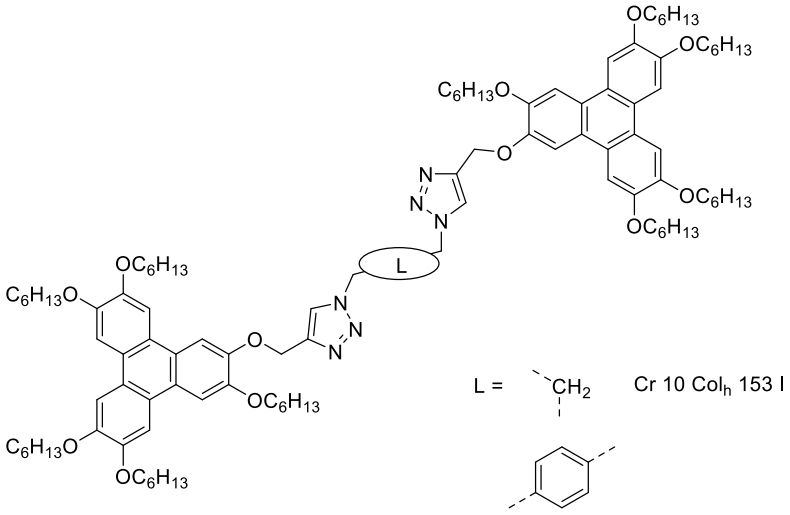


Figure 1.24: Triazole linked triphenylene diad.[43]

As these examples show, triphenylene diads show more ordered columnar mesophases over a wider temperature range than their counterpart monomers. The flexible spacer increases the order in the columnar mesophase by avoiding slippage from columns and fluctuation in the column. These properties led to the study being extended into the synthesis of triphenylene twins.

In 1998 the spiro twins **37** were synthesised,[45] it was thought that the twist in the spiro centre may stop the formation of columnar mesophases. However, it was found that this was not the case, columnar mesophases were seen and the compounds shown to have potential application in photo conductivity.

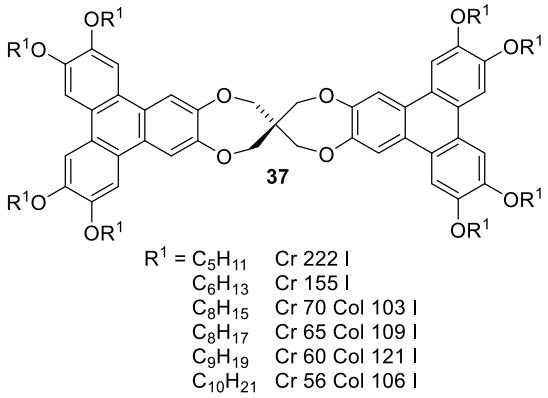


Figure 1.25: Triphenylene spiro twins [45]

Crown-ether linked triphenylene twin and triad were synthesised in 2010 by Cammidge *et al*.[39] They found that the twin compound **38** showed no mesophase behaviour, while the more flexible triad **39** showed columnar mesophases, with potential application in optoelectronic device applications.

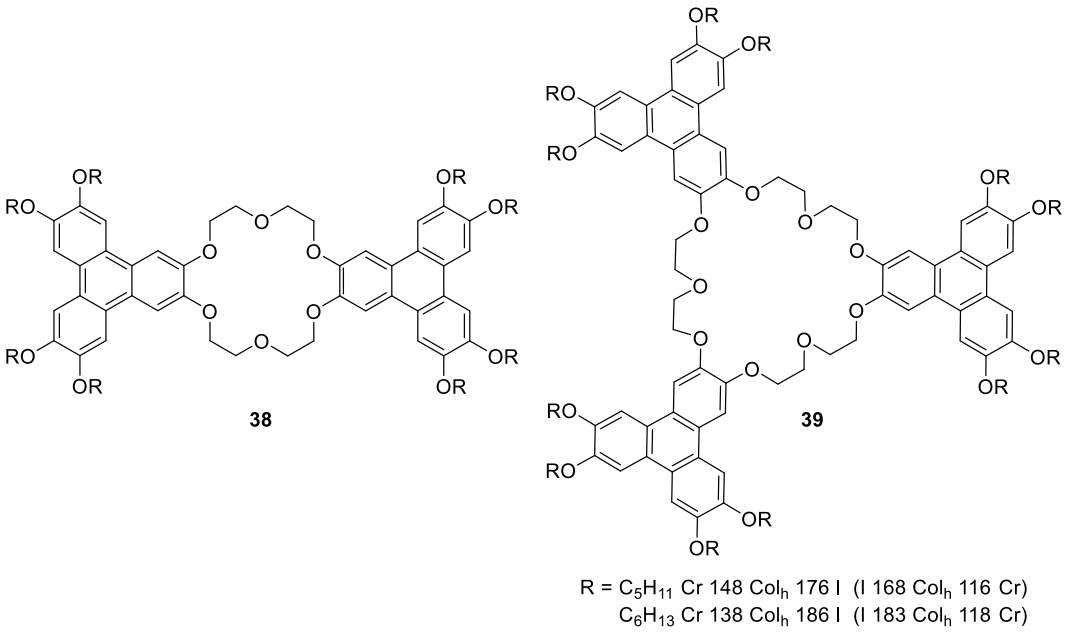


Figure 1.26: Crown-ether linked triphenylene twin and triad[39]

Antiaromatic triphenylene twins bridged by acetylenes were also synthesised in 2010 by Cammidge *et al*.[46] They originally followed a similar structure to the crown ether twin **38**, linking the triphenylenes through the *ortho*-sites, however they found that the twinned product readily decomposed through pericyclic reactions. Therefore, they synthesised the twin linked through 3,6-positions which avoided the decomposition problems but kept the antiaromatic core.

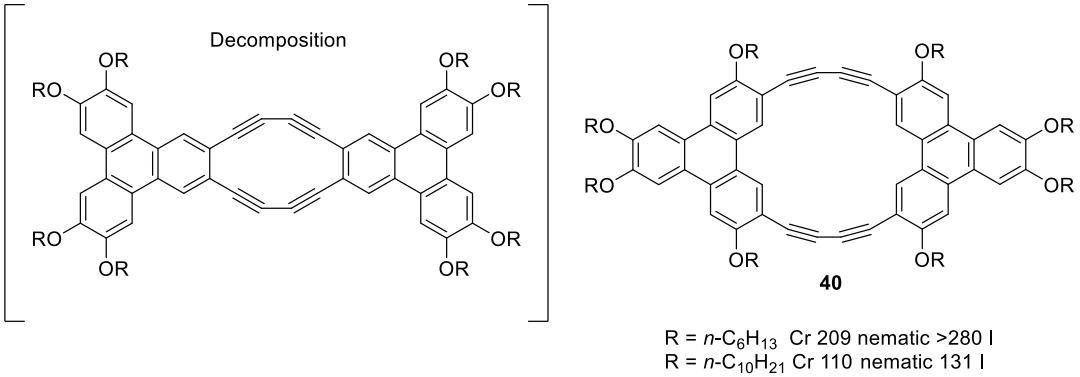


Figure 1.27: Antiaromatic triphenylene twin linked by acetylene bridges

This twin was shown to form a stable, planar, board-like molecule that formed a nematic mesophase on heating. The crystal structure showed an interesting property in how the molecules are packed in the crystal, column formation is not possible as this would leave a free space from the void in the twin, therefore the twins stack in an overlapping formation, as can be seen in the cartoon illustration in Figure 1.28. This accounts for the observed nematic mesophase, and means that communication is possible both through the columns and also along the rows.

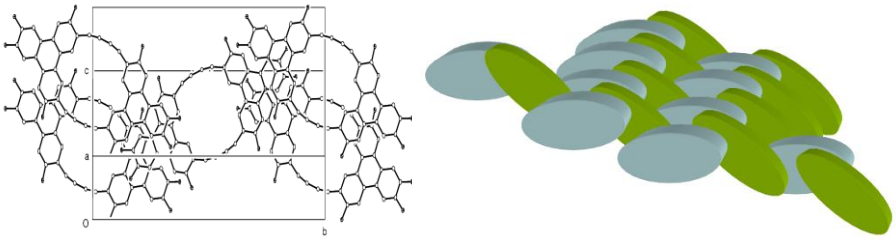


Figure 1.28: Crystal structure of **40** and cartoon of packing in crystal

Another class of acetylene bridged triphenylene twins was synthesised in 2011 (Figure 1.29).[47] The phenyl-substituted triphenylene twin formed well ordered 2D-structures, and was shown to be more conjugated in the ground state than in the excited state. This was postulated to be due to the constrained shape causing a bend in the diacetylene bridge.

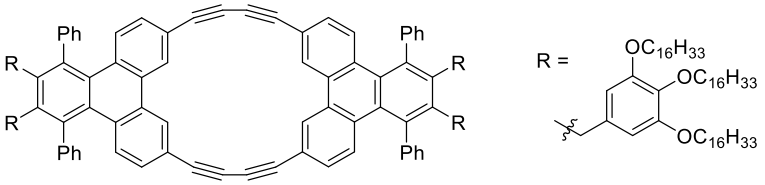
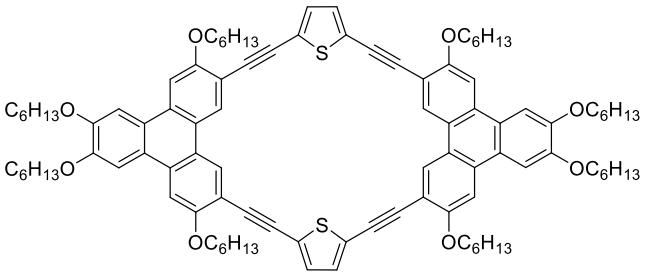


Figure 1.29: Phenyl-substituted triphenylene twin linked by acetylene units.

The idea of creating a void region in the centre of the twin to force nematic behaviour lead to further functionalised twins to be targeted. In 2012, Cammidge *et al*. published the synthesis of triphenylene twins linked through thiophene bridges, structure **41**.[48] Thiophene was chosen as it would allow communication through the twin, and would form a less strained twin than other aryl groups, for example phenyl. The twin showed only a nematic mesophase, and was again a formally antiaromatic system, which showed in its strong Stokes-shifted fluorescence at around 500 nm.

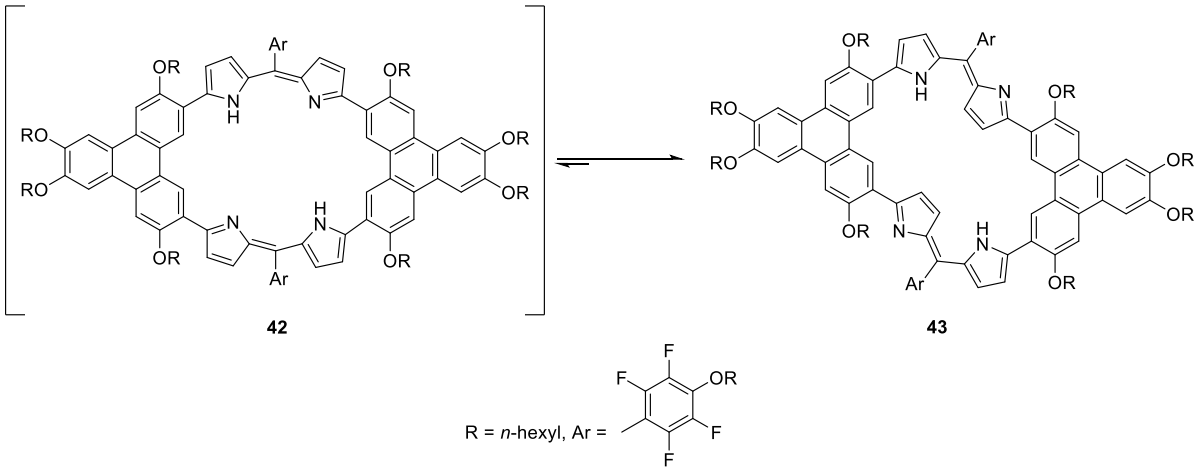


41

Cr 69 Cr 291 N_D 300

Figure 1.30: Thiophene linked triphenylene twin

Most recently, Cammidge *et al*. published the synthesis of a triphenylene twin linked by pyrrole.[49] The twin was targeted as it was thought to have a porphyrin-like structure, and would therefore have similar properties such as the ability to coordinate metals. However, the crystal structure showed that the molecule adopts a strain-free configuration where the pyrroles face in opposite directions. It was found that the twins shared more properties with dipyrromethenes, although whereas dipyrromethenes are generally unstable in air/light, the triphenylene twin had good stability in both. The twin was again formally antiaromatic, however this time the absorption spectra were similar to the spectra for the triphenylene diads, suggesting that the effect of conjugation is localised leading to little antiaromatic behaviour being observed. The twin was stable beyond 300 ^{o}C therefore observation of any mesophase formation was not possible.



Scheme 1.16: Pyrrole linked triphenylene twin, target **42** and preferred conformation **43**

1.6 Aims of Project

The scope of triphenylene twins has not been fully recognised, therefore in order to investigate these structures more throughly more ambitious targets have been created. Different methods of synthesising heterocyclicly linked triphenylene twins will be investigated. The twinning of triphenylene twins has been proven to force nematic behaviour and keep communication between the two triphenylene moieties. As discussed, nematic behaviour is rare in triphenylene derivatives as they more commonly stack into columns, however the prescence of a void prevents this. Our aim is to synthesise more complex twinned structures through creating new methodologies to introduce different functionalities to the triphenylene.

Chapter 2

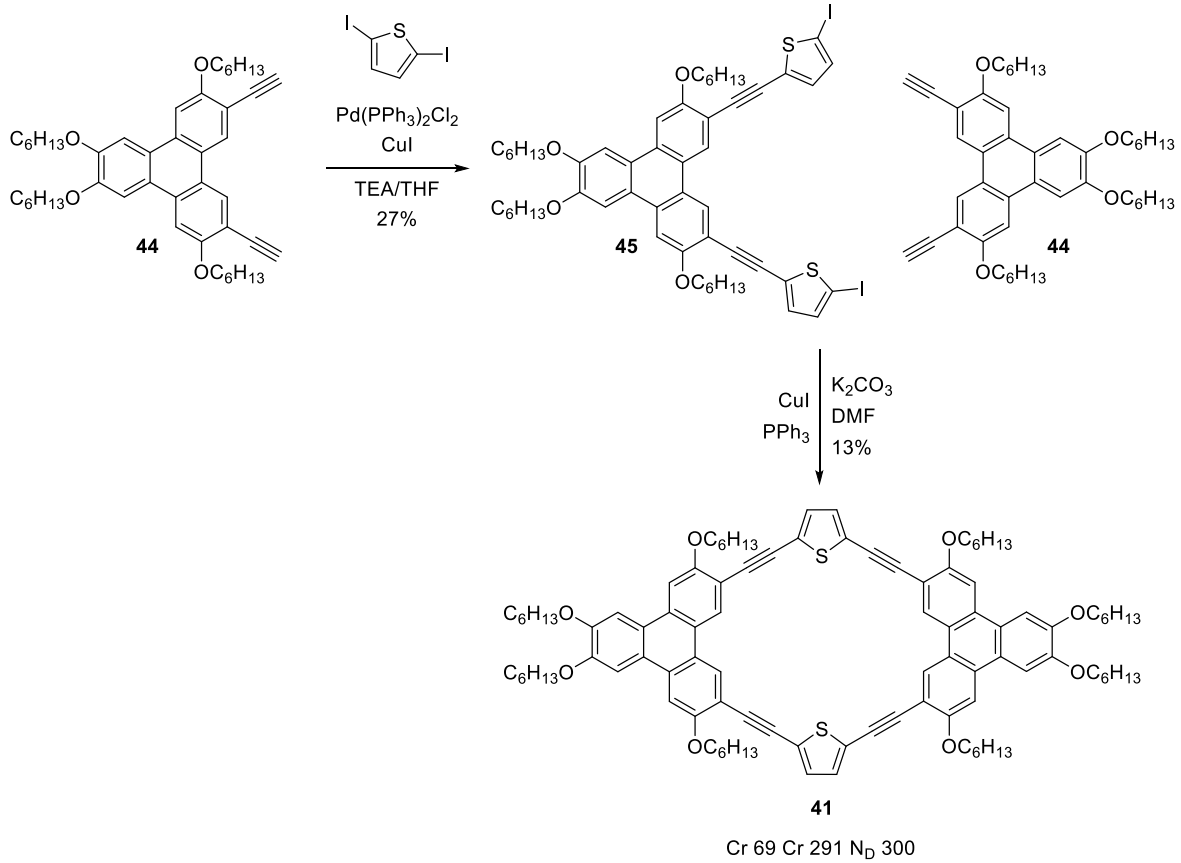
Results and Discussion

2.1 Synthesis of Dipyrrolyltriphenylene and Attempts at the Synthesis of Twins

2.1.1 Background and Previous Work from our Group

Our group has been interested in rigidly fused triphenylene twin structures for some time. The first such twin, **40**, displayed nematic behaviour,[46] and led to the design and investigation of more elaborate twins, for example those linked through heterocycles.

Work into the synthesis of heterocycle-linked triphenylene twins successfully included incorporation of thiophene units.[48] The synthesis of acetylene-thiophene twin **41** is shown in Scheme 2.1. The thiophene bridge was chosen as it allows communication throughout the twin; also the strain in the structure is minimal due to the matched bonding angles. The twin was synthesised in a stepwise fashion, starting by introducing the thiophene moiety *via* Sonogashira coupling between triphenylene diacetylene **44** and excess 2,5-diiodothiophene. Macrocyclisation to form the twin was achieved by another coupling between **45** and its precursor **44**. Nematic mesophase behaviour was also observed for this twin.



Scheme 2.1: Synthesis of acetylene-thiophene twin **41**

The next challenge, and the starting point for this project, targeted triphenylene twins where the linking heterocycles (thiophene and pyrrole) were directly bonded to the triphenylene units. Methine linkages then complete the macrocycle giving full conjugation (Figure 2.1).

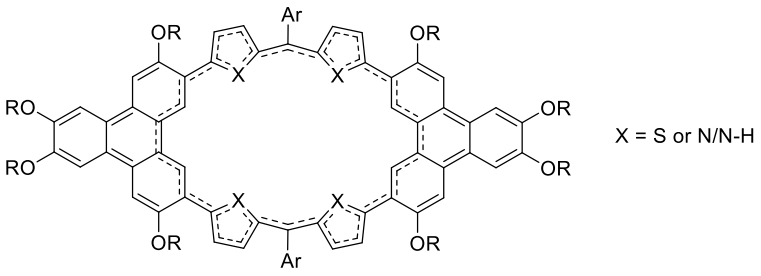
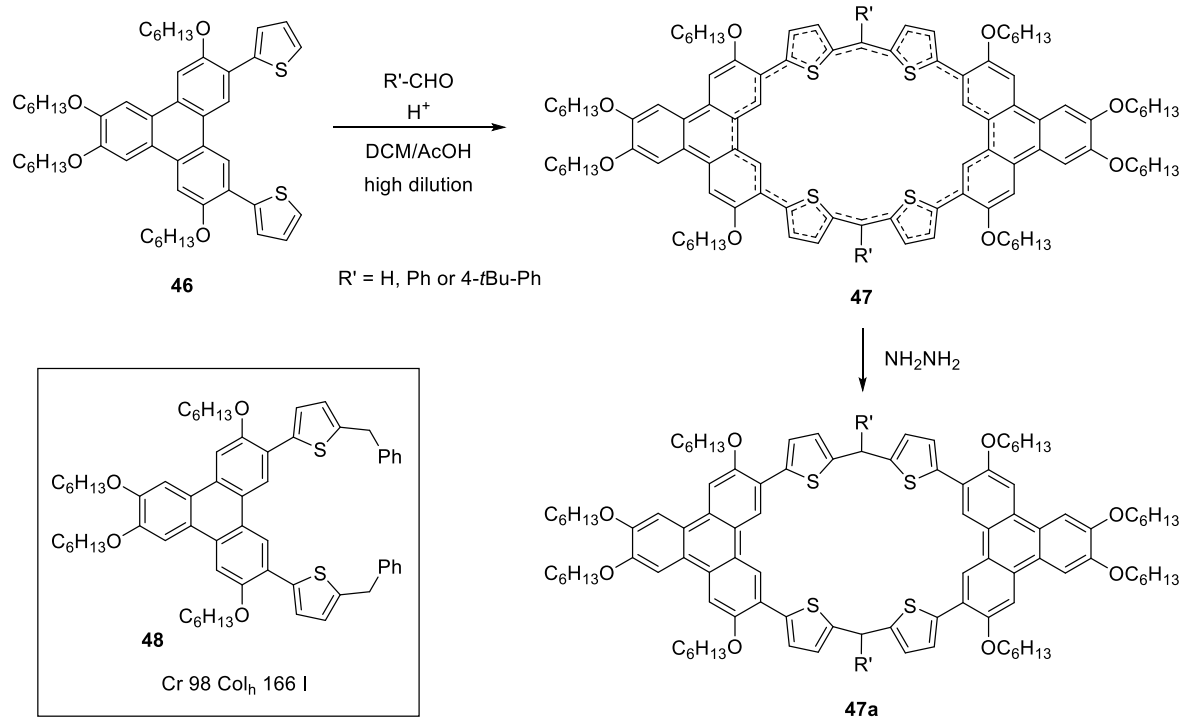


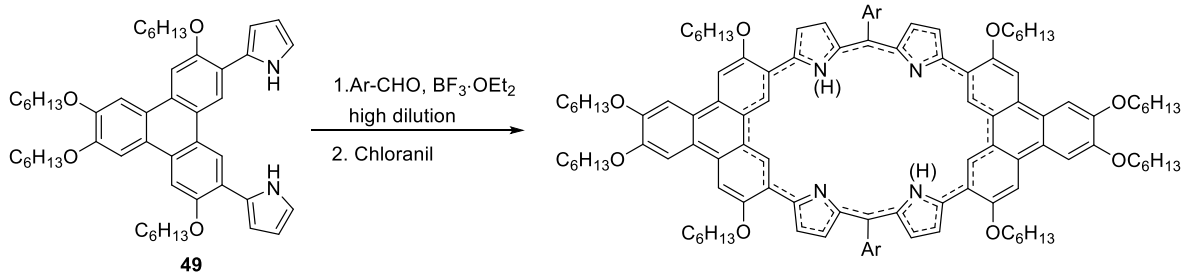
Figure 2.1: New triphenylene twin target structure

Some preliminary investigations had already revealed potentially interesting outcomes from synthesis of the twins. The synthesis of the thiophene-linked twin is shown in Scheme 2.2.[49] The reaction yielded a deep blue material with a mass spectrum corresponding to **47**. However, the samples gave no signals when analysed by ^{1}H-NMR spectroscopy making characterisation difficult. It is interesting to note that the reaction itself was further complicated by production of side products such as **48** (R′=Ph). Later, twin **47** was reduced with hydrazine to give the methylene-bridged system, twin **47a**, that was fully characterised.



Scheme 2.2: Condensation reaction to thiophene twin **47a**

Attention was then turned to the analogous pyrrole linked twins. Initial work highlighted similar difficulties to those encountered in the thiophene twin – blue products were obtained which gave expected mass spectra (Scheme 2.3).[49] However, as previously, further characterisation was challenging. The investigation was then split between variation of the aldehyde partner and the triphenylene precursor. The latter formed the initial phase of this project.



Scheme 2.3: Synthesis of pyrrole-linked twins

In our effort to improve solubility (and eventually lower melting points to uncover mesophase behaviour) the targets were derivatives bearing decyloxy chains (**50**, Figure 2.2).

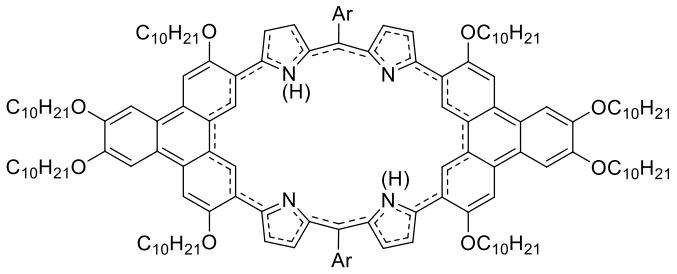
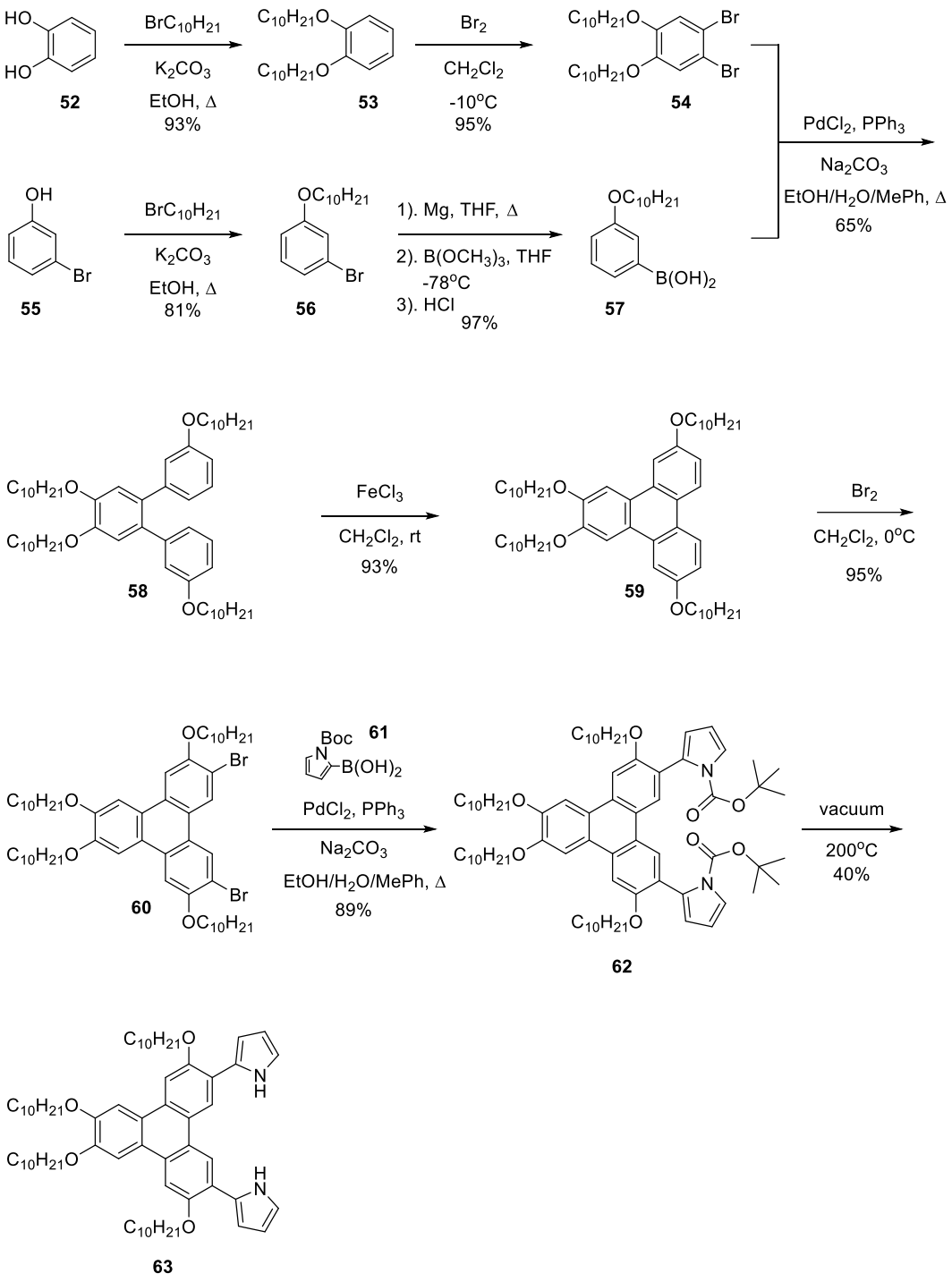


Figure 2.2: Pyrrole twin target structure **50**

2.1.2 Synthesis of 3,6,7,10-tetrakis(decyloxy)-2,11-bis(2-pyrrolyl) triphenylene 63

The key precursor to twin **50** is the dipyrrolyltriphenylene **63**. The full synthesis is shown in Scheme 2.4. The synthesis of the triphenylene moiety followed the procedure developed in our group in 2001,[3] and the synthesis starts from the relatively cheap and easy to handle 3-bromophenol **55** and catechol **52**. Pyrrole compounds are more difficult to handle than

thiophenes, so protecting steps were incorporated into the synthesis; the dipyrrolyltriphenylene was stored with the protecting group still in place, compound **62**, until it was needed for further synthesis.

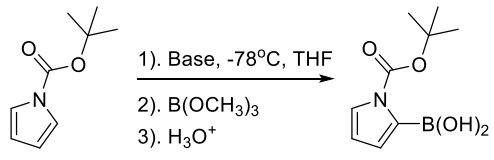


Scheme 2.4: Synthesis of dipyrrolyltriphenylene **63**

Catechol **52**, 1-bromodecane and potassium carbonate were stirred in ethanol under reflux to yield diether **53**. Subsequent bromination gave 1,2-dibromo-4,5-bisdecyloxybenzene **54**. Separately, 3-bromophenol **55** also underwent alkylation following the same conditions yielding **56**. Both compounds **53** and **56** were purified by vacuum distillation; the extension of the alkyl chain to ten carbons made distillation less straightforward, but the purifications were performed successfully and high yields were obtained.

Reaction of the bromide **56** with magnesium turnings formed the Grignard reagent which was reacted with trimethylborate to give the boronic acid **57** after work-up. A Suzuki-Miyaura cross coupling reaction was carried out between **54** and **57** yielding 1,2-bisdecyloxy-4,5-bis(3-decyloxyphenyl) benzene **58**. Ferric chloride induced oxidative ring closure of terphenyl **58** gave the corresponding triphenylene **59**, and another bromination gave 3,6-dibromo-2,7,10,11-tetrakis(decyloxy) triphenylene **60**.

In order to introduce the pyrrole moiety a Suzuki-Miyaura reaction was planned, meaning that the pyrrole boronic acid **61** needed to be synthesised. Initially, *n*-Boc-protected pyrrole **64** was bought and reacted first with LDA at -78^{o}C, then trimethylborate (Scheme 2.5). This gave us the desired pyrrole-boronic acid **61** after work-up, but the yield was poor (~38%). A literature search showed that higher yields had been obtained by using a more sterically hindered base formed from tetramethylpiperidine (TMP).[50] *n*-BuLi was added slowly to a solution of TMP in THF at -78^{o}C and the solution was warmed to 0^{o}C over 30 minutes, before being cooled again to -78^{o}C. *N*-Boc pyrrole **64** was then slowly added to the Li-TMP solution and the mixture stirred for 2 hours. Trimethylborate was added and the mixture allowed to warm to room temperature overnight. After an aqueous acidic work-up, *N*-Boc-pyrrole-2-boronic acid **61** was isolated in 70% yield. Boronic acid **61** was stored under a nitrogen atmosphere at -5^{o}C to avoid decomposition and prolong its usability.



64 **61**

Base = Yield = 38%

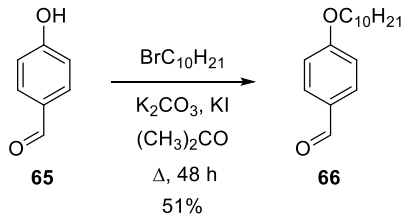
Yield = 70%

Scheme 2.5: Synthesis of *N*-Boc-pyrrole-2-boronic acid **61**

The planned Suzuki-Miyaura reaction was carried out between 3,6-dibromo-2,7,10,11-tetrakis(decyloxy) triphenylene **60** and *n*-Boc-pyrrole-2-boronic acid **61**, following the same conditions used to synthesise the terphenyl **58**. However, the reaction proved complicated and we discovered that the pyrrole product itself decomposed on prolonged heating. The reaction was monitored more carefully and worked-up immediately when it was deemed complete by TLC analysis. After purification by column chromatography, pyrrole **62** was stored at -5^{o}C under a nitrogen atmosphere until needed for subsequent reactions. When required, 3,6,7,10-tetrakis(decyloxy)-2,11-bis[2-(*N*-Boc-pyrrolyl)] triphenylene **62** was heated gradually to ~200^{o}C as a neat solid under vacuum. After cooling the product was rapidly purified by column chromatography yielding 3,6,7,10-tetrakis(decyloxy)-2,11-bis(2-pyrrolyl) triphenylene **63** as an off-white solid. This was used immediately in subsequent reactions.

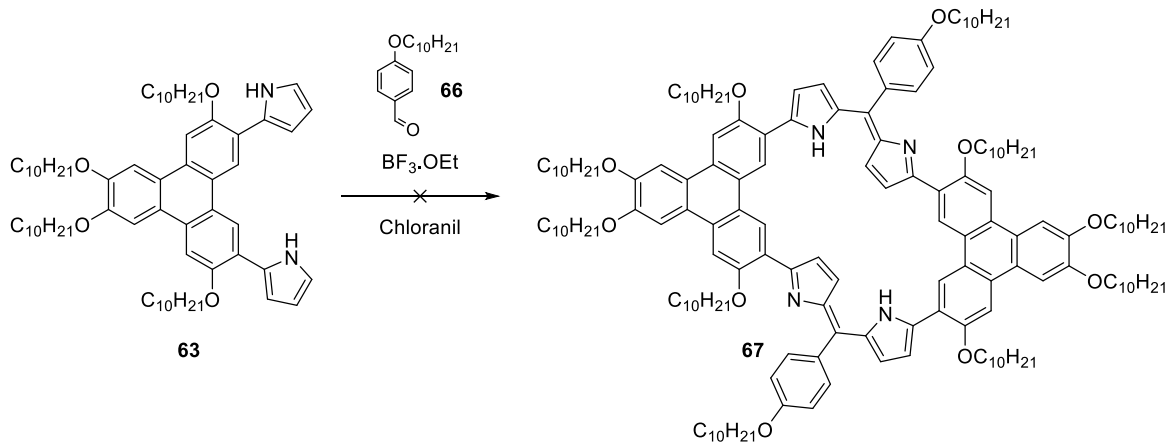
2.1.3 Attempt at Synthesis of Dipyrrole-Triphenylene Twin 69

For the initial attempts at synthesising the pyrrole twin **69**, 4-decyloxybenzaldehyde **66** was required for use in the condensation reaction. A simple alkylation of 4-hydroxybenzaldehyde **65** with 1-bromodecane gave benzaldehyde **66** in acceptable yield (Scheme 2.6).



Scheme 2.6: Synthesis of 4-decyloxybenzaldehyde **66**

Previous work on the synthesis of the hexyloxy-twin **43** had shown that high dilution conditions were necessary to promote the formation of the twinned compound over polymer products. These conditions were adopted for the synthesis of twin **67**.



Scheme 2.7: General conditions to synthesise pyrrole twin **67**

A 1:1 ratio of dipyrrolyltriphenylene **63** to benzaldehyde **66** was used and the mixture was dissolved in degassed dichloromethane and loaded into a syringe. The solution was added to a solution of boron trifluoride etherate in degassed dichloromethane, at a rate of 2 mL per hour (total addition time 10 hours). After the addition was complete, the reaction was stirred at room temperature for a further 24 hours. Chloranil was then added and the mixture stirred for another 2 hours. The mixture was neutralised with triethylamine and the solvents removed *in vacuo*. The crude product was analysed by MALDI-MS, but this showed no evidence for any twin products. The reaction was repeated, this time stirring the reaction for a further 48 hours before adding the chloroanil. The crude MALDI-MS analysis showed evidence of the desired twin (Figure 2.3). However, attempts at purification *via* column chromatography were unsuccessful, due to the formation of a large amount of side-products.

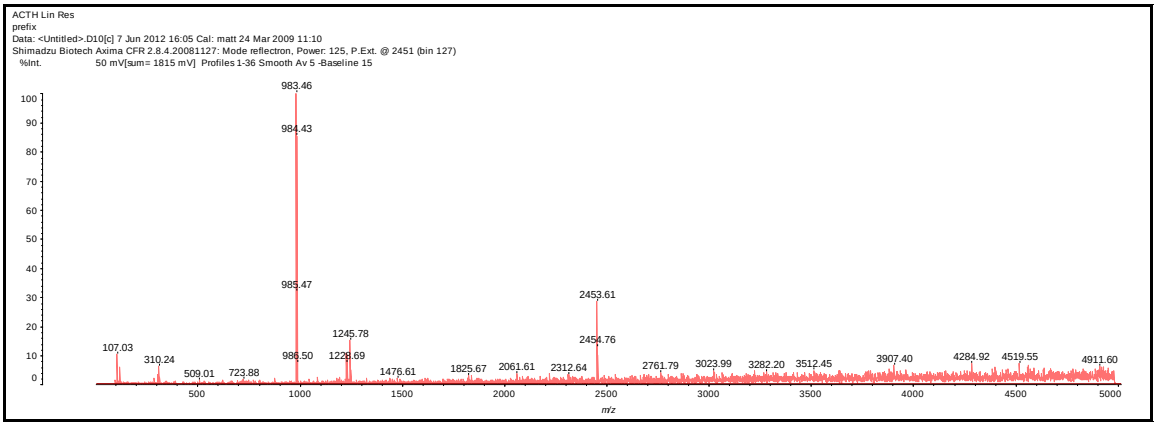


Figure 2.3: MALDI-MS possibly showing desired twin **67** with mass of 2254 amu.

In the next attempt, the aldehyde was changed to 4-*tert*-butylbenzaldehyde in order to simplify the twinning reaction. Also, the timing was increased to 72 hours and the reaction monitored closely by TLC. After the reaction had been stirred for 72 hours the crude product was analysed by MALDI-MS, showing evidence that the desired twin **68** was present (observation of a peak at 2252 *m/z*). Another significant peak was observed at 2111 *m/z* (Figure 2.5), this was found to represent the dipyrromethene-type twin **69** (Figure 2.4).

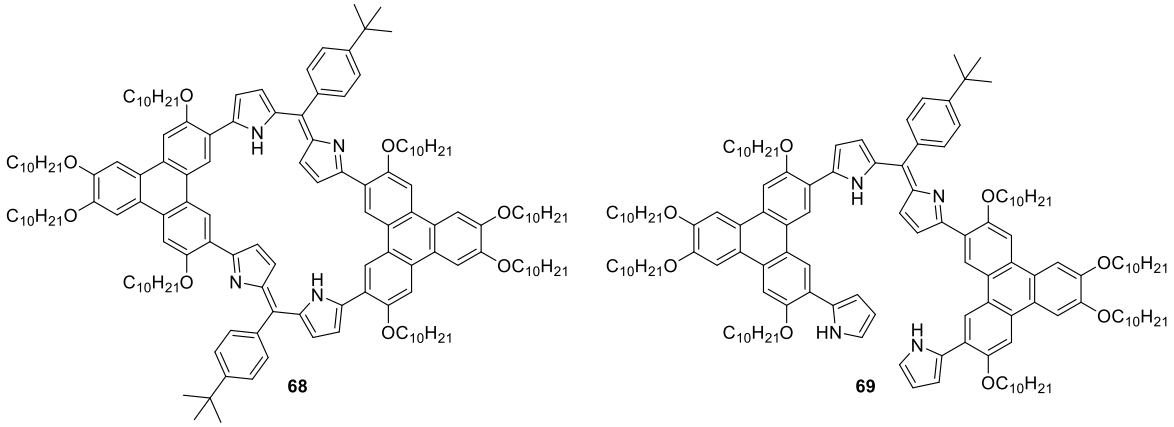


Figure 2.4: Structure of desired twin **68** and dipyrromethene-type twin **69**

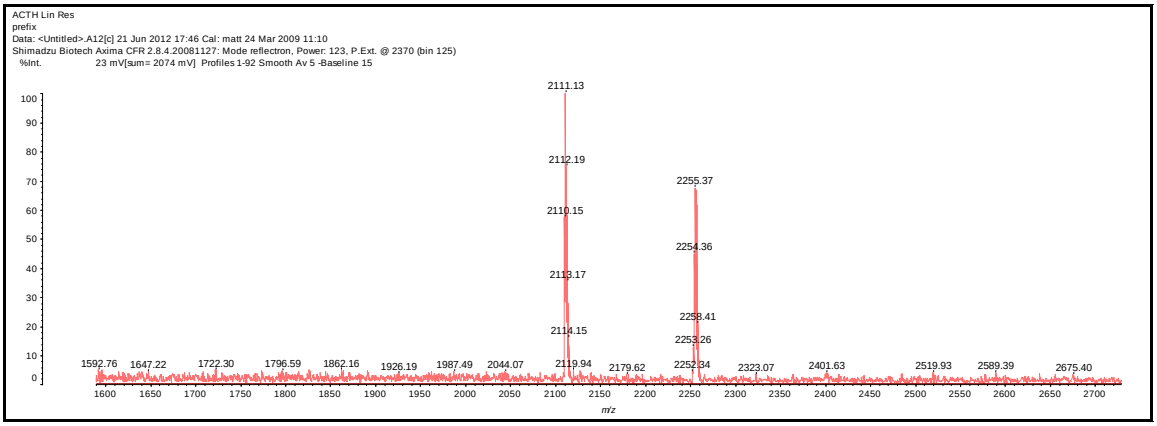
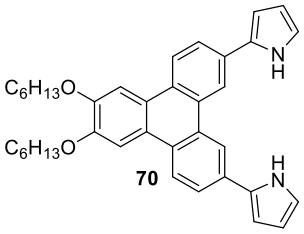


Figure 2.5: Crude MALDI-MS showing presence of twins **68** and **69**

Due to the presence of the desired twin **68**, the crude reaction was split into two; to one half a drop of the aldehyde was added (~10 mg), and to the other half, chloranil (~50 mg, 2 eq) was added. The aldehyde was added to push the reaction to form more of the desired twin, while the chloranil was added so that both compounds, as observed in MALDI-MS, could be isolated. However, again purification *via* column chromatography of both halves was not successful due to separation from the tar-like side products not being possible.

One possible reason for the twin not forming was the interference of the long alkyl chains, especially at the neighbouring positions to the pyrrole units. A new synthesis was designed to have just two alkyl chains on each triphenylene to remove this potential issue. Importantly though, we were particularly intrigued to see how the new, more board-like shape of the twins would affect its properties. We reverted to hexyloxy chains to simplify the synthetic manipulations. The key precursor that we targeted was therefore dipyrrolyltriphenylene **70** (Figure 2.6).



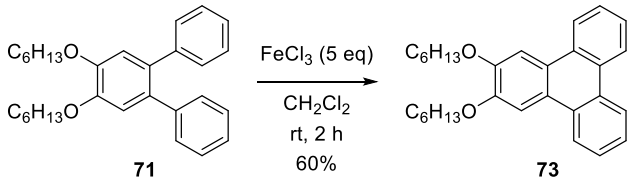
70

Figure 2.6: Key precursor dipyrrolyltriphenylene **70**

2.1.4 Development of the Synthesis of Dihexyloxytriphenylene 73

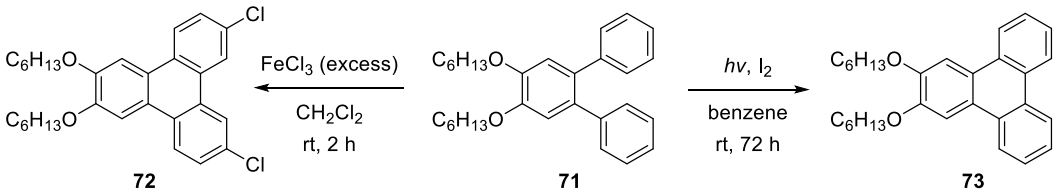
Previous work into the synthesis of 2,3-dialkoxytriphenylenes indicated complications with simple modification of our previously used method (synthesis of terphenyl and ring closure).[3] It was found that ring closure of the terphenyl **71** with ferric chloride in fact yielded the

chlorinated triphenylene product **72**. The desired triphenylene **73** could only be achieved by photochemical cyclisation (Scheme 2.8).[3] While photocyclisation is a useful tool in the synthesis of triphenylenes, it is also a slow reaction and difficult to scale up. For these reasons we decided to reinvestigate the original attempts at the synthesis of dihexyloxytriphenylene **73** *via* the ferric chloride method.



Scheme 2.8: Previous attempts at synthesis of dihexyloxytriphenylene **73**[3]

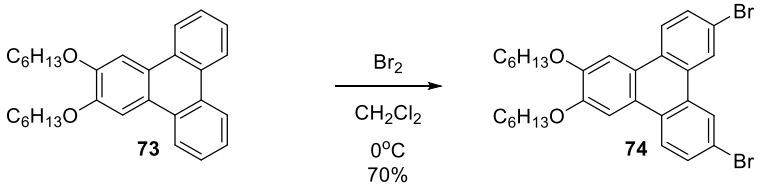
The reaction to form **72** was repeated following the original conditions, and it was found that the reaction did indeed give the chlorinated product **72**. When analysing the conditions used however, the ferric chloride was found to be used in great excess (around 30 equivalents). In the analogous reaction to form the C_{10}-triphenylene **59**, just 3 equivalents of ferric chloride were needed, showing that an excess was not necessary in the reaction. The reaction was performed again under more carefully controlled conditions. Terphenyl **71** was stirred in dichloromethane at room temperature. Ferric chloride (5 eq) was added slowly, ensuring the temperature did not rise, and the mixture stirred for 2 hours, monitoring closely by TLC. Upon completion, the mixture was cooled to -10 ^{o}C and methanol was added carefully. Work-up and purification *via* column chromatography gave the desired triphenylene **71** in good yield (~60%).



Scheme 2.9: Successful synthesis of triphenylene **71**

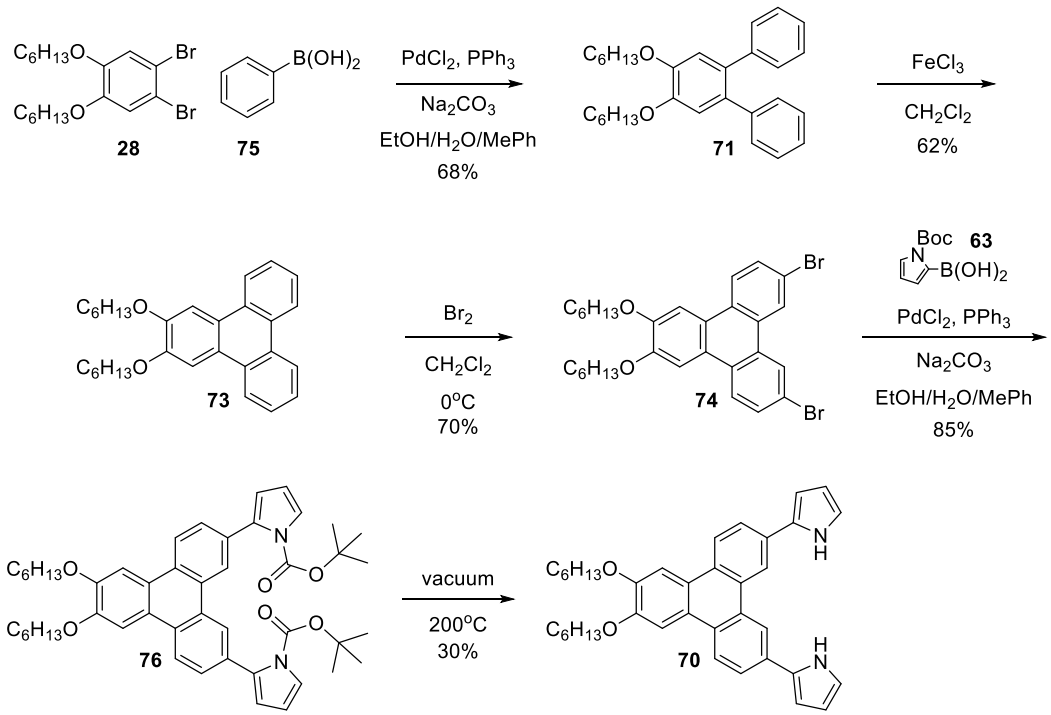
With the new synthesis of terphenyl **71** developed we were in a position to investigate routes to the target dipyrrolyltriphenylene **70**. To introduce the pyrrole groups *via* Suzuki-Miyaura coupling, as in the C_{10} route, we needed to brominate the triphenylene in positions 7 and 10. This bromination had the potential to form poly-brominated products, therefore more caution was necessary than in the bromination performed to synthesise the tetraalkoxy compound **60**.

The number of equivalents of bromine was kept at 2.01, and the reaction was performed at 0 ^{o}C. The reaction was monitored by TLC and worked-up when the reaction deemed complete. After washing with sodium metabisulphite solution, the organics were extracted with dichloromethane, dried over magnesium sulphate and then the solvent removed *in vacuo*. The most successful purification method was found to be recrystallisation from pentanol and this conveniently gave the dibrominated product **74** as a white powder in good yield (~70%).



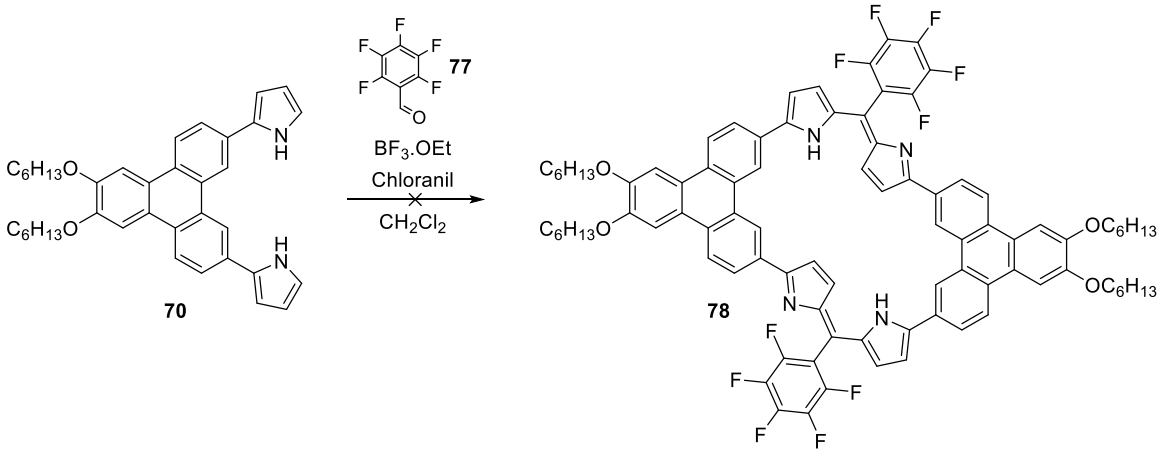
Scheme 2.10: Bromination of dialkoxytriphenylene **73**

Introduction of the pyrrole moieties *via* Suzuki-Miyaura coupling proceed smoothly, with the bis-*N*-Boc pyrrole-triphenylene **76** obtained in high yield. The Boc group was left in place, ready to be removed at high temperature under vacuum when required for subsequent reactions. The full synthesis of dipyrrolyltriphenylene **70** is shown in Scheme 2.11.



Scheme 2.11: Synthesis of two-chain dipyrrolyltriphenylene **70**

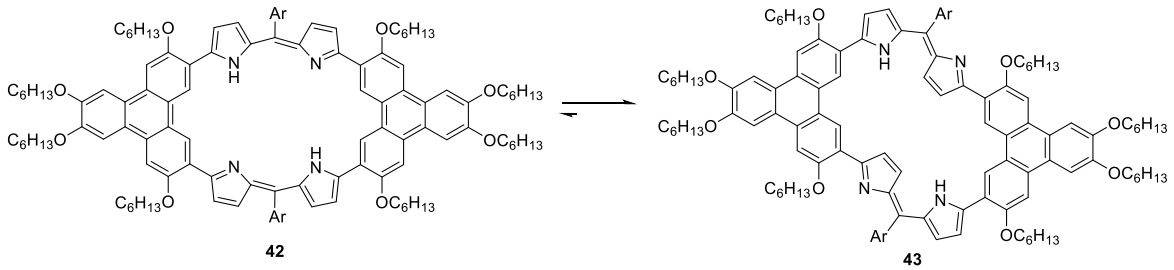
The twinning reaction was attempted with dipyrrolyltriphenylene **70**; pentafluorobenzaldehyde **77** was chosen for the condensation reaction to make ^{1}H-NMR analysis of the products more simple (Scheme 2.12). High dilution was again employed with the triphenylene and benzaldehyde added *via* syringe pump to a mixture of boron trifluoride etherate in degassed dichloromethane at a rate of 2 mL/hour. However, there were solubility issues with dipyrrolyltriphenylene **70**, presumably due to reduction to two alkyl chains, and the reaction was unsuccessful. Attempts to solve this issue, including changing the solvent and applying heat/sonication to dissolve, were unsuccessful in improving the solubility of the compound.



Scheme 2.12: Attempted synthesis of twin **78**

2.1.5 Conclusions to Dipyrrolyltriphenylene Twin Synthesis

At this point, the parallel investigation in the group managed to grow a crystal and obtain characterisable derivatives from the tetrahexyloxy analogues.[49] X-ray structures of both the reduced C_6-thiophene triphenylene twin **47a** and the C_6-pyrrole-triphenylene twin **43** were obtained. The crystal structure of compound **43** showed that the compound prefers a strain-free configuration where the pyrroles face in opposite directions with respect to the planar core, as shown in Scheme 2.13.[49] As attempts to synthesise twins for mesophase analysis were unsuccessful it was deemed appropriate to stop the project at this stage and move onto other twinned structures that were being developed more successfully.



Scheme 2.13: Correct structure of compound **42** shown as **43**[49]

2.2 Synthesis of 'Click' Twin Linked *via* Triazoles

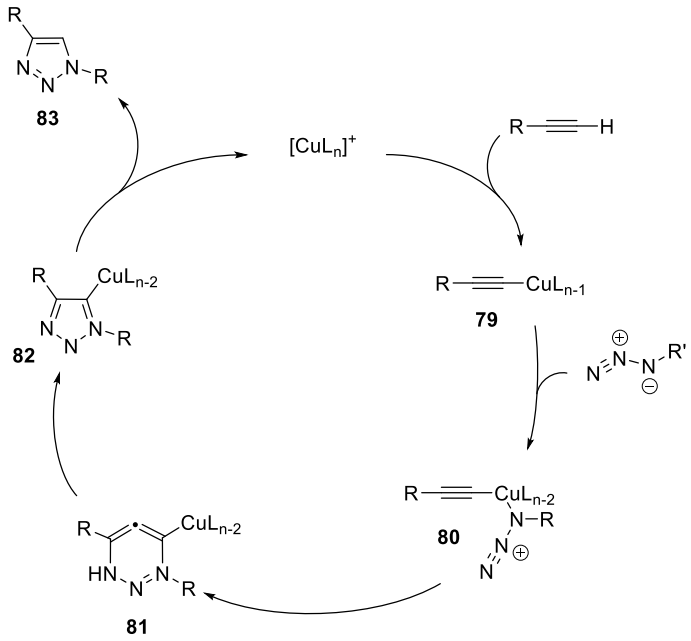
2.2.1 Introduction to Click Chemistry

Click chemistry has received wide interest in recent years; it was first described by Sharpless in 2001.[51] A 'click' reaction is one which is wide in scope and gives high yields with a range of starting materials. It must be easy to perform, insensitive to water and oxygen, and the work-up and purification must be simple, as in without the need for column chromatography. The reaction should also be stereoselective and have high atom economy. Click chemistry encompasses a wide range of reactions, they need to be thermodynamically driven with selectivity for the formation of one product. Some examples are cycloadditions of unsaturated species; e.g. Diels-Alder reactions, nucleophilic substitution reactions; ring-opening reactions of epoxides or aziridines for example, non-aldol type carbonyl chemistry; such as formation of ureas, heterocycles, hydrazones and amides, and additions to carbon-carbon multiple bonds; oxidative formation of epoxides and aziridines, also Michael additions.

One of the most widely known reactions in the area of click chemistry is Huisgen's 1,3-dipolar cycloaddition of alkynes and azides giving triazoles. The classic reaction itself cannot be classed as a click reaction as it requires elevated temperatures and often produces a mixture of two regioisomers. However, when the reaction is catalysed by either a copper or ruthenium catalyst, the reaction occurs at room temperature in aqueous conditions, and forms one regioisomer specifically, making it a click reaction.

2.1.1.1 Copper-Catalysed Azide-Alkyne Cycloaddition (CuAAC)

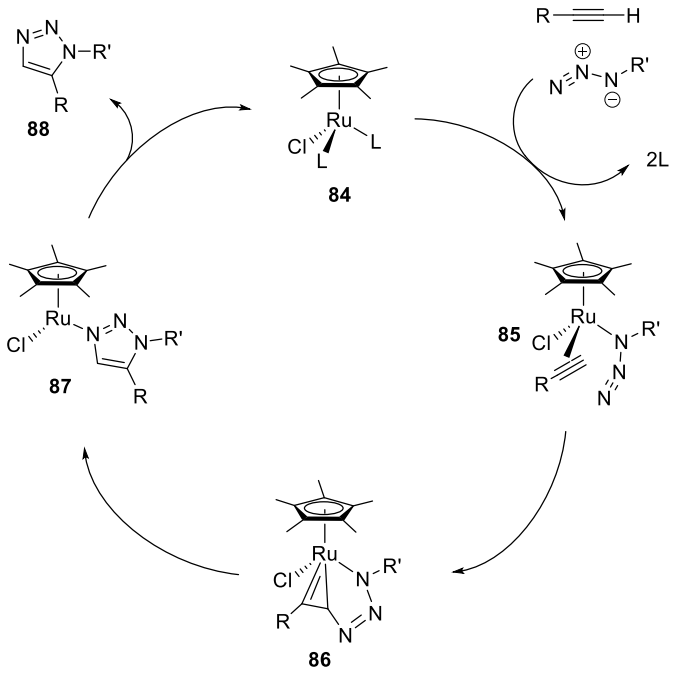
The first catalyst found to catalyse the Huisgen's 1,3-dipolar cycloaddition was a copper(I) catalyst.[52] Using a Cu(I) catalyst, the reaction proceeds regiospecifically to yield 1,4-disubstituted triazoles **83**. The active Cu(I) catalyst can be formed either from Cu(I) salts, or by *in situ* reduction of Cu(II) salts, which is the less costly option. The catalyst cycle starts with the formation of a copper acetylide **79**. The azide is then introduced, displacing a ligand and binding to the copper **80**. The next step forms the first C-N bond, in a strained copper metallocycle **81**. Ring contraction to the copper triazolide **82** forms the second C-N bond and finally protonolysis gives the triazoles **83**, regenerating the copper catalyst.



Scheme 2.14: Catalytic cycle of CuAAC reaction

2.1.1.2 Ruthenium-Catalysed Azide-Alkyne Cycloaddition (RuAAC)

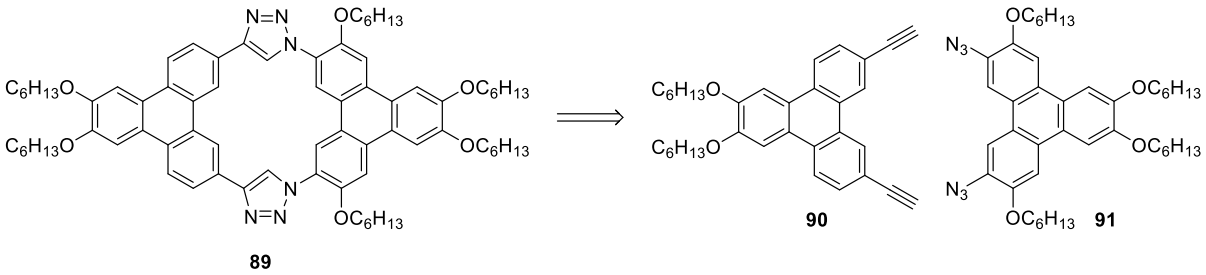
A second catalyst was discovered to facilitate the Huisgen 1,3-dipolar cycloaddition, η^5-pentamethylcyclopentadienylruthenium chloride **84** (Cp*RuCl), however this complex yields the 1,5-disubstituted triazoles **88** exclusively.[53] The mechanism starts with the displacement of two ligands by introduction of the azide and alkyne which forms the active complex **85**. Oxidative coupling between the azide and alkyne forms the first C-N bond between the terminal nitrogen and the more electronegative carbon to give the ruthenacycle **86**. Reductive elimination releases the triazole and regenerates the catalyst.



Scheme 2.15: Catalytic cycle of RuAAC reaction

2.2.2 Target 'Click' Triphenylene Twin 89

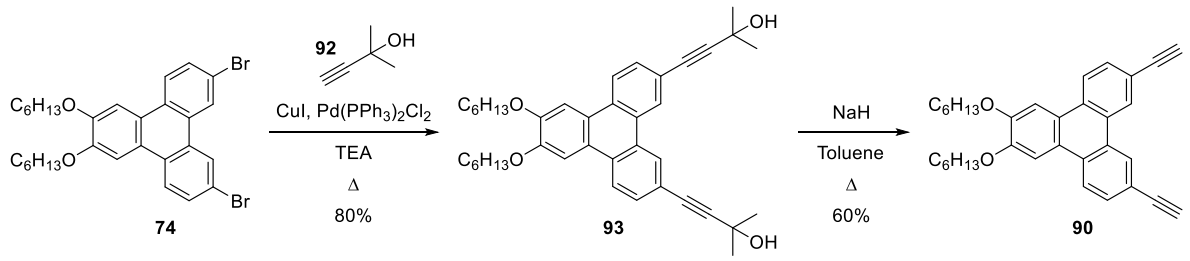
Due to the facile nature of these reactions and our desire to synthesis triphenylene twins linked *via* heterocycles, we devised a triazole linked triphenylene twin (Scheme 2.16). There was literature precedent for the introduction of both the acetylene unit, and azide unit onto the triphenylene ring. We decided that for ease of analysis of the twin we would have one triphenylene with two alkyloxy chains, the other with four. Due the shape of the desired twin, compound **89**, a 1,4-triazole would be needed to form the twin, therefore copper catalysis would be used.



Scheme 2.16: Retrosynthetic analysis of click twin **89**

2.2.3 Synthesis of Diacetylene-Triphenylene 90

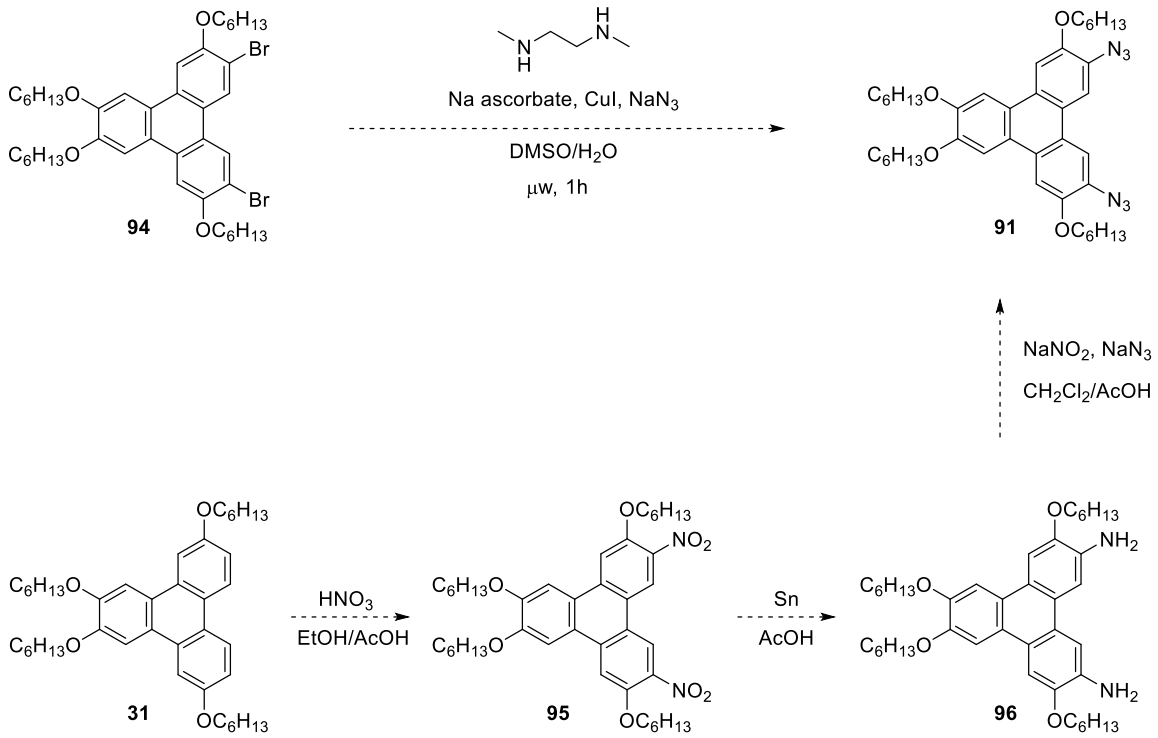
The acetylene-triphenylene was synthesised with two hexyloxy chains on the triphenylene core. Starting from 7,10-dibromo-2,3-bis(hexyloxy)triphenylene **74**, a Sonogashira reaction with 2-methyl-but-3-yn-2-ol **92**, gave 4,4'-(6,7-bis(hexyloxy)triphenylene-2,11-diyl)bis(2-methylbut-3-yn-2-ol) **93** in high yield once the right conditions for column chromatography were found. A mixture of dichloromethane, petroleum ether and ethyl acetate (3:1:1) gave the best separation. The deprotection step was performed with sodium hydride in toluene, work-up and purification *via* column chromatography gave 7,10-diethynl-2,3-bis(hexyloxy)triphenylene **90** in good yield.



Scheme 2.17: Synthesis of 7,10-diethynyl-2,3-bis(hexyloxy)triphenylene **90**

2.2.4 Attempted Synthesis of Diazide-Triphenylene 91 with an Interesting Result

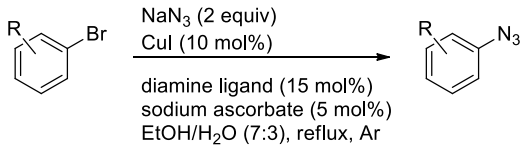
With the synthesis of the diacetylene-triphenylene complete, two routes to the diazide-triphenylene were considered. Firstly, a direct reaction from the brominated triphenylene **94** and the second from a nitration reaction with triphenylene **31** and subsequent manipulations to the diazide **91** (Scheme 2.18).



Scheme 2.18: Possible routes to diazide-triphenylene

In 2005 Anderson *et al*. developed a synthesis of aryl azides from aryl halides that could be performed under mild conditions.[54] The reaction is catalysed by copper iodide, with a diamine

ligand and is performed using microwave conditions to give the product azides in high yields (Scheme 2.19). They showed that the reaction can give high yields from short reaction times for a range of different aryl bromides containing many different functional groups (Table 2.1).



Scheme 2.19: Reaction of aryl halides to azides[54]

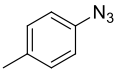
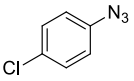
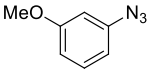
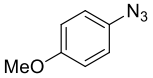
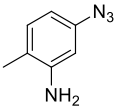
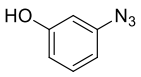
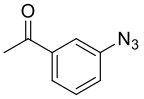
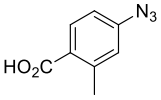
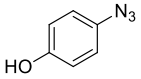
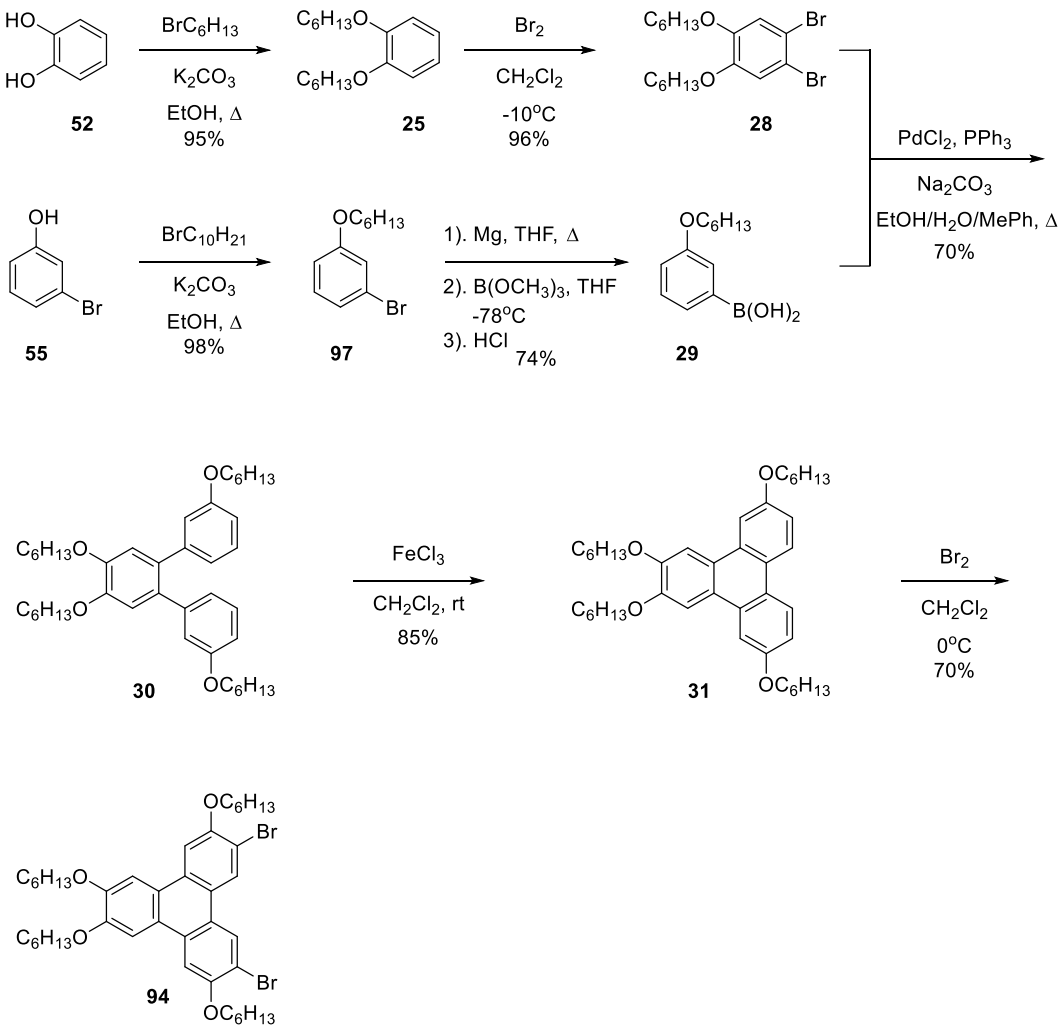
Product	Time (min)	Yield (%)	Product	Time (min)	Yield (%)
	10	89		20	84
	40	95		20	90
	30	99		30	99
	20	96		30	88
	60	82		40	99

Table 2.1: Table of different aryl azide products synthesised[54]

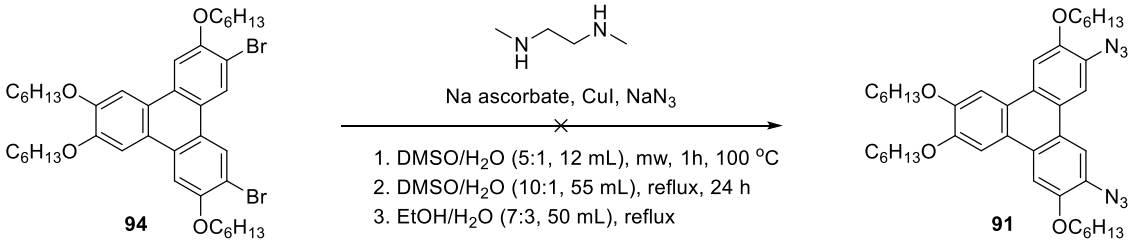
The starting point of the direct synthesis is the dibromide **94**. The synthesis of **94** was the same as that of the tetrakis(decyloxy) version, **60**, and the synthetic route is shown in Scheme 2.20. Details of the syntheses and characterisation for the compounds in Scheme 2.20 can be found in the experimental chapter.



Scheme 2.20: Synthesis of dibromide-triphenylene **94**

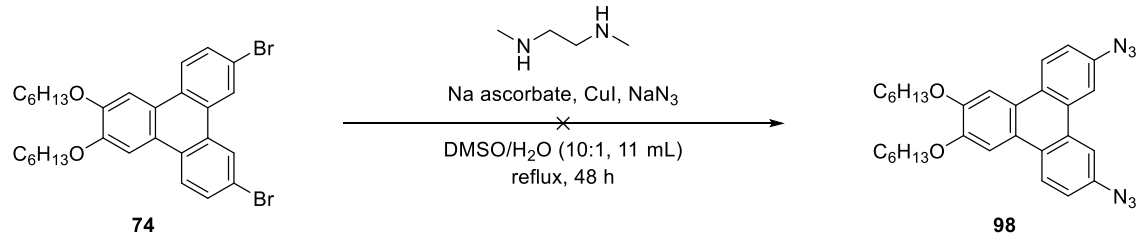
The direct route was attempted following the conditions used by Anderson, Scheme 2.21. The equivalents were doubled, due to the starting material being a dibromide, and the solvent system used was DMSO/H_2O (5:1, 12 mL). The paper showed that this was a comparable solvent system to EtOH/H_2O and was used as the starting material was more soluble in DMSO. The reaction was performed under microwave heating at 100 ^oC for 1 hour. After this time it was found that not all of the starting material had dissolved. The reaction was repeated, this time with conventional heating, with 55 mL of a 10:1 ratio of DMSO/H_2O to improve solubility. The reaction mixture was heated at reflux for 24 hours under a nitrogen atmosphere and after this time TLC analysis showed full consumption of the starting material. The reaction was worked-up and the IR spectrum of the crude product was analysed; a new peak was seen at 2223 cm^{-1} which indicated that an azide product was present. The crude product was purified *via* column chromatography, however none of the fractions collected contained

the desired diazide product. The reaction was repeated, changing the solvent to ethanol/water, however, as expected, the mixture did not fully dissolve even with heating.



Scheme 2.21: Attempts at direct synthesis of diazide triphenylene **91**

When the paper was consulted again, it was noticed that of all the examples of aryl halides used, there was no example with an electron donating group *ortho* to the halide. We postulated that this could be the reason the reaction was unsuccessful and tested this theory by trying the reaction on the bis(hexyloxy)triphenylene **74**.



Scheme 2.22: Attempted synthesis of dihexyloxy diazide-triphenylene **98**

The same conditions were followed and a solvent system of DMSO/H_2O (10:1, 11 mL) used. The reaction mixture was heated at reflux for 48 hours, after which TLC analysis showed full consumption of the starting material. The reaction mixture was worked-up and washed thoroughly with water. The crude ^{1}H-NMR spectrum looked promising so the crude mixture was separated by column chromatography using a solvent system of dichloromethane/petroleum ether/methanol (3:1.9:0.1). In the ^{1}H-NMR spectrum four aromatic proton signals were present, indicating the triphenylene protons, also the triphenylene protons either side of the azide were both shifted upfield (Figure 2.7). However, the IR spectra did not show any evidence of an azide.

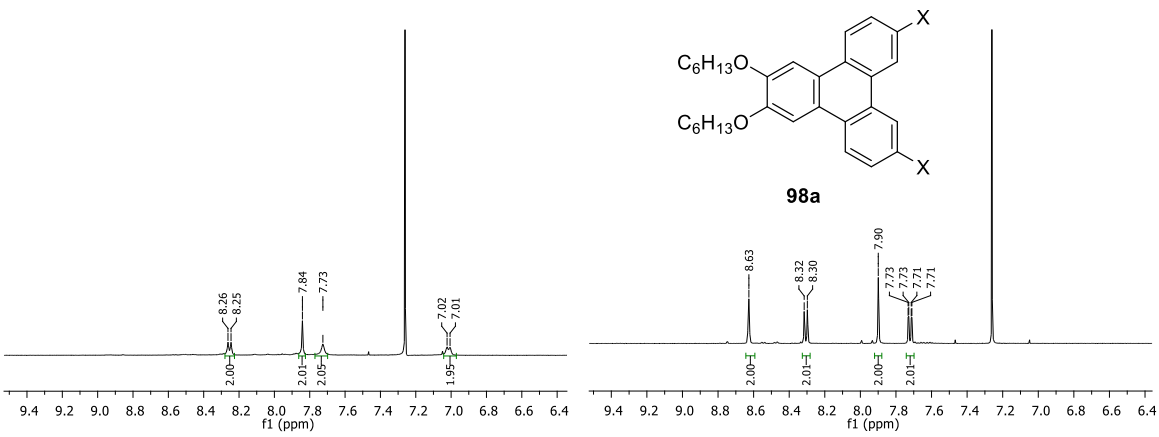
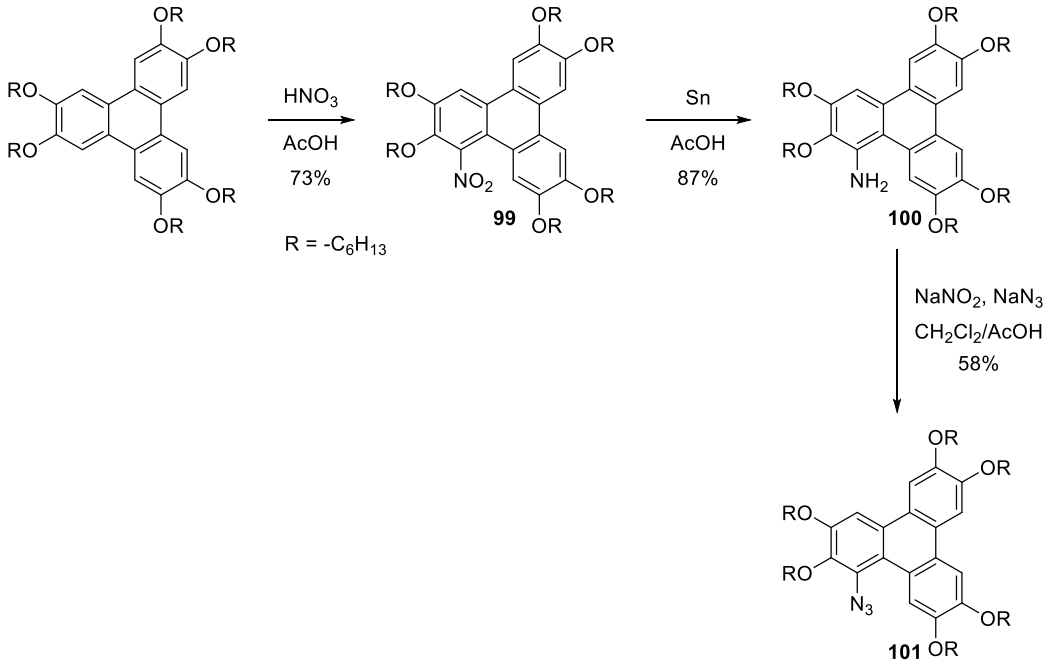


Figure 2.7: Comparison of ^{1}H-NMR aromatic regions of compounds **74** and **98a** respectively

The downfield shift of the triphenylene protons either side of the new functional group suggests that it is an electron-donating group. The IR spectrum suggested an amine was present, however this does not correspond with the NMR data, therefore the identity of the product is still unknown.

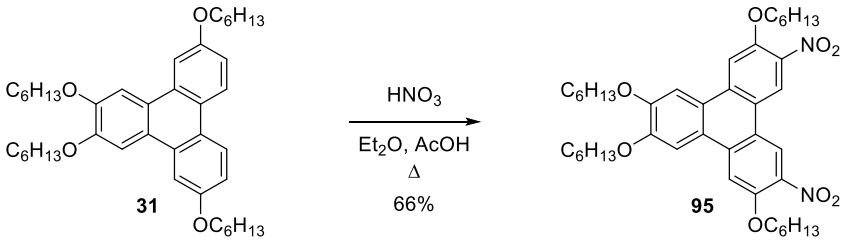
As this reaction was not going to yield the desired tetrahexyloxy-diazide-triphenylene, our focus moved to the second route *via* nitration.

Nitration of the triphenylene ring was described in 1995 by Bushby *et al*.[55,56] Using conc. nitric acid in diethyl ether and acetic acid at room temperature, they synthesised the mono α-nitrated triphenylene product **99** in high yield. With the nitro functionality in place they could functionalise the ring further, taking it through amine **100** to the azide **101**.



Scheme 2.23: Mono-α-nitration of triphenylene and further modification to azide **101**[55,56]

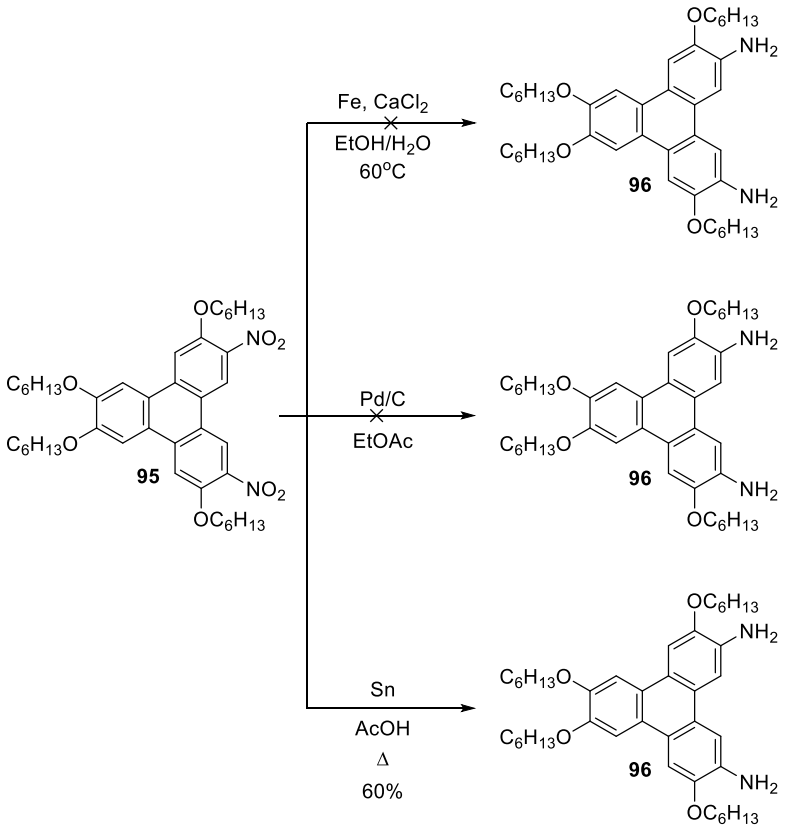
Following this route, the synthesis started from the triphenylene, compound **31**, prepared previously (Scheme 2.20). Triphenylene **31** was stirred in diethyl ether and acetic acid at room temperature with conc. nitric acid. After stirring for 15 minutes a precipitate had formed, which when isolated was the triphenylene starting material **31**. No nitrated product was observed by TLC analysis or ^{1}H-NMR spectroscopy of the crude product. Therefore, to aid the solubility of the triphenylene, the mixture was heated gently before the conc. nitric acid was added. After 2 hours of stirring at room temperature TLC analysis showed that no new product was present, only starting material. Adding another equivalent of conc. nitric acid and further stirring also did not yield the nitrated product. The reaction mixture was then heated at reflux overnight. When the crude reaction was analysed by TLC 16 hours later, new products were observed. Purification by column chromatography in dichloromethane and petroleum ether (3:7) gave dinitrated triphenylene, assumed to be **95**, in surprisingly high yield (66%) as a stable yellow, viscous oil.



Scheme 2.24: Synthesis of dinitro-triphenylene, presumed to be **95**

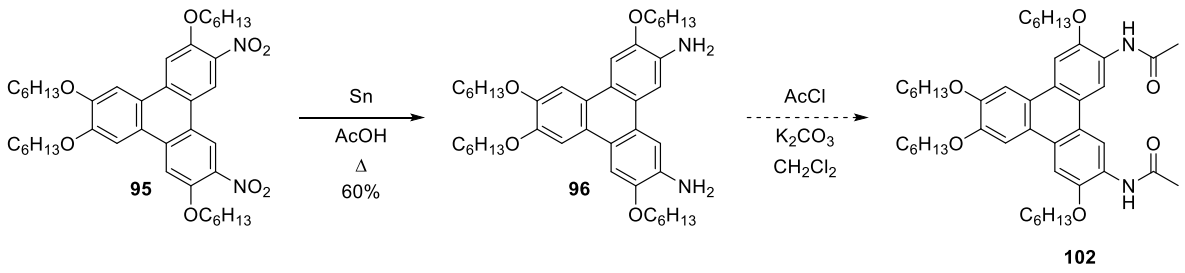
It was later found that this was not the product formed, the nitro group had been introduced in the 1- and 8- positions, as shown in scheme **2.28**. The correct structure is compound **103** and is discussed further later in this chapter.

The next step was to reduce the nitro group to the amine. The reaction performed in the literature was with tin in acetic acid and the same conditions were used on the dinitrated triphenylene. Tin powder and dinitro-triphenylene were stirred in acetic acid at reflux for 4 hours, after this time TLC analysis showed the formation of a new product and full consumption of the starting material, however, there were difficulties in purification. Initially recrystallization from ethanol was tried but was not successful. Purification *via* column chromatography was then attempted by running the column in dichloromethane and petroleum ether (1:9), however this again did not yield the pure product. Different reactions were used to try overcome these issues (Scheme 2.24). The dinitro-triphenylene was stirred in a mixture of ethanol and water, iron powder and calcium chloride were added and the reaction heated at 60^{o}C and monitored by TLC, but no reaction occurred. Hydrogenation was also tried and dinitro-triphenylene was dissolved in ethyl acetate in a hydrogenation vial, palladium on carbon (10 mol%) was added and the vial sealed. The reaction was run at 45 psi for 4 hours, however after this time TLC analysis showed that the starting material was still present and no new product formed. The reaction was run for longer but still no new product was observed.



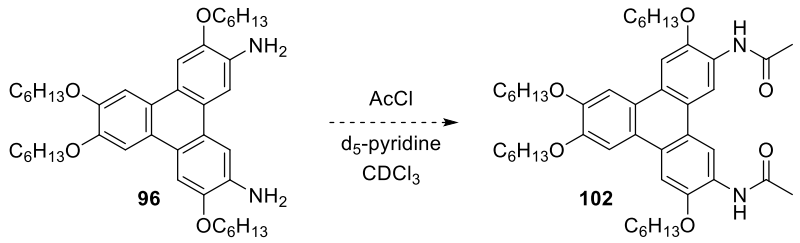
Scheme 2.25: Reduction of dinitro-triphenylene to diamino-triphenylene

As the tin reaction had given a new product it was run again, this time filtering the crude product through silica straight after work-up, this method isolated the pure product in good yield. However, the product decomposed rapidly meaning any further analysis other than proton NMR was unable to be obtained. For this reason we decided to take the diamino-triphenylene **96** through to diamide **102** to obtain a product that would be more stable and allow for further analysis.



Scheme 2.26: Reaction scheme to synthesise diamide-triphenylene **102**

Immediately after preparation, the diamino-triphenylene was dissolved in dichloromethane with potassium carbonate and acetyl chloride. The mixture was stirred at room temperature and after 30 minutes TLC analysis showed the starting material had been consumed and new spots were present. The crude mixture was filtered and the solvent removed *in vacuo*. The ^{1}H-NMR spectrum of the crude material showed that the NH_2 peak had disappeared and the Ar-H peaks had moved. However, even after purification by column chromatography the ^{1}H-NMR spectrum was hard to analyse and it was not clear whether the reaction was going too far and forming a bisimide-triphenylene, or not far enough. Therefore a ^{1}H-NMR spectroscopy experiment was run. The conditions were changed slightly with deuterated chloroform used as the solvent and deuterated pyridine used for the base (Scheme 2.27). An initial ^{1}H-NMR spectrum was run of diamino-triphenylene (presumed to be **96**) with deuterated pyridine (Figure 2.8), then another run straight after the addition of acetyl chloride. After this ^{1}H-NMR spectra were taken every 10 minutes.



Scheme 2.27: NMR study of the acylation reaction

The results were very interesting. As can be seen from Figure 2.8, the initial ^{1}H-NMR spectrum shows three peaks in the aromatic region from the triphenylene protons, and the broad NH_2 signal at 4.36 ppm. Straight after the addition of acetyl chloride, there is a change in the ^{1}H-NMR spectrum, the broad NH_2 peak has gone, the three aromatic peaks have shifted and a new peak appeared, possibly indicating that amide formed. A selection of the subsequent spectra are shown in Figure 2.9. Once the acylated product has formed no further reaction occurs and there is no decomposition. Even after 20 hours, the ^{1}H-NMR spectrum has hardly changed.

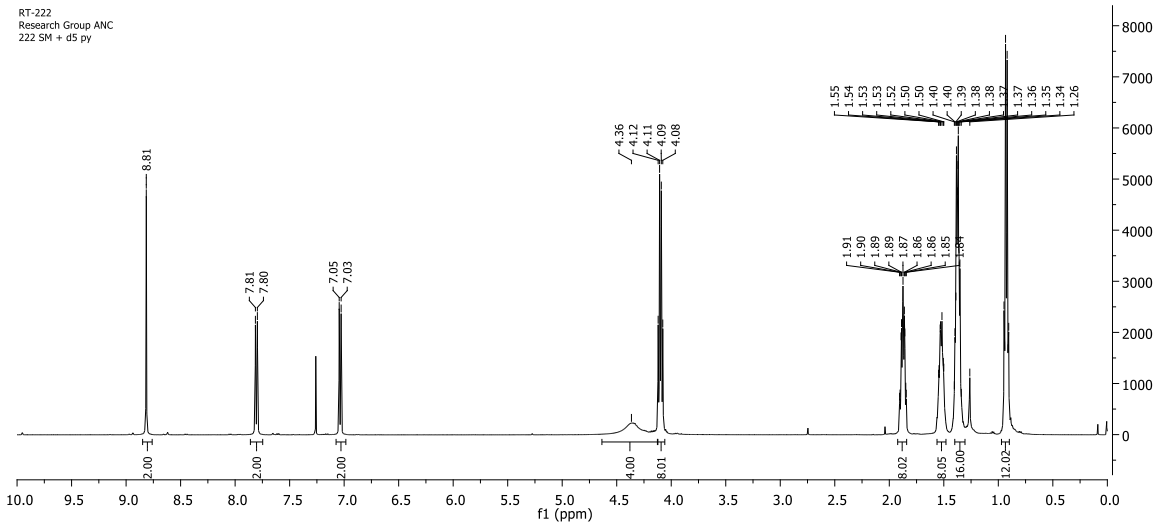


Figure 2.8: ^{1}H-NMR spectrum of the starting materials used in the NMR study

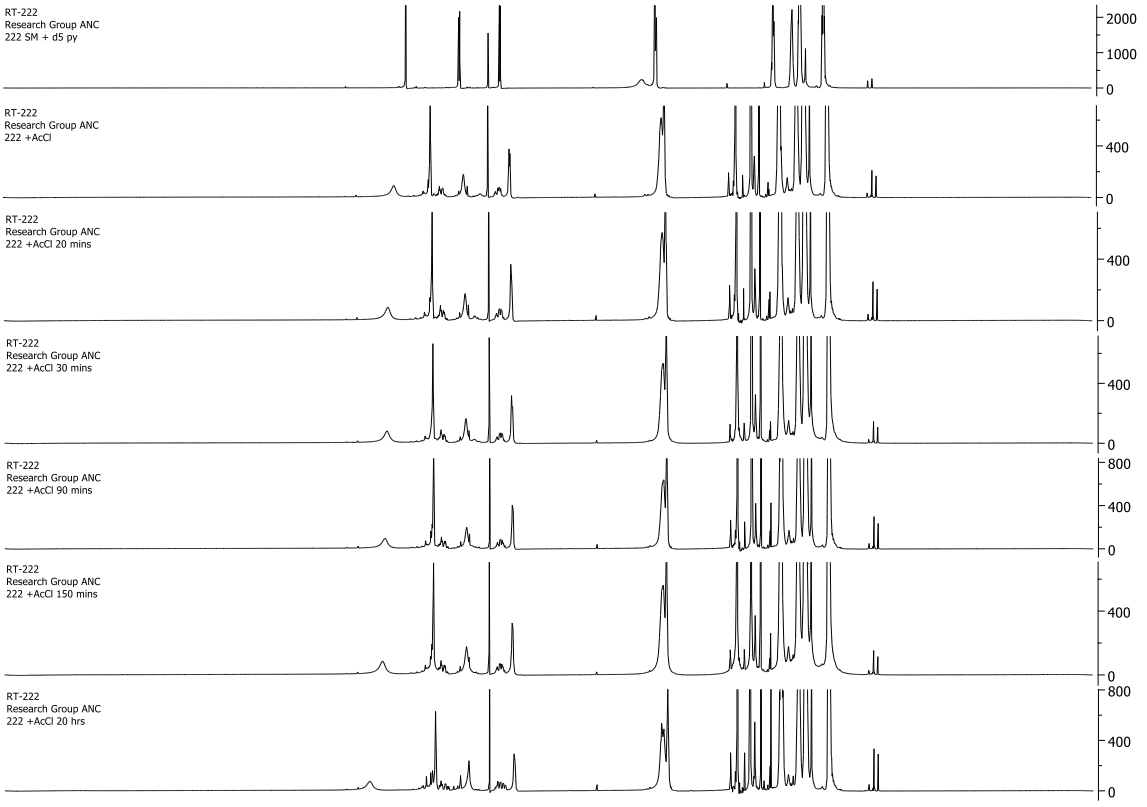


Figure 2.9: ^{1}H-NMR spectra from the NMR study showing progression of the reaction

One of the ^{1}H-NMR spectra obtained during the study has been integrated to show the significant peaks observed (Figure 2.10). There are four peaks in the aromatic region that have integrals for two protons. These were thought to be the six protons from the triphenylene ring, and two amide NH protons.

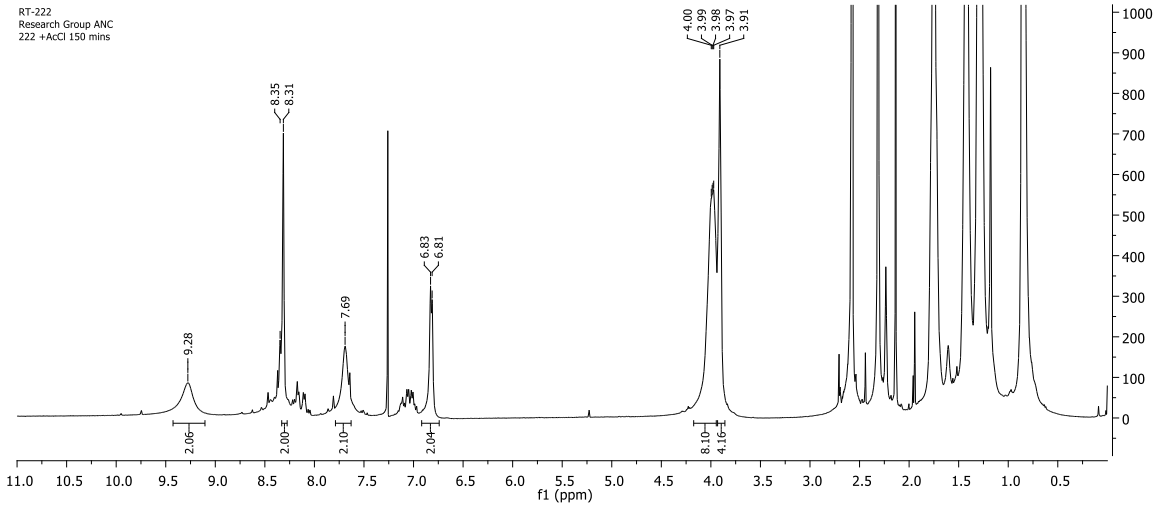


Figure 2.10: ^{1}H-NMR of amide crude product

With these encouraging results, the reaction was taken back to the laboratory and scaled up to preparative scale, using the same conditions as in the ^{1}H-NMR study. Diamino-triphenylene was prepared freshly and dissolved in chloroform with pyridine, then acetyl chloride added. The reaction was stirred at room temperature. After 30 minutes an aliquot was taken and the solvent removed *in vacuo* before obtaining a ^{1}H-NMR spectrum. The spectrum was messy and the peaks observed during the ^{1}H-NMR study were not obvious, therefore the reaction was left for longer. After 16 hours the crude ^{1}H-NMR spectrum suggested that there was a double addition of acetyl groups on each amine and the reaction was stopped. Purification by column chromatography was considered, but good separation could not be achieved, therefore recrystallisation was used instead. The crude product was dissolved in hot ethanol and crystals were grown. With these in hand we were able to gain the crystal structure of our compound and also obtain a clean set of data.

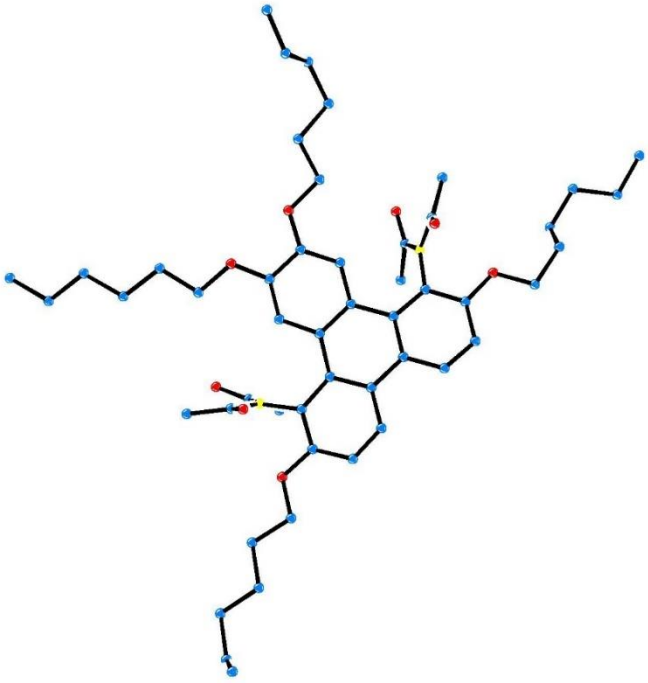


Figure 2.11: Crystal structure of bisimide **105**

The crystal structure proved the initial idea from ^{1}H-NMR spectrum that the bisimide-triphenylene had indeed been formed. However, it also showed something else that was very unexpected. Instead of the imides being in the 3- and 6- positions as anticipated, they were in fact in the 1-and 8- positions. This was puzzling as the bromination reaction, also being an electrophilic aromatic substitution reaction, gave exclusively the 3-, 6- product. The ^{1}H-NMR data obtained also showed this with two doublets (one hidden by the residual $CHCl_3$ peak) and one singlet being seen in the aromatic region, showing the splitting pattern between the protons in the 3-, 4- and 5-, 6- positions on the triphenylene (Figure 2.12).

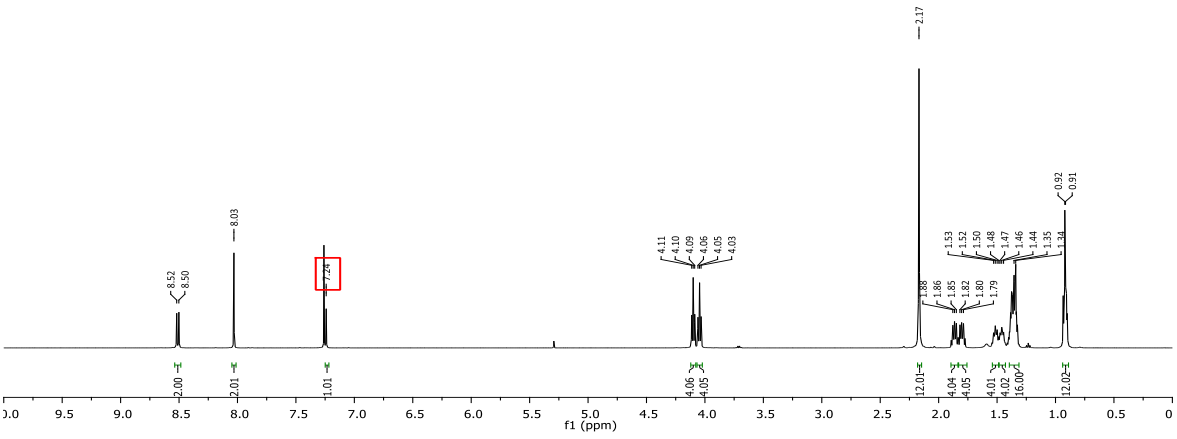
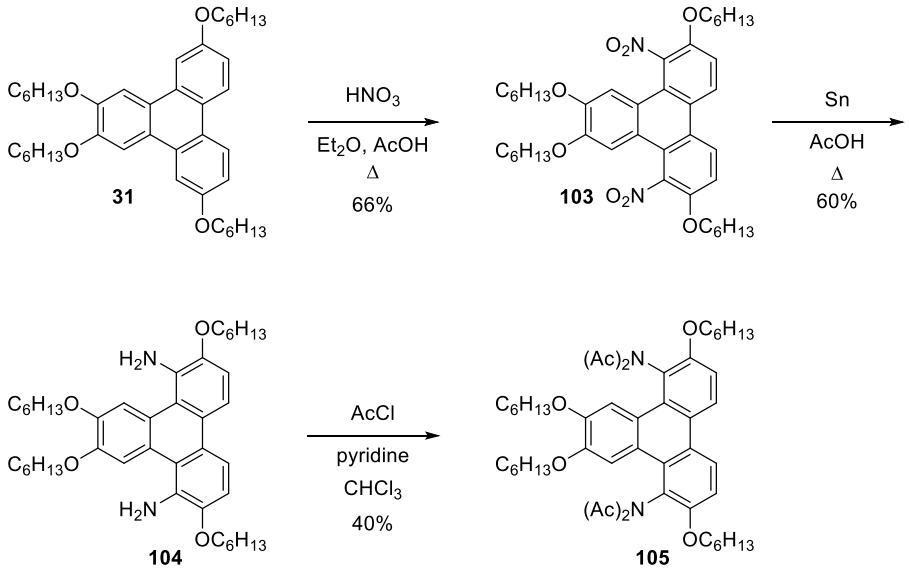


Figure 2.12: ^{1}H-NMR of bisimide **105**

This splitting was not so clearly observed originally in the ^{1}H-NMR of the di-nitro compound, hence our thought that the 3- 6- product was being formed. However, when these spectra were revisited the aromatic peaks were seen to be broad compared to the sharp peaks you would normally expect. The ^{1}H-NMR was re-run making sure the solution was dilute, and this time the aromatic splitting could be seen (Figure 2.12). Scheme 2.28 shows the correct synthesis for bisimide-triphenylene **105**.



Scheme 2.28: Synthesis of bisimide triphenylene **105**

The reason behind this unusual result is still not fully understood. The substitution is expected to occur in the 3- and 6- positions like the case for electrophilic bromination, Figure 2.13 shows the two intermediates. Reaction is hindered at the *ortho* position in intermediate **106** due to steric interactions, however this is where the nitration occurs. The difference in regiochemical outcome between bromination and nitration is remarkable – each process produces a single, but different isomer.

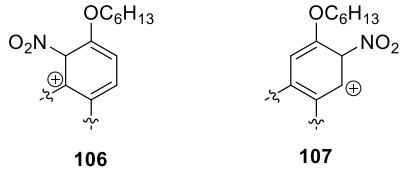
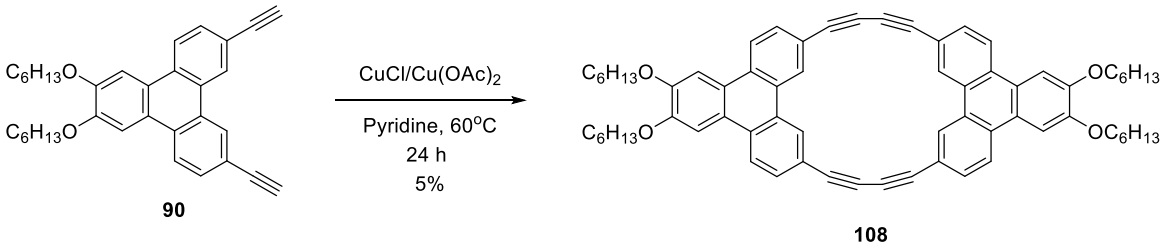


Figure 2.13: Intermediates formed during nitration of triphenylene

2.2.5 Synthesis of Diacetylene-Triphenylene Twin 108

This result meant that the desired diazide-triphenylene could not be synthesised following our proposed route, so we decided to twin the diacetylene-triphenylene **90** itself. The reaction procedure followed the high dilution conditions used previously in our group for the synthesis of the four chain version, compound **40**. Diacetylene-triphenylene **90** was dissolved in anhydrous pyridine and loaded into a syringe, the mixture was added to a flask of copper chloride and copper acetate in pyridine at a rate of 0.012 mL/min (total time 21 hours). The reaction mixture was heated at 60^{o}C, and stirred for a further 16 hours after the addition was complete.



Scheme 2.29: Synthesis of acetylene twin **108**

A crude sample was analysed by MALDI-MS, this showed a signal at 949 *m/z*, indicating the possible presence of the acetylene twin **108**. A work-up was attempted on a portion of the reaction but it was found that the compound was insoluble in almost all organic solvents. Some solubility was seen in THF, therefore a soxhlet extraction was implemented. The resulting THF solution was left to cool overnight and the pure product **108** was obtained by filtration as a yellow solid. Due to the poor solubility, analysis was only possible by VT-NMR spectroscopy. The ^{1}H-NMR spectrum was run in 1,1,2,2-tetrachloroethane-d_2 at 80 ^{o}C, the spectrum obtained proves the formation of the twinned compound **108**, Figure 2.14.

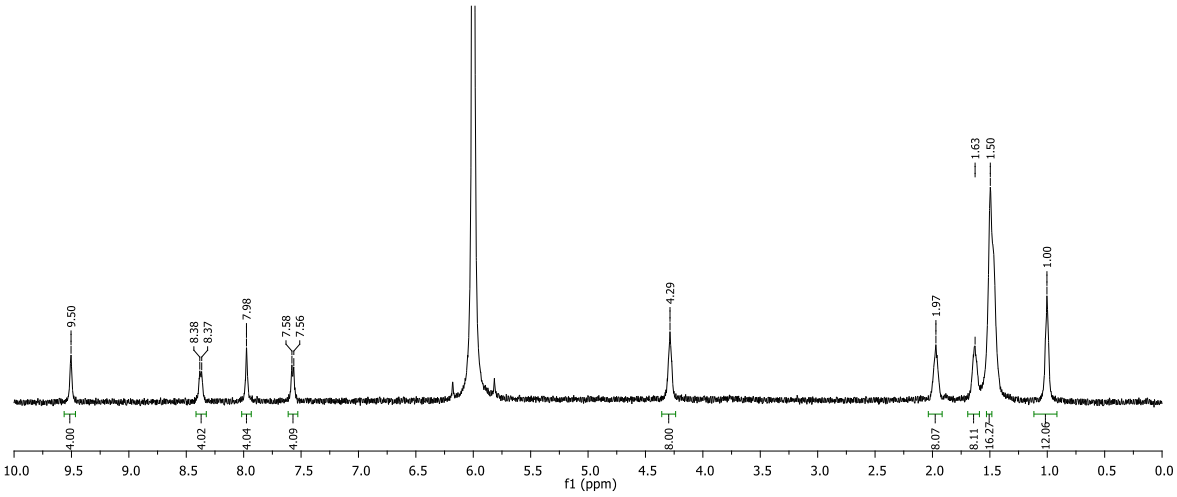


Figure 2.14: ^{1}H-NMR spectrum of acetylene twin **108**

A closer look at the aromatic regions of both the twin **108** and precursor **90** shows the effect on the chemical shift of the proton in the 4- and 5- positions (Figure 2.15). A normal spectrum is seen in the case of the diacetylene-triphenylene precursor **90**, however there is a significant shift downfield in the spectrum of the twin **108**, from 8.75 ppm to 9.50 ppm. This is due to the antiaromatic character of the twin, the deshielding effect of the inner ring current shifts the proton downfield. This is the opposite of the effect seen in aromatic materials, where the inner ring current shields the protons within the aromatic ring, causing a shift upfield.

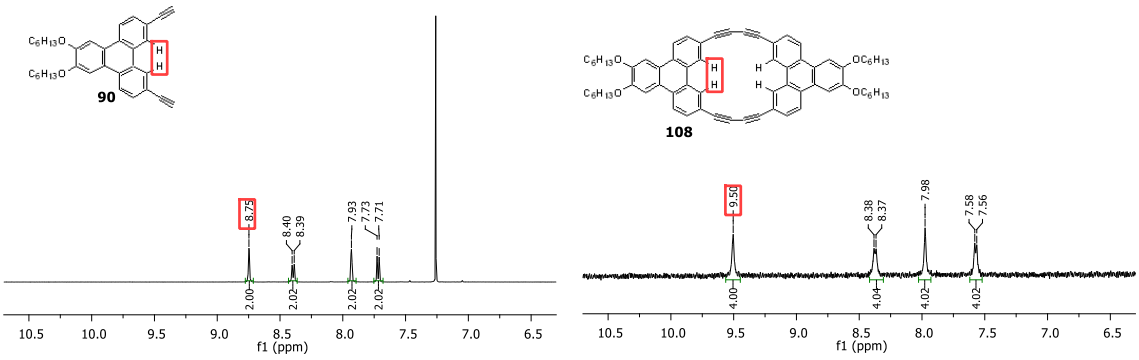


Figure 2.15: Aromatic region of ^{1}H-NMR spectra of compounds **90** and **108**

The melting point of the twin was taken, to see whether there was any evidence of liquid crystallinity, however the twin remained crystalline beyond 300^{o}C, therefore any potential mesophase behaviour could not be observed.

As the twin was obtained as a yellow solid the UV/Vis spectrum was run, as well as the fluorescence spectrum. As you can see from the emission spectra (Figure 2.17) the compound is fluorescent, the emission spectra were run at two excitation wavelengths, 360nm and 410 nm, both had a high (qualitative) fluorescence intensity.

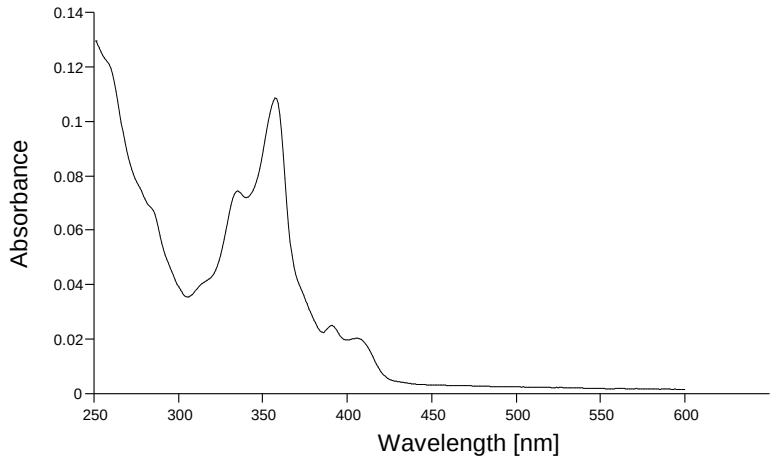


Figure 2.16: UV/Vis spectra of acetylene twin **108**

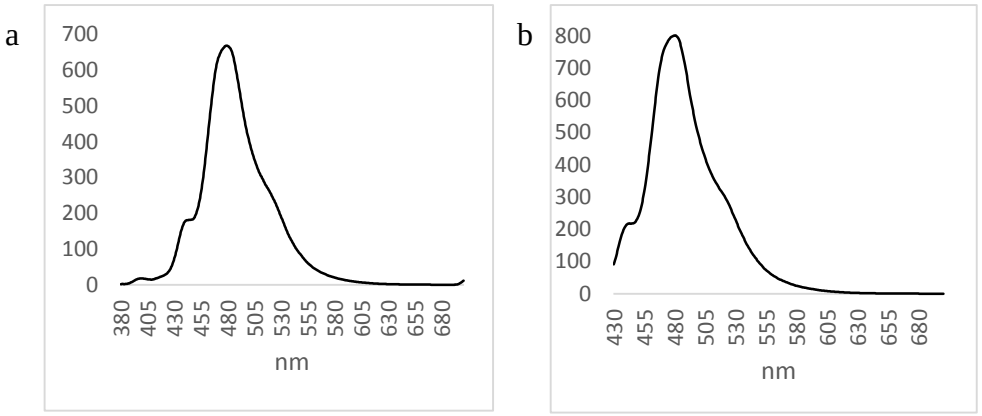


Figure 2.17: Emission spectra from excitation wavelengths of a) 360 nm and b) 410 nm respectively

It was thought that there was potential for the formation of higher order oligomers during the twinning reaction, the possibilities are shown in Figure 2.18. However, as can be seen in the MALDI-MS data (Figure 2.19), no such structures were observed, the twin was isolated exclusively.

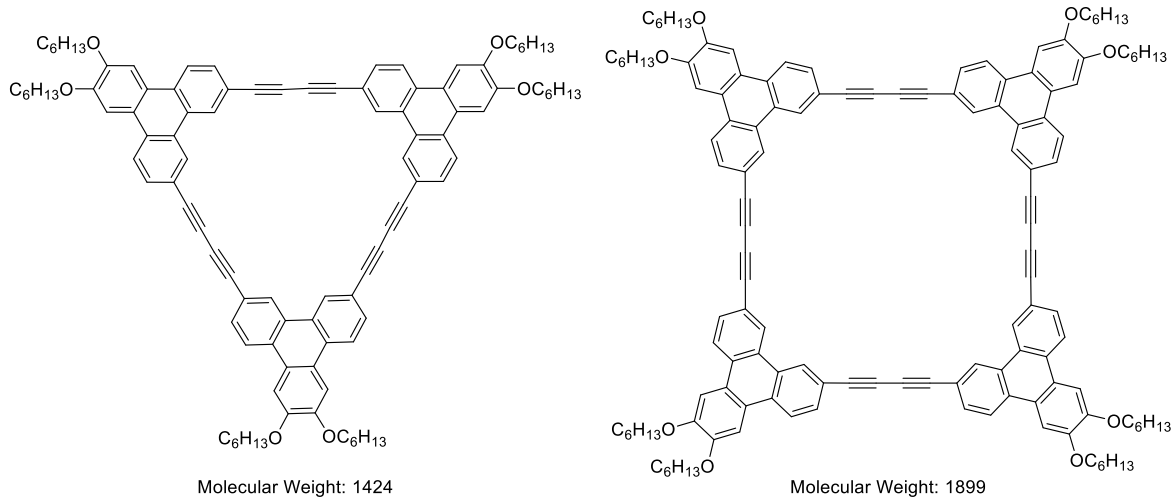


Figure 2.18: Possible oligomer structures from twinning reaction

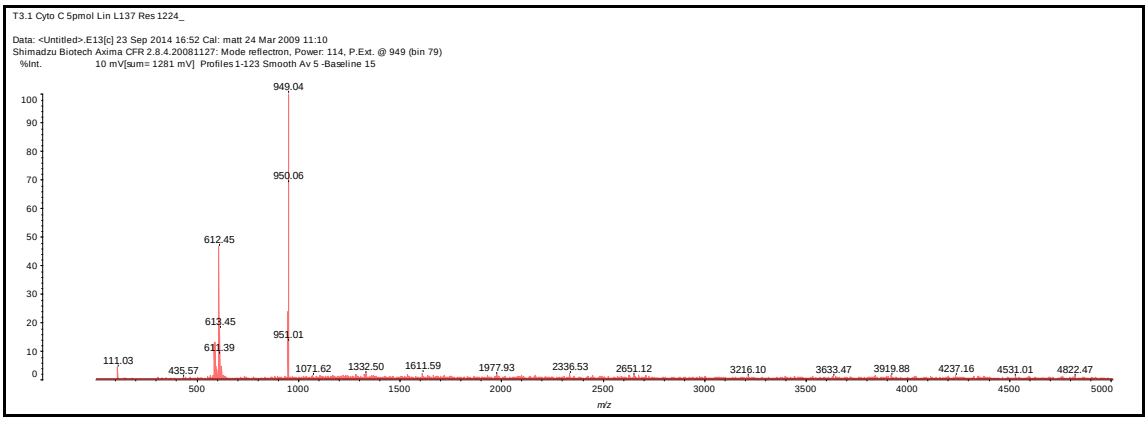
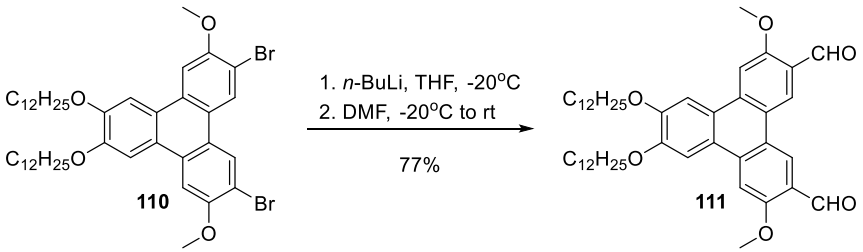


Figure 2.19: MALDI-MS spectra of acetylene twin **108** (*m/z* 949)

2.3 Synthesis of bis-BODIPY Triphenylene Hybrid and Diamine Triphenylene Twin

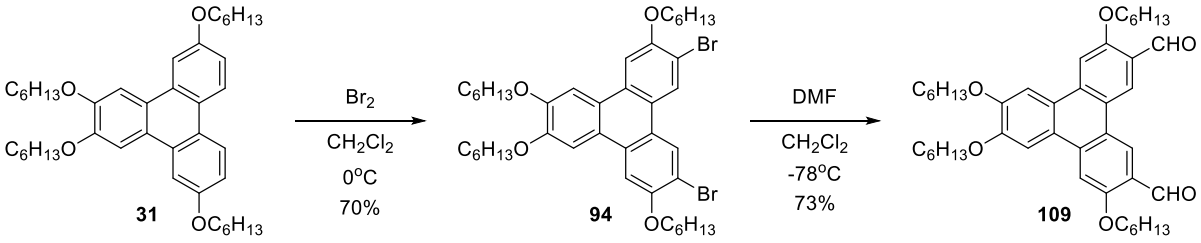
2.3.1 Formylation of Triphenylene

Our aim of synthesising triphenylene derivatives with high functionality and potential as materials, lead us to create more routes by which to introduce different functional groups. One very useful moiety is the aldehyde, it is a versatile functional group that can undergo many different transformations to give a wide range of new compounds. Our group had previously investigated the reaction of triphenylenes with a formylating agent to introduce aldehyde units into the 3- and 6- positions of the triphenylene. The reaction was tried on the tetra-alkylated triphenylene and no formylated product was seen. In 2013 a paper was published detailing a synthesis of a triphenylene-containing macrocycle that was made *via* the aldehyde.[57] The route started from the 3-6-dibromotriphenylene **110** (Scheme 2.30), this underwent a lithium-halogen exchange, quenching with excess dimethylformamide (DMF) yielded the desired dialdehyde product **111**.



Scheme 2.30: Formylation reaction of triphenylene **110** to yield aldehyde **111**

Taking 2,3,6,11-tetrakis(hexyloxy)triphenylene **31**, the synthesis of which was shown in Scheme 2.19, we performed the bromination following the established conditions, and followed the paper for the formylation (scheme 2.31). Dibromotriphenylene **94** was dissolved in anhydrous THF and the mixture cooled to -78 °C, *n*-BuLi was added and the mixture stirred for 4 hours when TLC analysis showed full consumption of the dibromide. Anhydrous DMF was added and the reaction left to stir overnight and allowed to warm to room temperature. The reaction mixture was quenched with water and extracted with dichloromethane, the crude residue was recrystallised from dichloromethane and ethanol giving the dialdehyde triphenylene **109** in a very good yield.



Scheme 2.31: Bromination and subsequent formylation of dialdehyde triphenylene **109**

From this point there were a number of routes we wanted to investigate. The main target being the synthesis of triphenylene-BODIPY hybrids.

2.3.2 Introduction to BODIPY Compounds

4,4-Difluoro-4-boro-3a,4a-diaza-*s*-indacenes (BODIPYs) are a class of small organic molecules that are highly fluorescent. They are strongly UV-absorbing, and have many spectral characteristics including high quantum yields and a sharp fluorescence emission. They are also relatively insensitive to environmental conditions such as polarity and pH, making them useful fluorophores in the labelling of biological molecules such as proteins.

Treibs and Kreuzer first discovered BODIPY's in 1968,[58] however the unsubstituted BODIPY **112** wasn't synthesised until 2009 due to the unsubstituted dipyrromethene being susceptible to nucleophilic attack.

The BODIPY moiety has eight sites for substitution, two β-positions and one α-position on each pyrrole, then the meso-position between the joined pyrroles. The numbering system is different to the parent dipyrromethane **113**/dipyrromethene **114** compounds, Figure 2.20.

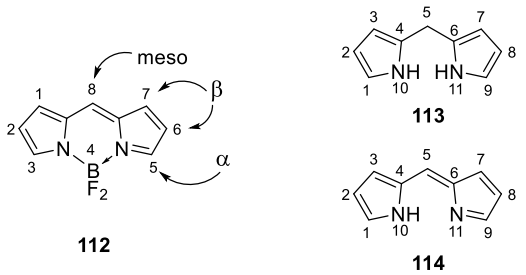
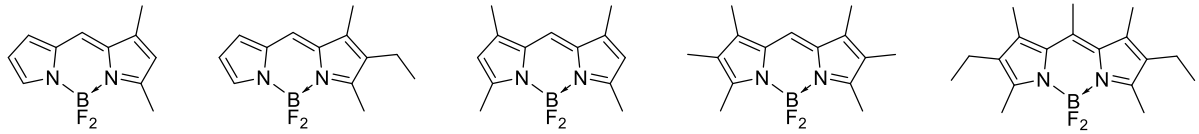


Figure 2.20: Comparison of numbering systems for BODIPY and dipyrromethane/ene

Looking at a number of simple alkylated BODIPY compounds a trend can be seen where increased substitution leads to an increase in absorption and emission wavelength (a red-shifted absorption and emission). Figure 2.21 demonstrates this trend.



EtOH ϕ 0.70
$\lambda_{max\ abs}$ 499 nm
$\lambda_{max\ emiss}$ 509 nm

EtOH ϕ 0.40
$\lambda_{max\ abs}$ 510 nm
$\lambda_{max\ emiss}$ 520 nm

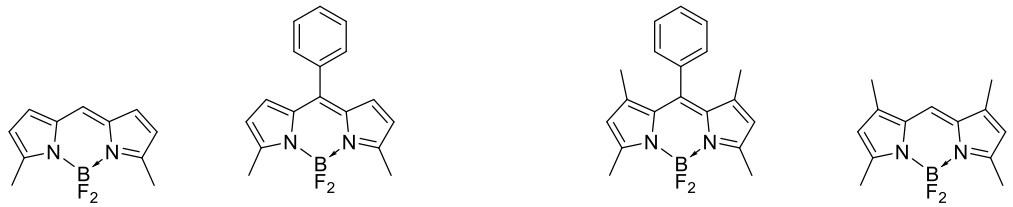
EtOH ϕ 0.80
$\lambda_{max\ abs}$ 505 nm
$\lambda_{max\ emiss}$ 516 nm

EtOH ϕ 0.56
$\lambda_{max\ abs}$ 528 nm
$\lambda_{max\ emiss}$ 535 nm

EtOH ϕ 0.70
$\lambda_{max\ abs}$ 517 nm
$\lambda_{max\ emiss}$ 546 nm

Figure 2.21: BODIPY compounds showing trend towards red-shifted absorption with increased substitution.

The introduction of an aryl group in the *meso* position has been shown to not affect the absorption or emission wavelength, however it has been shown to have a large effect on the quantum yield[59,60] (Figure 2.22).



EtOH ϕ 0.81
$\lambda_{max\ abs}$ 507 nm
$\lambda_{max\ emiss}$ 520 nm

115

MeOH ϕ 0.19
$\lambda_{max\ abs}$ 508 nm
$\lambda_{max\ emiss}$ 521 nm

116

MeOH ϕ 0.65
$\lambda_{max\ abs}$ 498 nm
$\lambda_{max\ emiss}$ 508 nm

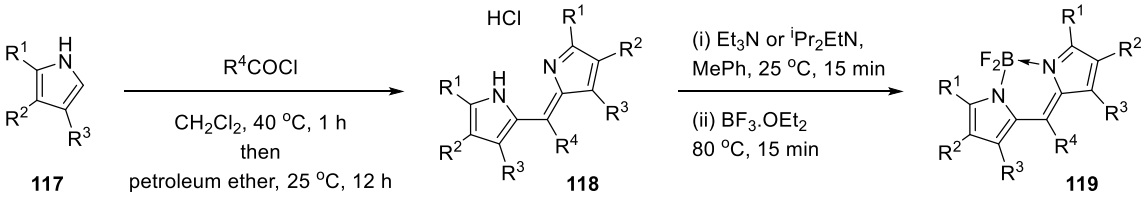
EtOH ϕ 0.80
$\lambda_{max\ abs}$ 505 nm
$\lambda_{max\ emiss}$ 516 nm

Figure 2.22: BODIPY structures showing effects of *meso*-substitution with an aryl group

Comparing the *meso*-aryl compounds to the non-*meso*-substituted versions shows that there is little change in the wavelengths of absorption/emission. Comparing the two *meso*-aryl compounds, **115** and **116**, shows the effect on the quantum yield. The 1,7-substituents in **116** stop the free rotation of the phenyl group which reduces the amount of energy loss from the excited states through non-radiative motion, thus increasing the efficiency of the fluorescence process. *Ortho*-substituents on the phenyl ring have also been shown to increase the quantum yield, further proving this effect.

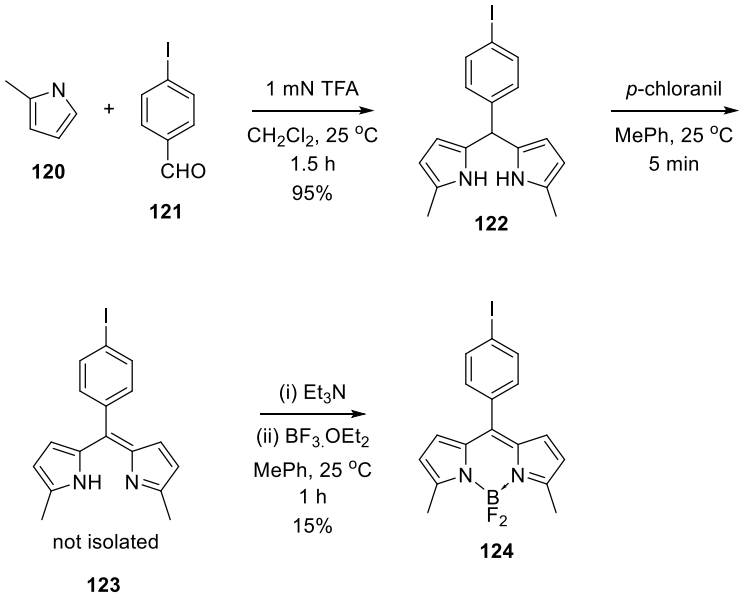
2.3.2.1 Syntheses of BODIPY Compounds

There are a number of known syntheses for BODIPY compounds, differing with the amount of substitution required. One method for synthesising BODIPYs with eight substituents, including the *meso*-position, is from acid chlorides.[61] A condensation reaction with the substituted pyrrole **117** and acyl chloride yields the dipyrromethene hydrochloride salt intermediate **118**, this is unstable so is not usually isolated. Complexation with boron gives the fully substituted BODIPY compound **119**.



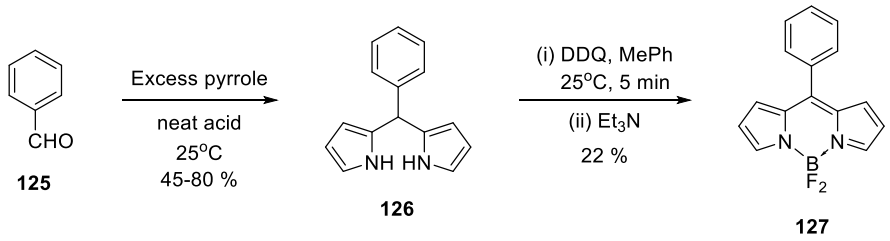
Scheme 2.32: BODIPY synthesis from acyl chlorides

Another method is from pyrroles and aldehydes, it follows a similar route to the acyl chloride but requires an extra oxidation step.[62] A condensation reaction between the pyrrole **120** and aldehyde **121** gives the dipyrromethane compound **122**, oxidation with *p*-chloranil yields the dipyrromethene **123**, which is not isolated. This is then taken onto the BODIPY **124** by complexation with boron. As can be seen from the example given in Scheme 2.33, this method allows for the introduction of useful functionalities on the phenyl group such as the iodine shown, this could then be used in further reactions, for example cross coupling.



Scheme 2.33: BODIPY synthesis from pyrroles and aldehydes

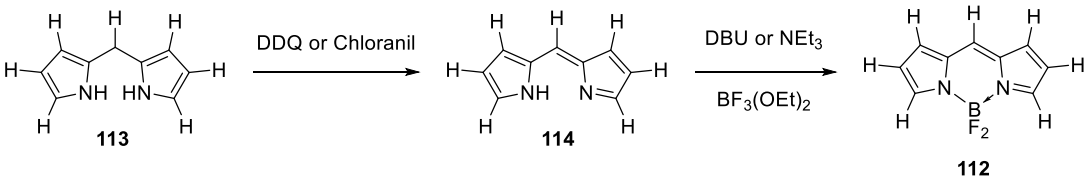
A similar synthesis was devised to give α/β-unsubstituted BODIPY compounds.[62] Benzaldehyde **125** was dissolved in excess pyrrole at room temperature and acid was added, yielding the dipyrromethene **126** exclusively. This was then oxidised with DDQ (*p*-chloranil did not completely oxidise the dipyrromethane so a more potent oxidant was required) and the BODIPY **127** obtained by complexation with boron. This reaction is particularly useful given the lack of side products formed in the initial condensation step.



Scheme 2.34: Synthesis of α/β-unsubstituted BODIPY compounds

2.3.2.2 Synthesis of Unsubstituted BODIPY

As mentioned earlier, the unsubstituted BODIPY compound **112** was not synthesised until 2009 when Tram *et al*. published its synthesis and crystal structure.[63] Due to the unsubstituted dipyrromethene **114** being sensitive to nucleophilic attack they decided to perform the oxidation reaction to form dipyrromethene at -78^{o}C to prevent decomposition. Upon completion of the oxidation, the dipyrromethene was allowed to react with boron trifluoride diethyl etherate, also at -78^{o}C, for one hour before being heated under reflux in dichloromethane. They reported yields of 5-10% of the unsubstituted BODIPY **112** as a bright red solid.



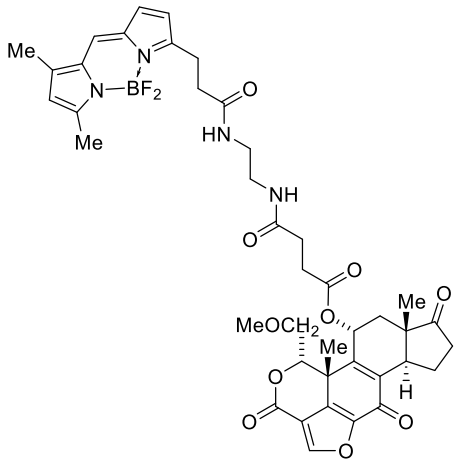
Scheme 2.35: Synthesis of unsubstituted BODIPY **112**

2.3.2.3 Uses/Applications

The fluorescent properties of BODIPY compounds lends them to a range of applications; such as protein labelling, fluorescent switches, chemosensors, cellular imaging and laser dyes, some of these will be discussed further.

2.3.2.3.1 Labelling of Proteins

The labelling of proteins is a useful application of BODIPY derivatives due to their high fluorescence and their insensitivity to solvent polarity and pH. In 1994 a study was conducted to discover the potential of using BODIPY compounds in protein labelling, they discovered that the electronic transition at around 500 nm was shifted away from overlapping absorption bands from both proteins and lipids.[64] The study concluded that BODIPY derivatives linked with proteins would be useful to study conformational changes and interactions with other proteins through energy migration. Later in 2005 a paper reported the synthesis of a BODIPY-Wortmannin compound **128** (Figure 2.23).[65] Wortmannin is a steroid fungal metabolite that is a specific, covalent inhibitor of protein and lipid kinases. The BODIPY-Wortmannin compound was shown to exhibit similar reactivity to Wortmannin itself, with the added ability to permeate cells, allowing for the labelling of proteins within cells. This also meant that analysis of Wortmannin-sensitive proteins in cells could be carried out.



128

Figure 2.23: Structure of BODIPY-Wortmannin compound **128**

2.3.2.3.2 Fluorescent Switches

Light-driven molecular switches are of great interest to the electronics industry, it is a process that exists in nature that chemists have been attracted to due to the convenience of using light to trigger a signal. In 2005 Golovkova *et al*. reported the synthesis of a photochromic dithienylethene moiety attached to iodo-BODIPY *via* a phenylacetylene linker (Figure 2.24).[66]

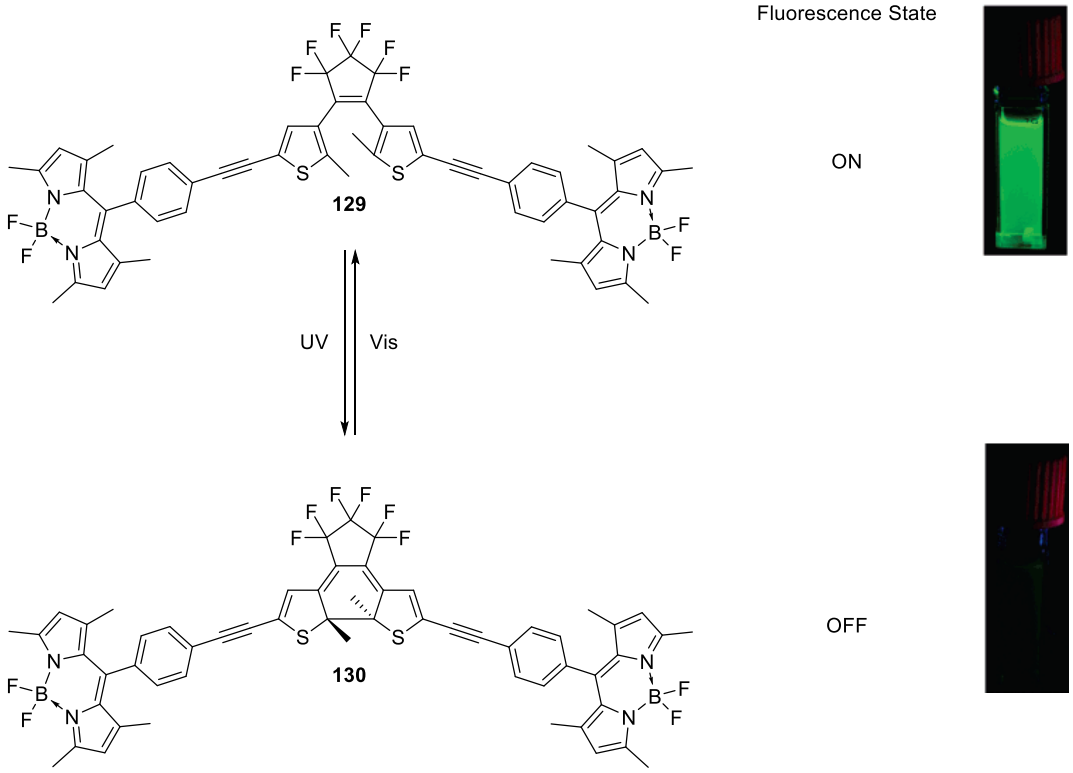
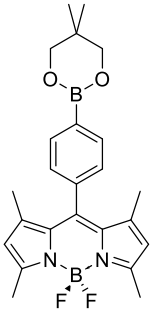


Figure 2.24: Isomerisation of **129**

UV light induces the isomerisation of **129** which turns the fluorescence off (Figure 2.24). The fluorescence can then be recovered with visible light and the process can be repeated without loss of intensity. The compound works well as a photo switch as the open-ring isomer **129** is highly emissive, whereas the fluorescence is significantly quenched in the closed-ring isomer **130**.

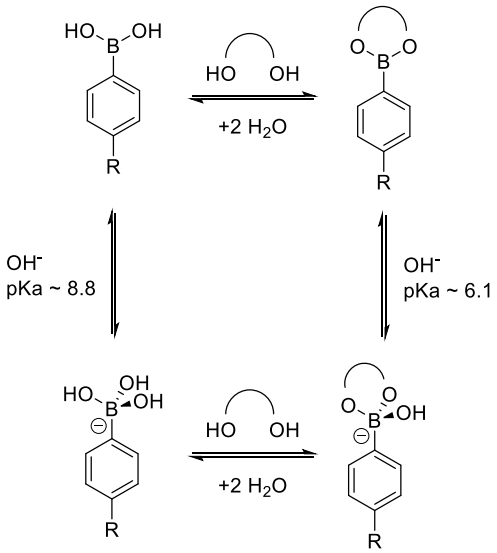
2.3.2.3.3 Chemosensors

BODIPY compounds also lend themselves to be used as chemosensors. In 2001 a highly fluorescent probe for sugars was synthesised of a BODIPY compound functionalised with a boronic acid moiety **131** (Figure 2.25).[67] The detection of sugar in the body is important for the treatment of diabetes, boronic acids are known for their interactions with diols and have been developed as probes for sugars. The boronic acid forms a fast, reversible interaction with the sugar, this forms the anionic form which causes a decrease in the pK_a (Scheme **2.36**). The anionic form is electron rich, and it is this change in the electronic properties that induces a spectral change in the fluorophore. They observed a blue shift of the absorption and also an increase of the absorption coefficient as the concentration of sugar increased.



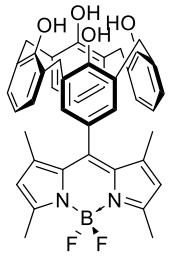
131

Figure 2.25: Structure of fluorescent sugar probe **129**



Scheme 2.36: Equilibrium between boronic acid and sugar/pH

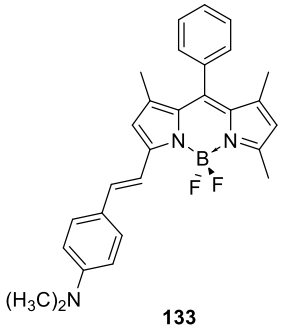
A BODIPY/calixarene complex **132** was synthesised as a pH probe.[68] The near neutral pH molecule signals pH changes by a change in the emission intensity at 509 nm. The emission peak itself at 509 nm is unaltered and the intensity is entirely pH dependent. The fluorescence signal that occurs on pH change is fully reversible.



132

Figure 2.26: Structure of Calix[4]arene-BODIPY pH sensor

Rurack *et al*. synthesised **133** the first unsymmetrically substituted BODIPY dye containing an analyte-responsive receptor conjugated to the core. They found that the compound could be used to probe the solvent polarity and acidity through measuring the fluorescence. As the polarity of the solvent increases, the fluorescent band broadens and shifts to the near infrared, indicating intramolecular charge-transfer processes. In terms of measuring the acidity, protonation of the dimethylamino group alters its electron-donating properties which stops any charge-transfer processes from occurring. This gives typical BODIPY absorption/emission bands; narrow and structured.



133

Figure 2.27: Structure of 3-dimethylaminostyryl functionalised BODIPY **133**

2.3.2.3.4 Cellular Imaging

Fluorescence imaging of living cells is a vital procedure in biomedical research. For this process a fluorescent probe is required that has a high fluorescent quantum yield, BODIPY dyes fit this role and have been developed by Zheng *et al.* for this purpose.[59] BODIPY compounds also have the *meso*-position which can be used to attach specific functional groups in order to label specific biological targets. Zheng synthesised a range of BODIPY compounds (Figure 2.28) and found that they were readily taken up by the cells. Also, the treatment of cells with the fluorophores did not cause any morphological damage showing that the compounds are non-toxic.

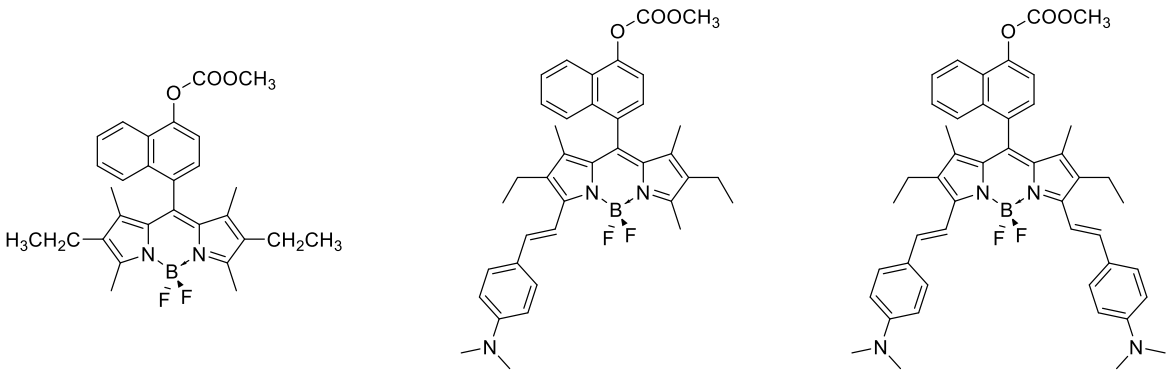
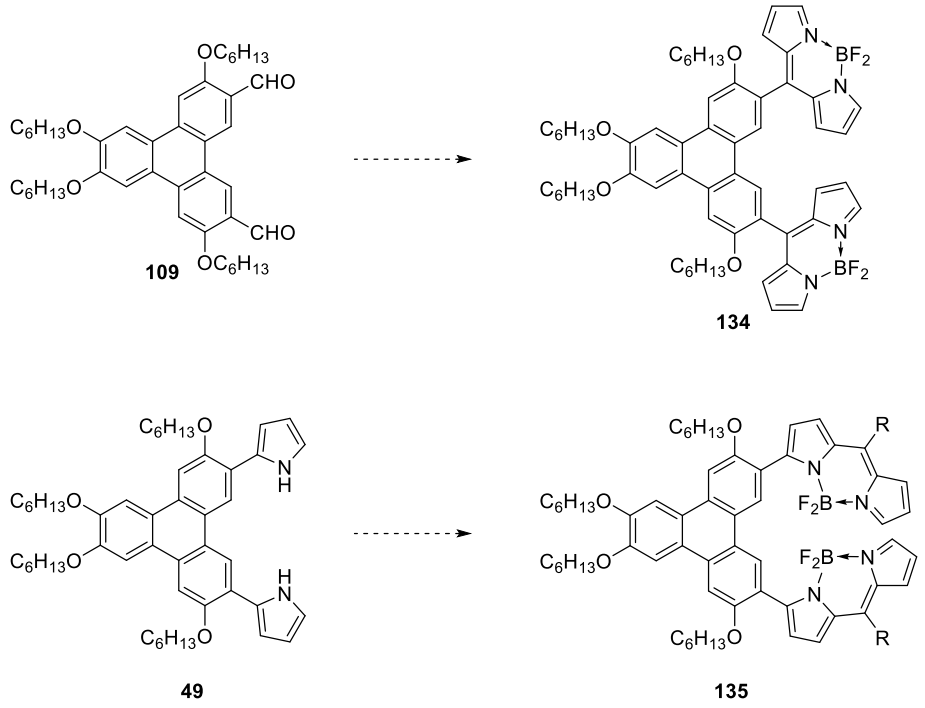


Figure 2.28: BODIPY compounds synthesised for cellular imaging

2.3.3 BODIPY-Triphenylene Target Compounds

The aim of this project was to incorporate the BODIPY moiety onto the triphenylene scaffold, to create a hybrid molecule that has the fluorescent properties of the BODIPY with the self-organising properties of the triphenylene.

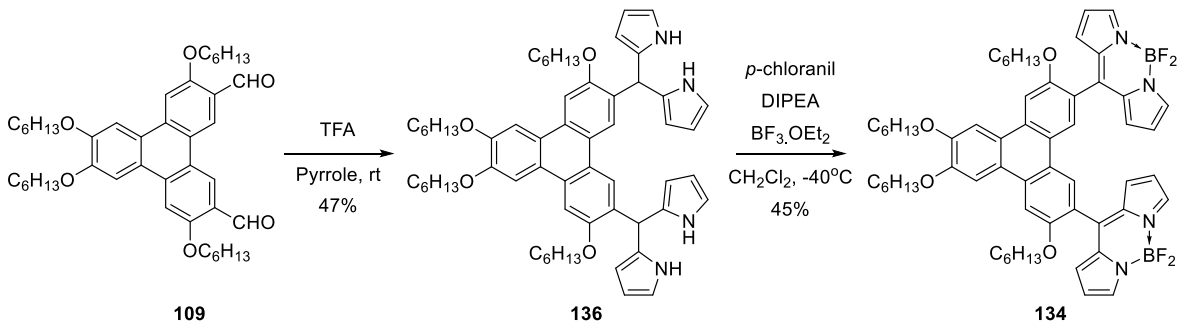
We had two BODIPY-triphenylene target structures, one from the dialdehyde-triphenylene **109**, and the other from the dipyrrolyltriphenylene **49**. The dipyrrolyltriphenylene derivative **49** had been synthesised in the group previously, following the same conditions shown in Scheme 2.4, and the synthesis of the dialdehyde-triphenylene **109** is shown in Scheme 2.31. From the aldehyde, the BODIPY fragment would be attached *via* the central *meso*-carbon to give compound **134**, and from the pyrrole, the BODIPY would be attached from the alpha positions of the pyrrole giving **135**.



Scheme 2.37: BODIPY-triphenylene hybrid structures

2.3.4 Synthesis of Triphenylene-bisBODIPY 134 *via* Dialdehyde-Triphenylene 109

The dialdehyde-triphenylene route was followed first. This was seen to be the simplest synthesis as the reaction should stop at the formation of the dipyrromethane **136**, as an excess of pyrrole was to be used. The reaction was run in freshly distilled pyrrole, the dialdehyde-triphenylene **109** was added along with trifluoroacetic acid (TFA) and the mixture stirred at room temperature. After 45 minutes, TLC analysis showed full consumption of the dialdehyde. A simple work-up of dilution with dichloromethane and a sodium hydroxide wash, then concentration *in vacuo* gave the crude product. The excess pyrrole was distilled off, and the remaining residue was recrystallised from dichloromethane and ethanol, giving the pure product **136** as a light brown powder. Full analysis was carried out and the compound was found to decompose over time, therefore it was taken straight through to the more stable bis-BODIPY product **134**.

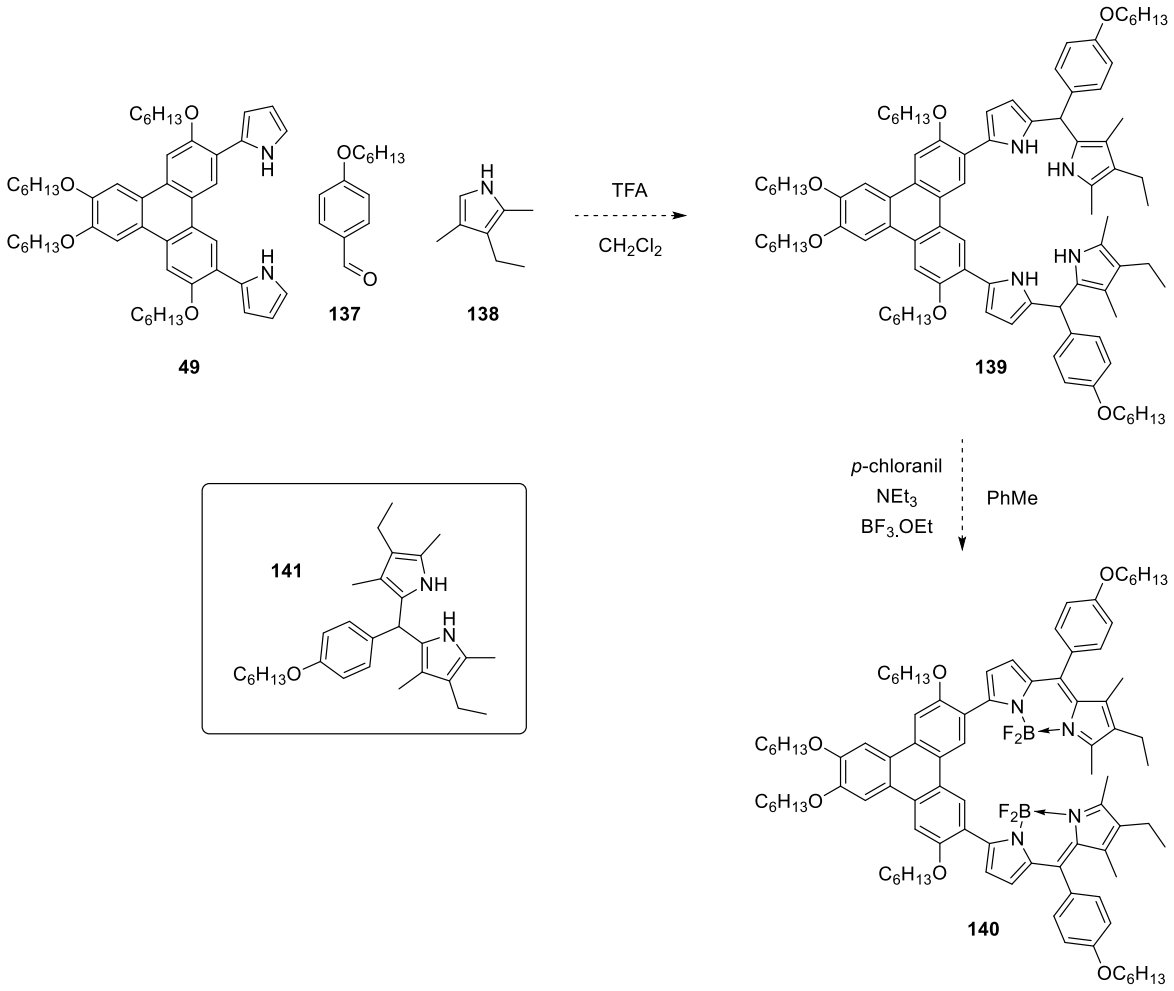


Scheme 2.38: Synthesis of BODIPY-triphenylene **134**

Dipyrromethane-triphenylene **136** was added dropwise *via* an addition funnel to a mixture of *p*-chloranil in anhydrous dichloromethane, the mixture was stirred at -40°C for 3 hours. DIPEA was then added, then 30 minutes later boron trifluoride was added and then the reaction allowed to warm to room temperature overnight. Filtration through celite and a wash with aqueous $NaHCO_3$ gave the crude product. This was then recrystallised from dichloromethane and ethanol to give the pure product **134** as a highly coloured dark red solid.

2.3.5 Attempted synthesis of Triphenylene-bisBODIPY 140 *via* Dipyrrolyltriphenylene 49

The synthesis of the BODIPY *via* the dipyrrolyltriphenylene was perceived to be trickier due to there being many possible products, with the formation of polymer type products also possible. Kryptopyrrole **138** was chosen for the reaction as only the alpha position on the pyrrole is available for the BODIPY formation, which should discourage the potential polymer formation.



Scheme 2.39: Synthetic route to BODIPY **140**

The reaction was performed in anhydrous dichloromethane. Dipyrrolyltriphenylene **49**, hexyloxybenzaldehyde **137** and kryptopyrrole **138** were added and the reaction mixture degassed with argon for 30 minutes. TFA was then added and the mixture stirred at room temperature for 1 hour. After this time a sample was taken and analysed by MALDI-MS, the spectra showed evidence of the desired dipyrromethane-triphenylene **139** with a peak at 1383

m/z, a large peak at 433 *m/z* was also observed, possibly corresponding to the kryptopyrrole-dipyrromethane, **141**.

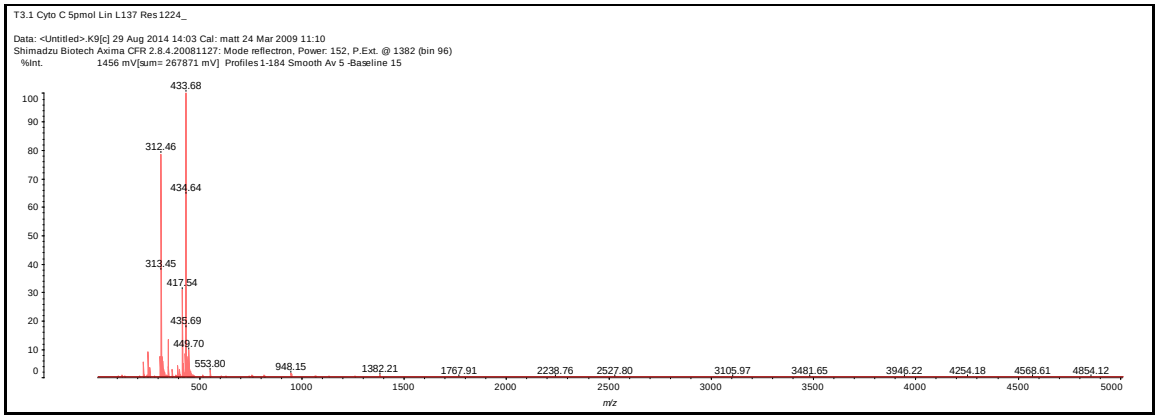


Figure 2.29: MALDI-MS of crude dipyrromethane-triphenylene **139** mixture

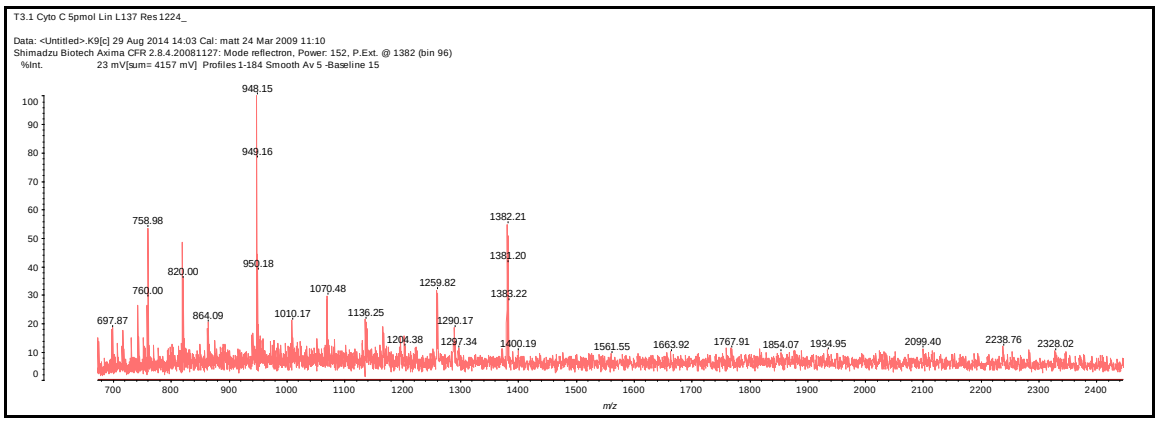


Figure 2.30: Expansion of MALDI-MS showing **139** at 1383 *m/z*

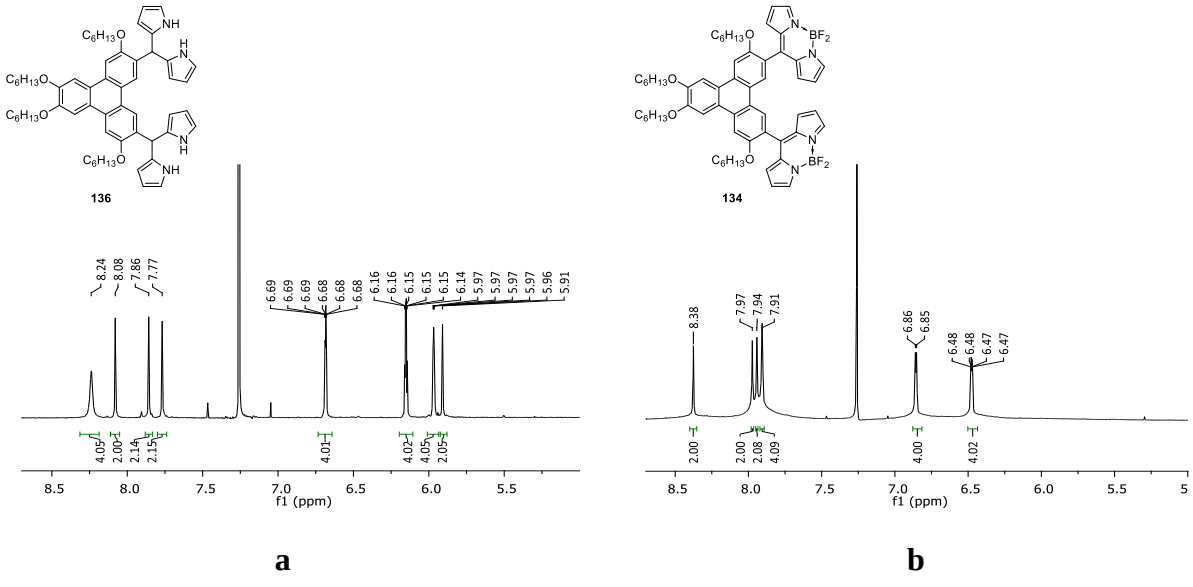
On the basis of this data the reaction was stopped and worked-up, washing with aqueous sodium hydroxide solution and extracting with dichloromethane. Many different purification methods were tried, including recrystallisation from dichloromethane and ethanol, however, the product was not isolated

The reaction was repeated but the order of reaction slightly modified. It was thought that having the concentration of kryptopyrrole increase gradually through the reaction would discourage the formation of the kryptopyrrole-dipyrromethane **141**. The reaction was again performed in anhydrous dichloromethane, with the dipyrrole-triphenylene and benzaldehyde added and the mixture degassed with argon. TFA was then added and the kryptopyrrole added dropwise over a period of 30 minutes. After an hour, a sample was taken and the MALDI-MS spectrum run, again the dipyrromethane-triphenylene was seen along with the

kryptodipyrromethane. The reaction was left to stir at room temperature for 48 hours and the MALDI-MS spectrum was taken of a sample, the dipyrromethane-triphenylene peak was more significant. A sample was worked-up and a TLC ran to isolate the correct spot. The TLC spots were analysed by MALDI-MS, however the peak corresponding to the dipyrromethane-triphenylene was not observed. The difficulties encountered with this reaction were found to be too great to continue the study, therefore the focus was kept on BODIPY **134** synthesised *via* the aldehyde route.

2.3.6 Characterisation of BODIPY-Triphenylene 134

The ^{1}H-NMR-data of BODIPY-triphenylene **134** was realtively simple to analyse. The aromatic regions of both the dipyrromethane **136** and the BODIPY **134** are shown in Figure 2.31. The spectrum simplifies significantly with compound **134** giving six aromatic peaks, three for the triphenylene protons, and three for the BODIPY protons. The dipyrromethane spectrum includes peaks for the NH protons as well as the protons at the *meso* position of the dipyrromethane.



a **b**

Figure 2.31 a and b: Comparison of the aromatic regions of ^{1}H-NMR spectra of compounds **136** and **134** respectively

As discussed previously, BODIPYs are highly fluorescent compounds, therefore we ran studies to investigate the potential fluorescent properties of triphenylene-BODIPY **134**. The UV/Vis spectrum (Figure 2.32) of the highly coloured compound has an absorption maxima

at 504 nm. This is consistant with the observation that the more substitution on the BODIPY causes a red shift in absorption, compound **134** has only *meso* susbitution, and a $\lambda_{max\ abs}$ 504 nm is at the lower end of the examples in Figure 2.21.

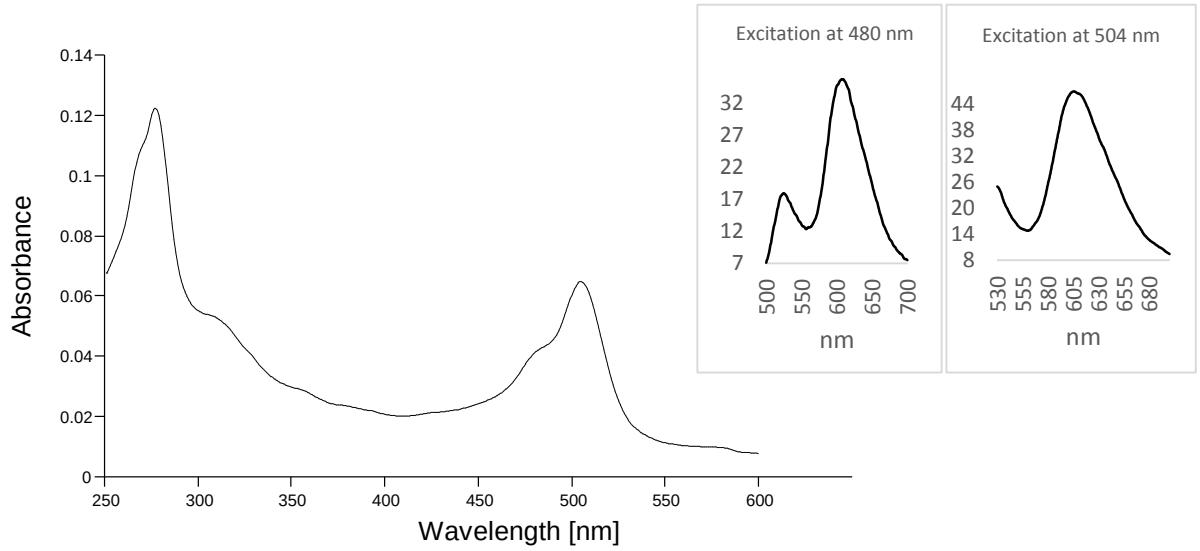


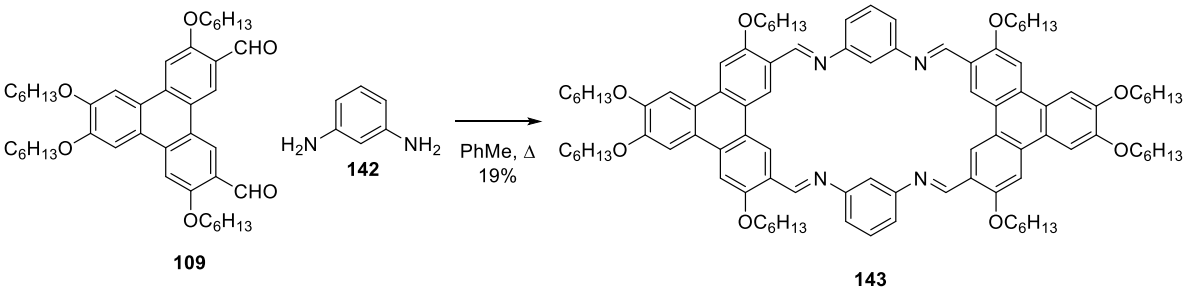
Figure 2.32: UV/Vis and emission spectra of triphenylene-BODIPY **134**

Two excitation wavelengths were used to obtain the emission spectra, 480 nm and 504 nm. As you can see from the spectra the compound does not have a strong emission, the fluorescence intensities are relatively low.

Compound **134** also had potential mesophase behaviour, due to the presence of the triphenylene moiety, however when observed under crossed polarising microscopy the compound was seen to melt with decomposition at 150-160^{o}C.

2.3.7 Synthesis of Imine-Triphenylene Twin 143

The success of the dialdehyde-triphenylene synthesis lead to a new twin target **143**, linking the two triphenylene units *via* imines (Scheme 2.40). The triphenylene **109** and *m*-phenylenediamine **142** were heated at reflux in degassed toluene under a nitrogen atmosphere using a Dean-Stark trap. After 24 hours a sample was taken and analysis by MALDI-MS showed the presence of the desired twin. Another aliquot was taken from the reaction and a small work-up performed. The sample was cooled to room temperature, filtered, and washed with methanol. The ^{1}H-NMR spectrum of the aliquot was run which also confirmed the presence of the twin, the reaction was left for a further 72 hours to push the reaction to completion. After this time, the reaction mixture was cooled to room temperature and filtered, washing with methanol then hexane. The pure product **143** was obtained as a yellow solid, in a 19% yield. The aromatic region of the ^{1}H-NMR spectrum is shown in Figure 2.33.



Scheme 2.40: Synthesis of triphenylene-diamine twin **143**

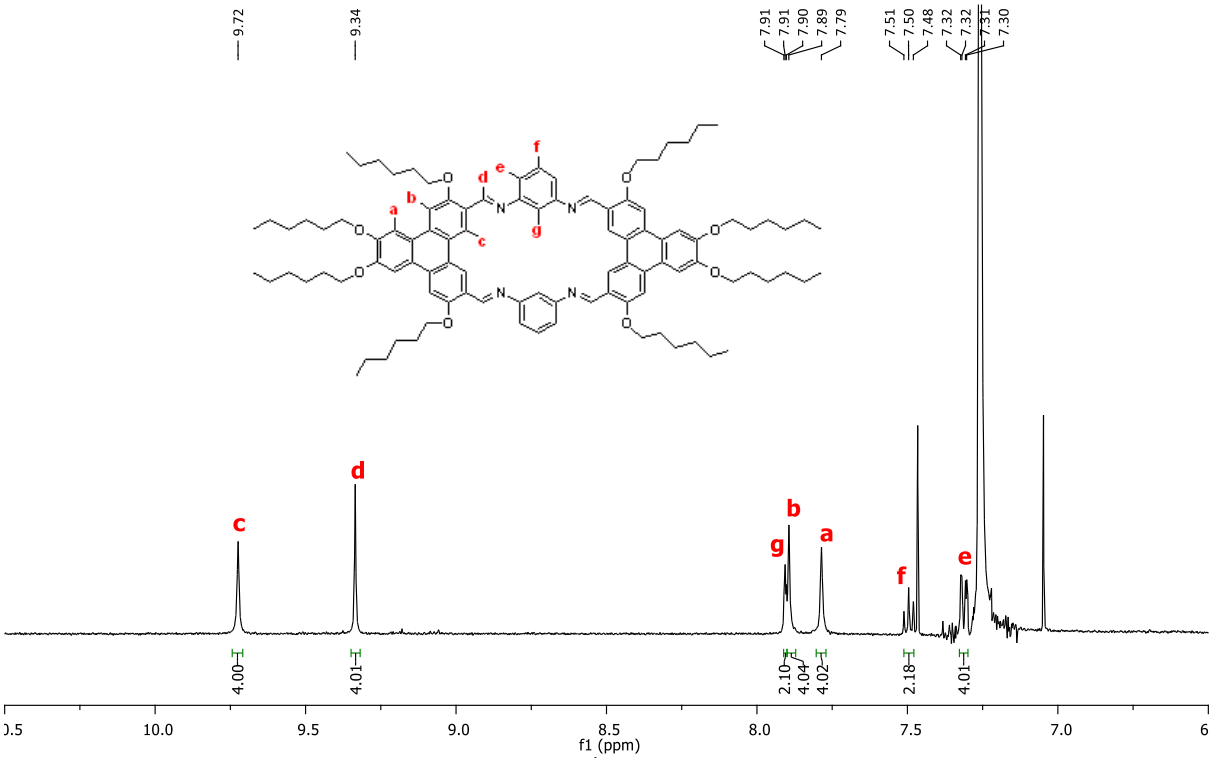


Figure 2.33: Aromatic region of ^{1}H-NMR spectrum of compound **143**

This novel twinned structure retains a central "void" region that we assume will disfavour columnar organisation. The compound was observed under a crossed polarising microscope for any potential mesophase behaviour. Pleasingly, the diamine twin exhibited only a stable nematic discotic mesophase up to 300 ^{o}C [275.7 ^{o}C - 300 ^{o}C], identified by its characteristic schlieren texture and low viscosity (Brownian motion was also observed).

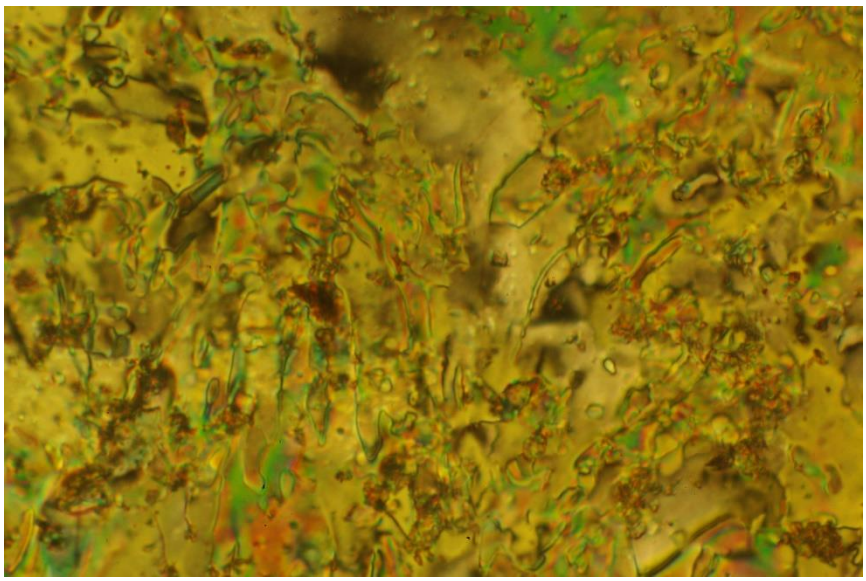


Figure 2.34: Nematic discotic phase of twin **143** as observed by polarising optical microscopy (300 ^{o}C, 100x)

2.4 Conclusions

The synthesis of new triphenylene twins has been investigated, introducing modifications at the triphenylene (side-chain length and number) and in the linking group itself. Our initial work focused on synthesising triphenylene twins linked by pyrroles. The twins bearing hexyloxy chains proved difficult to characterise by spectroscopic techniques, possibly due to aggregation. The corresponding dipyrrolyltriphenylene precursor bearing longer, decyloxy side chains was prepared successfully in an attempt to prepare a more soluble, lower-melting analogue. However, the twinning reaction was unpredictable and the final products could not be unambiguously characterised. At this stage a parallel investigation within the group led to complete characterisation by crystallography of the analogous twins. The data obtained showed the interesting strain-free configuration the compound adopts, where the pyrroles face in opposite directions with respect to the planar core.

The synthesis of a triphenylene twin linked by a triazole was next attempted, reasoning that twin formation could be achieved by a simple "click" reaction between a triphenylene bearing two acetylenes and a partner triphenylene bearing two azide substituents. The triphenylene diacetylene precursor was successfully synthesised but problems were encountered in the azide synthesis. The planned synthesis route involved conversion of a triphenylene-3,6-diamine into the corresponding diazide using diazonium chemistry. The amine itself was to be prepared for the corresponding dinitrotriphenylene. However, nitration of 2,3,6,11-tetraalkoxytriphenylenes unexpectedly yielded the unwanted 1,8- disubstituted product. The regiochemistry was unambiguously proved through a series of synthesis manipulations eventually yielding a crystalline bisimide. Crystals were grown and the x-ray structure was obtained, confirming the structure and regiochemical assignment. A novel twin linked by acetylenes was synthesised from the diacetylenetriphenylene partner but it did not melt beyond 300 °C so any potential mesophase behaviour could not be observed.

Aldehyde groups were successfully introduced at the triphenylene 3,6-positions following a bromination-lithiation-formylation sequence. This precursor allowed synthesis of both a bis-BODIPY triphenylene hybrid, as well as a novel triphenylene twin linked *via* imines. The bis-BODIPY triphenylene hybrids have potential to be an interesting class of compounds, combining the self-organising properties of the triphenylene with the fluorescence of the BODIPY. The imine twin showed a nematic discotic mesophase confirming our hypothesis that twinned structures with a "void" region will disfavour columnar organisation.

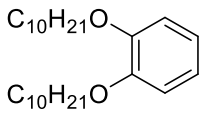
Chapter 3

Experimental

General Procedures

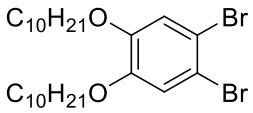
Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F_{254} aluminium backed sheets and was visualised with UV light. NMR spectra were measured in $CDCl_3$, CD_3OD or $(Cl_2CD)_2$ solutions at 500 MHz for ^1H and 126 MHz for ^{13}C. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards for chemical shift determinations. IR spectra were recorded on a Fourier transform interferometer; only diagnostic and/or intense peaks are reported. Melting points were measured on a Reichart hot stage apparatus and are uncorrected. HRMS analyses were performed at the EPSRC National Mass Spectrometry Service Centre at Swansea University. MALDI-MS analyses were recorded on AXIMA-CFRplus equipment. All reagents and solvents were purchased from commercial sources and were purified using standard methods were required, or otherwise used as purchased. Toluene and tetrahydrofuran were both dried over sodium and benzophenone ketal. Dichloromethane and pyridine were both dried over calcium hydride. The petroleum ether used refers to that fraction boiling in the range of 40 – 60 ^oC. Anhydrous dimethyl formamide was bought from Sigma-Aldrich with a purity of 99.8%.

1,2-Bis(decyloxy)benzene 53[69]



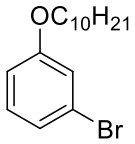
Catechol (20.00 g, 0.182 mol), 1-bromodecane (100.43 g, 0.454 mol) and potassium carbonate (75.31 g, 0.545 mol) were dissolved in ethanol (250 mL). The reaction mixture was stirred and heated at reflux for 48 hours under nitrogen. On completion the mixture was filtered under suction and washed with dichloromethane. The filtrate was collected and the solvent removed *in vacuo*. The crude product was purified using vacuum distillation, collecting the fraction at 185 ^{o}C (2 mm Hg), giving the pure product **53** as an oil that crystallised on standing to give a cream solid (66.16 g, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 4H), 4.05 (t, *J* = 6.6 Hz, 4H), 1.85 (m, 4H), 1.46 (m, 4H), 1.35 (m, 24H), 0.90 (m, 6H) ppm.

1,2-Dibromo-4,5-bis(decyloxy)benzene 54[70]



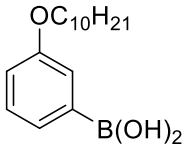
1,2-Bis(decyloxy)benzene **53** (36.13 g, 0.130 mol) was stirred in dichloromethane (300 mL) at -10^{o}C. Bromine (17.53 mL, 54.4 g, 0.340 mol) was added dropwise *via* syringe, and the mixture was stirred at 0 ^{o}C for 1 hour. On completion, the mixture was washed with sodium metabisulphite solution (20%, 200 mL). The organics were extracted with dichloromethane and dried over magnesium sulphate. The solvent was removed *in vacuo*, and the pure product **54** obtained as an orange oil (67.63 g, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 2H), 3.94 (t, *J* = 6.6 Hz, 4H), 1.83-1.76 (m, 4H), 1.48-1.41 (m, 4H), 1.36-1.27 (m, 24H), 0.90-0.87 (m, 6H) ppm.

1-Bromo-3-decyloxybenzene 56[46]



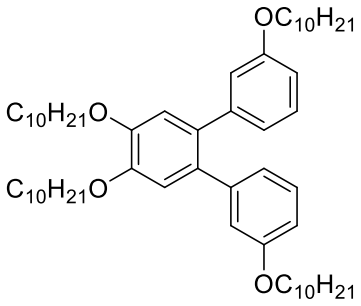
3-Bromophenol (49.60 g, 0.287 mol), 1-bromodecane (95.15 g, 0.430 mol) and potassium carbonate (59.43 g, 0.430 mol) were dissolved in ethanol (250 mL). The reaction mixture was stirred and heated at reflux for 24 hours under nitrogen. On completion the mixture was filtered under suction and washed with dichloromethane. The filtrate was collected and the solvent removed *in vacuo*. The crude product was purified using vacuum distillation, collecting the fraction at 165 ^{o}C (2 mm Hg), giving the pure product **56** as a colourless oil (72.71 g, 81%).^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15-7.07 (m, 3H), 6.85-6.83 (m, 1H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.80-1.77 (m, 2H), 1.48-1.45 (m, 2H), 1.39-1.31 (m, 12H), 0.92-0.91 (m, 3H) ppm.

3-Decyloxyphenyl boronic acid 57[46]



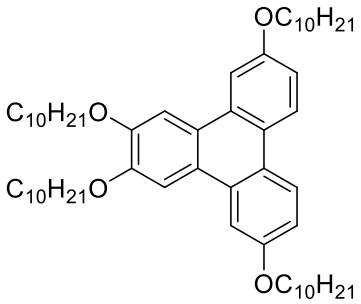
Magnesium turnings (6.20 g, 0.255 mol) were stirred in anhydrous tetrahydrofuran (200 mL). 1-Bromo-3-decyloxybenzene **56** (72.71 g, 0.232 mol) was added slowly *via* addition funnel. Once addition was complete, the reaction was heated at reflux for 90 minutes. Trimethylborate (48.24 g, 0.464 mol) was stirred in anhydrous tetrahydrofuran (200 mL) at -78°C, under nitrogen. The prepared Grignard reagent was added dropwise *via* syringe, keeping the temperature below -60°C, and the mixture stirred for 16 hours. On completion, HCl (~300 mL, 2M) was added to the mixture. The organics were extracted with diethyl ether and dried over magnesium sulphate. The solvent was removed *in vacuo*, and the crude product recrystallized from petroleum ether, giving the pure product **57** as a cream solid (62.29 g, 97%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15-7.06 (m, 3H), 6.84-6.82 (m, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.81-1.74 (m, 2H), 1.47-1.25 (m, 14H), 0.91 (t, *J* = 6.4 Hz, 3H) ppm.

3,3'',4',5'-Tetrakis(decyloxy)-1,1':2',1''-terphenyl 58[46]



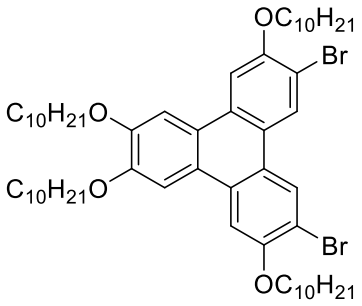
1,2-Dibromo-4,5-bis(decyloxy)benzene **54** (10.00 g, 18.2 mmol), 3-decyloxyphenyl boronic acid **57** (10.15 g, 36.5 mmol), palladium (II) chloride (0.259 g, 1.46 mmol), triphenylphosphine (1.53 g, 5.83 mmol) and sodium carbonate (5.80 g, 54.7 mmol) were stirred in a 1:1:1 mixture of toluene, ethanol and water (240 mL). The reaction mixture was heated to reflux under nitrogen for 24 hours. After this time, the following reagents were added to the mixture, 3-decyloxyphenyl boronic acid **57** (10.15 g, 36.5 mmol), palladium (II) chloride (0.259 g, 1.46 mmol), triphenylphosphine (1.53 g, 5.83 mmol) and sodium carbonate (5.80 g, 54.7 mmol). The reaction was heated under reflux for a further 48 hours. On completion, the reaction was quenched with HCl (100 mL, 2M) and extracted with dichloromethane. The solvents were removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63µ). The column was eluted using a 3:17 mixture of dichloromethane/petroleum ether, and removal of the solvents gave the pure product **58** as a colourless oil (10.07 g, 65%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 7.9 Hz, 2H), 6.96 (s, 2H), 6.74-6.66 (m, 6H), 4.06 (t, *J* = 6.6 Hz, 4H), 3.74 (t, *J* = 6.6 Hz, 4H), 1.88-1.81 (m, 4H), 1.68-1.64 (m, 4H), 1.51-1.45 (m, 4H), 1.37-1.28 (m, 52H), 0.91-0.86 (m, 12H) ppm.

2,3,6,11-Tetrakis(decyloxy)triphenylene 59[46]



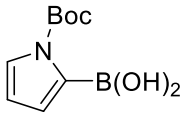
3,3'',4',5'-Tetrakis(decyloxy)-1,1':2',1''-terphenyl **58** (4.87 g, 5.69 mmol) was stirred in dichloromethane (200 mL) at room temperature. Iron (III) chloride (2.77 g, 17.1 mmol) was added slowly, and the resulting mixture stirred for two hours. On completion, the reaction was washed with methanol (200 mL) and water (3x 200 mL), the organics were extracted with dichloromethane and the solvents removed *in vacuo*. The crude product was recrystallized from methanol, giving the pure product **59** as a pale yellow solid (4.52 g, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 9.0 Hz, 2H), 7.91 (s, 2H), 7.85 (d, *J* = 2.5 Hz, 2H), 7.20 (dd, *J* = 2.5, 9.0 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 4.17 (t, *J* = 6.6 Hz, 4H), 1.99-1.87 (m, 8H), 1.58-1.51 (m, 8H), 1.41-1.24 (m, 48H), 0.90-0.82 (m, 12H) ppm.

2,11-Dibromo-3,6,7,10-tetrakis(decyloxy)triphenylene 60[46]



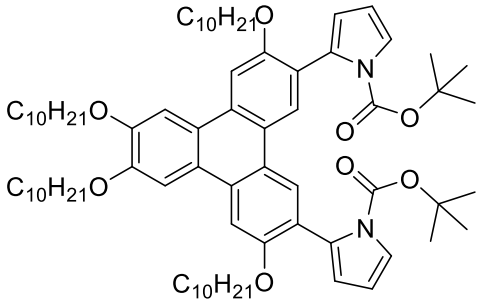
2,3,6,11-Tetrakis(decyloxy)triphenylene **59** (4.00 g, 4.69 mmol) was stirred in dichloromethane (100 mL) at 0°C. Bromine (1.51 g, 0.485 mL, 9.422 mmol) was added dropwise and the reaction stirred for 90 minutes. On completion, the mixture was washed with sodium metabisulphite solution (20%, 70 mL). The organics were extracted with dichloromethane and dried over magnesium sulphate. The solvent was removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63μ). The column was eluted with a 3:7 mixture of dichloromethane/petroleum ether. After removing the solvents *in vacuo* the pure product **60** was obtained as a pale yellow solid (4.50 g, 95%) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 2H), 7.78 (s, 2H), 7.64 (s, 2H), 4.25-4.20 (m, 8H), 1.97-1.94 (m, 8H), 1.63-1.56 (m, 8H), 1.45-1.22 (m, 48H), 0.90-0.87 (m, 12H) ppm.

(1-(*Tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)boronic acid 61[50]



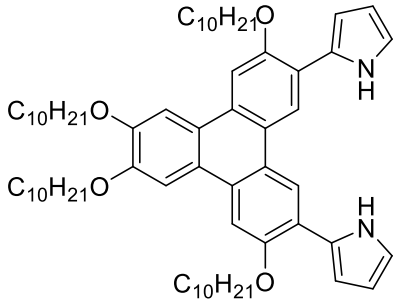
2,2,5,5-Tetramethylpiperidine (22.30 g, 0.158 mol) was stirred in tetrahydrofuran (100 mL) at -78ºC under a nitrogen. *n*-BuLi (2.5 M in hexanes, 63.16 mL, 0.158 mol) was added dropwise to the reaction, keeping the temperature below -70ºC, and the mixture was stirred for 10 minutes. After this time, the reaction mixture was allowed to warm to 0ºC over 30 minutes and then cooled again to -78ºC. A solution of N-Boc-pyrrole (24 g, 0.144 mol) in tetrahydrofuran (100 mL) was added dropwise, keeping the temperature below -70ºC. The reaction mixture was stirred for 2 hours, at -78ºC. Trimethyl borate (44.74 g, 0.431 mol) in tetrahydrofuran (200 mL) was added dropwise, and the mixture allowed to warm to room temperature overnight. On completion, HCl (200 mL, 2M) was added, the volatiles were removed *in vacuo* and the residue was extracted with diethyl ether. The combined organic extracts were washed with water and dried over magnesium sulphate. The solution was slowly concentrated until a solid began to precipitate and then cooled to 0ºC before filtering off the solid and washing with cold diethyl ether. The pure product **61** was obtained as an off-white solid (21.2 g, 70%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 1.6, 3.2 Hz, 1H), 7.19 (s, 2H), 7.10 (dd, *J* = 1.6, 3.2 Hz, 1H), 6.26 (t, *J* = 3.2 Hz, 1H), 1.62 (s, 9H) ppm.

Di-*tert*-butyl 2,2'-(3,6,7,10-tetrakis(decyloxy)triphenylene-2,11-diyl)bis(1*H*-pyrrole-1-carboxylate) 62



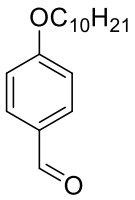
2,11-Dibromo-3,6,7,10-tetrakis(decyloxy)triphenylene **60** (5.00 g, 4.95 mmol), (1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)boronic acid **61** (10.44 g, 49.5 mmol), palladium(II) chloride (0.0701 g, 0.3956 mmol), triphenylphosphine (0.145 g, 1.58 mmol) and sodium carbonate (5.241 g, 49.5 mmol) were stirred in a 1:1:1 mixture of toluene, ethanol and water (120 mL). The reaction mixture was heated to reflux under a nitrogen for 6 hours. On completion, the reaction was washed with water and the organics extracted with dichloromethane, then dried over magnesium sulphate. The solvents were removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63µ). The column was eluted using a 2:3 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **62**, was obtained as a colourless oil (5.214 g, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 2H), 7.94 (s, 2H), 7.77 (s, 2H), 7.41 (t, *J* = 2.6 Hz, 2H), 6.28 (d, *J* = 2.6 Hz, 4H), 4.27 (t, *J* = 6.5 Hz, 4H), 4.11 (t, *J* = 6.5 Hz, 4H), 2.0-1.93 (s, 4H), 1.80-1.73 (m, 4H), 1.64-1.55 (m, 4H), 1.46-1.28 (m, 70H), 0.91-0.88 (m, 12H) ppm.

2,2'-(3,6,7,10-Tetrakis(decyloxy)triphenylene-2,11-diyl)bis(1*H*-pyrrole) 63



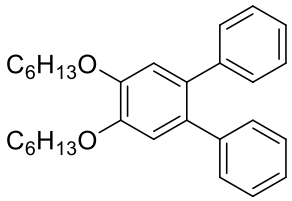
Di-*tert*-butyl 2,2'-(3,6,7,10-tetrakis(decyloxy)triphenylene-2,11-diyl)bis(1*H*-pyrrole-1-carboxylate) **62** (5.00 g, 4.85 mmol) was heated at 200°C as a neat oil under reduced pressure for 90 minutes. The crude material was cooled and loaded onto a silica gel column (pore size 40-63μ), eluting with a 2:3 mixture of dichloromethane/petroleum ether. After removal of the solvents, the pure product **63** was obtained an off-white solid (1.66 g, 40%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 2H), 8.79 (s, 2H), 7.80 (s, 2H), 7.76 (s, 2H), 6.95-6.91 (m, 4H), 6.41, (d, *J* = 3.3 Hz, 2H), 4.30 (t, *J* = 6.3 Hz, 4H), 4.22 (t, *J* = 6.5 Hz, 4H), 2.06-1.91 (m, 8H), 1.62-1.54 (m, 8H), 1.48-1.30 (m, 48H), 0.91-0.88 (m, 12H) ppm.

4-(Decyloxy)benzaldehyde 66[71]



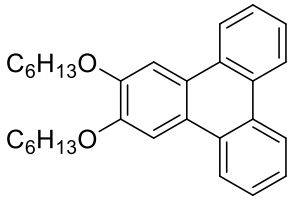
4-Hydroxybenzaldehyde (2.00 g, 16.38 mmol), 1-bromodecane (5.43 g, 24.57 mmol), potassium carbonate (4.53 g, 32.75 mmol) and potassium iodide (0.19 g, 1.15 mmol) were stirred in acetone (30 mL) under nitrogen. The mixture was heated at reflux for 48 hours. On completion, the reaction mixture was filtered and washed with dichloromethane. The filtrate was collected and concentrated *in vacuo*. The crude product was distilled under vacuum, collecting the fraction at 210 ^{o}C (1 mm Hg), giving the pure product **66** as a colourless oil (2.23 g, 51%) ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.82-1.75 (m, 2H), 1.48-1.41 (m, 2H), 1.35-1.26 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm.

4',5'-Bis(hexyloxy)-1,1':2'',1''-terphenyl 71[3]



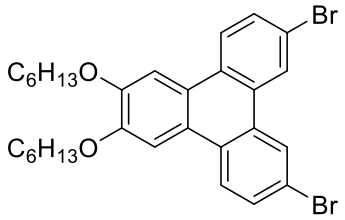
1,2-Dibromo-4,5-bis(hexyloxy)benzene **28** (10 g, 0.0229 mol), benzene boronic acid (8.39 g, 0.0687 mol), palladium chloride (0.3252 g, 1.83 mmol), triphenylphosphine (1.9226 g, 7.34 mmol) and sodium carbonate (7.29 g, 0.0684 mol) were stirred in a mixture of toluene, ethanol and water (1:1:1, 240 mL). The reaction was heated at reflux for 16 hours. After 16 hours, benzene boronic acid (8.39 g, 0.0687 mol), palladium chloride (0.3252 g, 1.83 mmol), triphenylphosphine (1.9226 g, 7.34mmol) and sodium carbonate (7.29 g, 0.0684 mol) were added to the reaction mixture, to ensure the reaction went to completion. After 40 hours, the reaction was quenched with hydrochloric acid (200 mL, 2M). The organics were extracted with dichloromethane and dried over magnesium sulphate. The solvents were removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63μ). The column was eluted using a 1:9 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **71** was obtained as a colourless oil (6.71 g, 68%). IR (thin film) ν 2930, 2859, 1602 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.22-7.11 (m, 10H), 6.95 (s, 2H), 4.07 (t, *J* = 6.6 Hz, 4H), 1.88-1.82 (m, 4H), 1.56-1.46 (m, 4H), 1.37-1.33 (m, 8H), 0.93-0.90 (m, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 148.4, 141.6, 133.1, 130.0, 127.8, 126.1, 116.2, 69.5, 31.6, 29.3, 25.7, 22.6, 14.0 ppm.

2,3-Bis(hexyloxy)triphenylene 73[3]



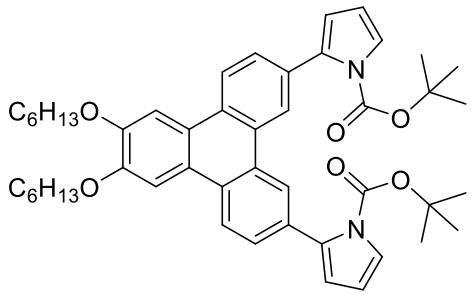
A solution of 4',5'-bis(hexyloxy)-1,1':2'',1''-terphenyl **71** (5.68 g, 0.0136 mol) in dichloromethane (250 mL) was stirred at room temperature. Iron (III) chloride (10.697 g, 0.0660 mol) was added and the reaction mixture was stirred for a further two hours. The reaction mixture was cooled to -10^{o}C and methanol (50 mL) was added. The solvents were removed *in vacuo*, and the resulting crude residue dissolved in dichloromethane. This was then washed with water (4 x 100 mL) and the organics were collected then dried over magnesium sulphate. The solvents were removed *in vacuo* and the crude product was loaded onto a silica gel column (pore size 40-63µ). The column was eluted using a 1:9 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **73** was obtained as a white solid (3.62 g, 62%). IR (thin film) ν 2926, 2856, 1613, 1185 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 1.1, 8.0 Hz, 2H), δ 8.51 (dd, *J* = 1.1, 8.0 Hz, 2H), 8.03 (s, 2H), 7.67-7.59 (m, 4H), 4.26 (t, *J* = 6.6 Hz, 4H), 2.01-1.96 (m, 4H), 1.63-1.59 (m, 4H), 1.48-1.42 (m, 8H), 1.02-0.99 (m, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 149.7, 129.7, 129.2, 127.0, 126.2, 124.3, 123.4, 122.9, 106.8, 69.4, 31.8, 29.4, 25.9, 22.8, 22.8, 14.2 ppm.

7,10-Dibromo-2,3-bis(hexyloxy)triphenylene 74[72]



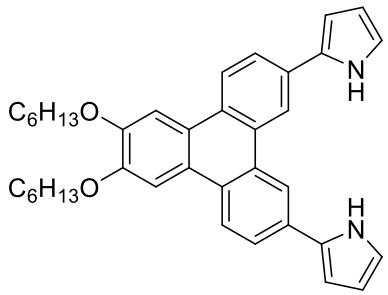
2,3-Bis(hexyloxy)triphenylene **73** (3.4 g, 7.93 mmol) was stirred in dichloromethane (150 mL) at 0°C. Bromine (0.89 mL, 2.79 g, 0.017 mol) was added dropwise *via* pipette and the mixture stirred for a further 2 hours at 0°C and then allowed to warm to room temperature. The reaction mixture was washed with sodium metabisulphite solution (20%, 100 mL) and the crude product extracted with dichloromethane. The combined organic layers were dried over magnesium sulphate, and the solvent removed *in vacuo*. The crude product was recrystallized from pentanol, giving the pure product **74** as a white powder (3.26 g, 70%). IR (thin film) ν 2927, 2857, 1614, 1189 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.0 Hz, 2H), 8.32 (d, *J* = 9.0 Hz, 2H), 7.91 (s, 2H), 7.73 (dd, *J* = 2.0, 9.0 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 1.98-1.92 (m, 4H), 1.60-1.53 (m, 4H), 1.44-1.37 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 150.1, 130.6, 129.6, 128.7, 126.2, 124.7, 123.6, 120.6, 106.5, 69.4, 31.7, 29.3, 25.8, 22.7, 14.1 ppm.

Di-*tert*-butyl 2,2'-(6,7-bis(hexyloxy)triphenylene-2,11-diyl)bis(1*H*-pyrrole-1-carboxylate) 76



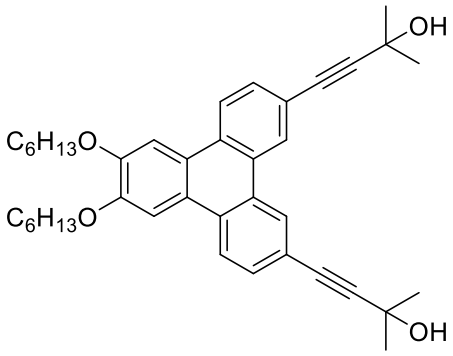
7,10-Dibromo-2,3-bis(hexyloxy)triphenylene **74** (1.54 g, 2.63 mmol), (1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)boronic acid **61** (5.55 g, 20.6 mmol), palladium(II) chloride (0.04 g, 0.21 mmol), triphenylphosphine (0.22 g, 0.84 mmol) and sodium carbonate (2.79 g, 20.6 mmol) were stirred in a 1:1:1 mixture of toluene, ethanol and water (60 mL). The reaction mixture was heated to reflux under nitrogen for 7 hours. On completion, the reaction was washed with water and the organics extracted with dichloromethane then dried over magnesium sulphate. The solvents were removed *in vacuo* and loaded onto a silica gel column (pore size 40-63µ). The column was eluted using a 1:1 mixture of dichloromethane and petroleum ether. After removal of solvents, the pure product, **76**, was obtained as a colourless oil (1.71 g, 85 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 1.6 Hz, 2H), 8.46 (d, *J* = 8.7 Hz, 2H), 8.02 (s, 2H), 7.63 (dd, *J* = 1.6, 8.7 Hz, 2H), 7.42 (dd, *J* = 1.8, 3.3, 2H), 6.33 (dd, *J* = 1.8, 3.3 Hz, 2H),6.90 (t, *J* = 3.3 Hz, 2H), 4.26 (t, *J* = 6.6 Hz, 4H), 1.99-1.93 (m, 4H). 1.62-1.56 (m, 4H), 1.43-1.36 (m, 8H), 1.32 (s, 18H), 0.94 (t, *J* = 7.0 Hz, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 149.8, 149.6, 135.2, 132.4, 128.9, 128.6, 128.6, 124.3, 123.8, 122.9, 122.1, 115.0, 110.9, 107.0, 83.8, 69.5, 41.5, 31.8, 29.5, 27.8, 26.0, 22.8, 22.8, 14.2 ppm.

2,2'-(6,7-Bis(hexyloxy)triphenylene-2,11-diyl)bis(1*H*-pyrrole) 70



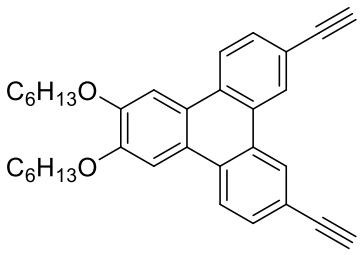
Di-*tert*-butyl 2,2'-(6,7-bis(hexyloxy)triphenylene-2,11-diyl)bis(1*H*-pyrrole-1-carboxylate) **76** (1.6 g, 2.11 mmol) was heated at 200°C as a neat oil under reduced pressure for 90 minutes. The crude material was cooled and loaded onto a silica gel column (pore size 40-63μ), eluting with a 2:3 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **70** was obtained as an off-white solid (0.35 g, 30%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 2H), 8.63 (s, 2H), 8.39 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 2H), 6.72 (s, 2H), 6.40 (d, *J* = 2.5 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 4H), 1.97-1.91 (m, 4H), 1.59-1.54 (m, 4H), 1.43-1.38 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 6H) ppm.

4,4'-(6,7-Bis(hexyloxy)triphenylene-2,11-diyl)bis(2-methylbut-3-yn-2-ol) 93



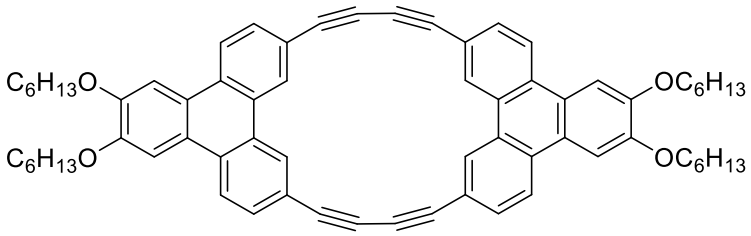
A mixture of 7,10-dibromo-2,3-bis(hexyloxy)triphenylene **74** (1.37 g, 2.33 mmol), copper iodide (0.027 g, 0.14 mol) and bis(triphenylphosphine)palladium(II) dichloride (0.098 g, 0.14 mol) were stirred in degassed triethylamine (50 mL) under nitrogen. The reaction mixture was heated at reflux for 30 minutes. 2-Methyl-but-3-yn-2-ol (1.13 ml, 0.98 g, 0.012 mol) was added *via* syringe and the reaction heated under reflux for 16 hours. On completion, the crude mixture was washed with water and the organics were extracted with dichloromethane. The organic extracts were combined and dried over magnesium sulphate. The solvent was removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63µ). The column was eluted using a 3:1:1 mixture of dichloromethane, ethyl acetate and petroleum ether respectively. After removal of solvents, the pure product **93** was obtained as a pale yellow solid (1.10 g, 80%). Mp. 148-150 ^{o}C; IR (thin film) ν 3351, 2931, 2859, 1614 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 2H), 8.37 (d, *J* = 8.6 Hz, 2H), 7,92 (s, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 2.14 (br s, 2H), 1.97-1.92 (m, 4H), 1.72 (s, 12H), 1.59-1.55 (m, 4H), 1.42-1.38 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 150.1, 130.1, 129.6, 128.3, 127.2, 124.2, 123.0, 120.5, 106.8, 94.5, 82.7, 69.5, 66.0, 31.8, 31.8, 31.2, 29.4, 25.9, 22.8, 14.2 ppm; HRMS (ASAP (Solid)) *m/z* calculated for $C_{40}H_{48}O_4$ $[M]^+$: 592.3547; found: 592.3533.

7,10-Diethynyl-2,3-bis(hexyloxy)triphenylene 90



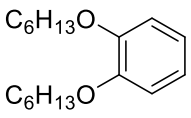
4,4'-(6,7-Bis(hexyloxy)triphenylene-2,11-diyl)bis(2-methylbut-3-yn-2-ol) **93** (1.0 g, 1.69 mmol) was stirred in anhydrous toluene (50 mL) under nitrogen, and the mixture heated to reflux. Sodium hydride (0.18 g, 7.59 mmol) was added portion-wise, and after the addition was complete, the reaction was heated at reflux for a further 3 hours. Upon completion the reaction was poured onto cold water, and extracted with dichloromethane. The organic extracts were combined and dried over magnesium sulphate, and the solvent removed *in vacuo*. The crude product was loaded onto a silica gel column (pore size 40-63µ) and the column was eluted with a 1:9 mixture of ethyl acetate/petroleum ether. After removal of solvents, the pure product **90** was obtained as a yellow solid (0.48 g, 60%). Mp. 92-94 ^{o}C; IR (thin film) ν 3287, 2926, 2857, 2105, 1614 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 2H), 8.40 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 4H), 1.98-1.92 (m, 4H), 1.61-1.56 (m, 4H), 1.42-1.39 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 150.3, 130.5, 130.1, 128. 3, 127.8, 124.2, 123.1, 120.0, 106.8, 84.2, 77.9, 69.5, 31.8, 29.4, 25.9, 22.8, 14.2 ppm; HRMS (ASAP (Solid)) *m/z* calculated for $C_{34}H_{36}O_2$ $[M+H]^+$: 477.2788; found: 477.2788.

Di-acetylenetriphenylene twin 108



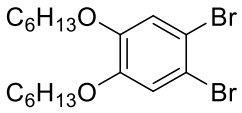
Copper chloride (187 mg, 1.89 mmol) and copper acetate (377 mg, 1.89 mmol) were stirred in anhydrous pyridine (50 mL) at 60 ^{o}C under nitrogen. 7,10-Diethynyl-2,3-bis(hexyloxy)triphenylene **90** (400 mg, 0.839 mmol) dissolved in anhydrous pyridine (15 mL), was added *via* syringe to the reaction at a rate of 0.012 mL/min. After addition was complete, the reaction was stirred at 60^{o}C for a further 24 hours. Upon completion, the solvent was removed *in vacuo* and the crude product underwent soxhlet extraction with THF. The THF solution was left to stand overnight, and the pure product **108** obtained by filtration as a yellow solid (30 mg, 5%). Mp. > 300 ^{o}C; ^{1}H-NMR (500 MHz, $(Cl_2CD)_2$, 80^{o}C) δ 9.51 (s, 4H), 8.37 (d, *J* = 8.4 Hz, 4H), 7.98 (s, 4H), 7.57 (d, *J* = 8.4 Hz, 4H), 4.29 (s, 8H), 1.97 (s, 8H), 1.63 (s, 8H), 1.48 (s, 16H), 1.01 (s, 12H) ppm; MS (MALDI): *m/z* 948.5 (M^+, 100%).

1,2-Dihexyloxybenzene 25[11]



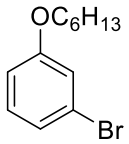
Catechol (10 g, 0.09 mol), 1-bromohexane (37.48 g, 0.227 mol) and potassium carbonate (31.38 g, 0.227 mol) were stirred in ethanol (120 mL) under nitrogen. The reaction mixture was heated at reflux for 36 hours. On completion the mixture was filtered under suction and washed with dichloromethane. The filtrate was collected and the solvent removed *in vacuo*. The crude product was distilled, collecting the fraction at 180^{o}C (2 mmHg) giving the pure product **25** as a clear orange oil (24 g, 95%). IR (thin film) ν 2931, 2859, 1597 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 4H), 4.01 (t, *J* = 6.63 Hz, 4H), 1.7-1.81 (m, 4H), 1.53-1.48 (m, 4H), 1.39-1.37 (m, 8H), 0.95-0.92 (m, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 149.4, 121.1, 114.2, 69.4, 31.74, 29.5, 25.9, 22.7, 14.1 ppm.

1,2-Dibromo-4,5-bis(hexyloxy)benzene 28[3]



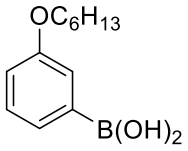
1,2-Dihexyloxybenzene **25** (24 g, 0.085 mol) was stirred in dichloromethane (120 mL) at 0^{o}C. Bromine (8.75 mL, 27.29 g, 0.171 mol) was added dropwise *via* syringe, and the mixture was stirred at 0^{o}C for 1 hour. On completion, the mixture was washed with sodium metabisulphite solution (20%, 100 mL). The organics were extracted with dichloromethane and dried over magnesium sulphate. The solvent was removed *in vacuo*, and the pure product **28** obtained as an orange oil (35 g, 96%). IR (thin film) ν 2930, 2859, 1586 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 3.94 (t, *J* = 6.58 Hz, 4H), 1.81-1.76 (m, 4H), 1.48-1.42 (m, 4H), 1.34-1.31 (m, 8H). 0.90 (t, *J* = 6.9 Hz, 6H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 149.1, 118.0, 114.7, 69.6, 31.6, 29.1, 25.7, 22.7, 14.1 ppm.

1-Bromo-3-hexyloxybenzene 97[73]



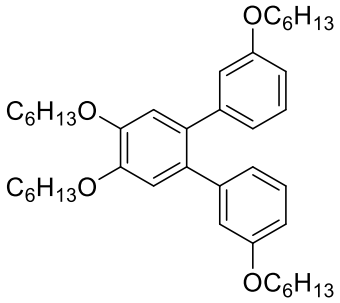
3-Bromophenol (44.86 g, 0.259 mol), 1-bromohexane (64.20 g, 0.389 mol) and potassium carbonate (53.75 g, 0.389 mol) were dissolved in ethanol (250 mL). The reaction mixture was stirred and heated at reflux for 16 hours, under nitrogen. On completion the mixture was filtered under vacuum and washed with dichloromethane. The filtrate was collected and the solvent removed *in vacuo*. The crude product was purified using vacuum distillation, collecting the fraction at 126 ^{o}C (2 mmHg), giving the pure product **97** as a colourless oil (65.35 g, 98%). IR (thin film) ν 2932, 2859, 1589 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.15-7.07 (m, 3H), 6.85-6.83 (m, 1H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.81-1.76 (m, 2H), 1.48-1.44 (m, 2H), 1.39-1.35 (m, 4H), 0.96-0.93 (m, 3H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 160.1, 130.5, 123.6, 122.9, 117.8, 113.6, 68.3, 31.7, 29.2, 25.8, 22.7, 14.2 ppm.

3-Hexyloxyphenyl boronic acid 29[73]



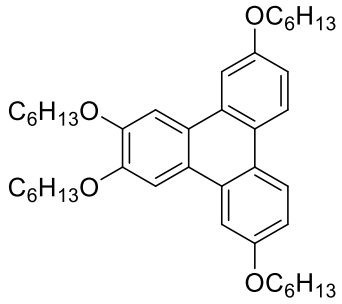
Magnesium turnings (6.90 g, 0.280 mol) were stirred in anhydrous THF (200 mL) under nitrogen. 1-Bromo-3-hexyloxybenzene **97** (65.35 g, 0.255 mol) was added dropwise *via* addition funnel. After addition was complete, the reaction was heated under reflux for two hours. Trimethyl borate (53.0 g, 0.510 mol) was stirred in anhydrous THF (200 mL), under nitrogen at -78°C. The Grignard reagent was added dropwise *via* syringe to the reaction mixture, keeping the temperature of the reaction below -50^{o}C, and the reaction mixture stirred for 24 hours at -78 ^{o}C. On completion, 2M HCl (~300 mL) was added to the reaction until the white precipitate dissolved to give a pale yellow solution. The organics were extracted with diethyl ether and dried over magnesium sulphate. The solvent was removed *in vacuo*, and the crude product recrystallised from petroleum ether, giving the pure product **29** as a cream solid (41.8 g, 74%). IR (thin film) ν 3253, 2931, 2423 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.24 (m, 3H), 6.92 (s, 1H), 3.98-3.95 (m, 2H), 1.76-1.74 (m, 2H), 1.51-1.45 (m, 2H), 1.38-1.35 (m, 4H), 0.94-0.91 (m, 3H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 160.0, 129.7, 127.0, 120.4, 117.6, 68.9, 32.8, 30.5, 26.9, 23.7, 14.4 ppm.

3,3'',4',5'-Tetrakis(hexyloxy)-1,1':2',1''-terphenyl 30[3]



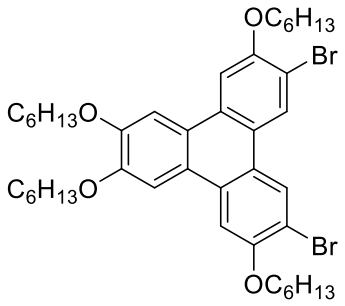
1,2-Dibromo-4,5-bis(hexyloxy)benzene **28** (11.80 g, 0.027 mol), 3-hexyloxyphenyl boronic acid **29** (18.02 g, 0.081 mol), palladium (II) chloride (0.384 g, 2.16 x10^{-3} mol), triphenylphosphine (2.27 g, 8.65 x10^{-3} mol) and sodium carbonate (8.60 g, 0.081 mol) were stirred in a mixture of toluene, ethanol and water (1:1:1, 240 mL). The reaction was heated at reflux for 16 hours. After 16 hours, 3-hexyloxyphenyl boronic acid **29** (18.02 g, 0.081 mol), palladium (II) chloride (0.384 g, 2.16 x10^{-3} mol), triphenylphosphine (2.27 g, 8.65 x10^{-3} mol) and sodium carbonate (8.60 g, 0.081 mol) were added to the reaction mixture, to ensure the reaction went to completion. After 40 hours, the reaction was quenched with hydrochloric acid (200 mL, 2M) and the organics were extracted with dichloromethane then dried over magnesium sulphate. The solvents were removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63μ). The column was eluted using a 1:4 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **30** was obtained as a colourless oil (12.03 g, 70%). IR (thin film) ν 2931, 2859, 1600 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.9 Hz, 2H), 6.96 (s, 2H), 6.74-6.67 (m, 6H), 4.06 (t, *J* = 6.6 Hz, 4H), 3.74 (t, *J* = 6.6 Hz, 4H), 1.88-1.82 (m, 4H), 1.69-1.64 (m, 4H), 1.54-1.47 (m, 4H), 1.40-1.27 (m, 20H), 0.93-0.89 (m, 12H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 158.7, 148.5, 143.0, 133.2, 128.9, 122.3, 116.1, 116.1, 113.1, 69.6, 68.0, 31.7, 31.7, 29.5, 29.2, 25.9, 25.8, 22.8, 22.8, 14.2, 14.2 ppm.

2,3,6,11-Tetrakis(hexyloxy)triphenylene 31[3]



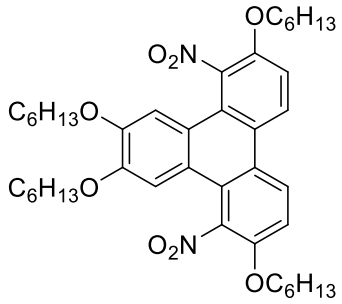
A solution of 3,3'',4',5'-tetrakis(hexyloxy)-1,1':2',1''-terphenyl **30** (11.5 g, 0.0182 mol) in dichloromethane (250 mL) was stirred at room temperature. Iron (III) chloride (8.87 g, 0.0547 mol) was added slowly and the reaction mixture was stirred for a further two hours. Methanol (50 mL) was added to the reaction mixture, which was then washed with water (4 x 100 mL). The organic extracts were collected and the solvents removed *in vacuo*. The product was recrystallised from methanol giving the pure product **31** as a yellow solid (9.74 g, 85%). IR (thin film) ν 2928, 2855 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.0 Hz, 2H), 7.91 (s, 2H), 7.85 (d, *J* =2.5 Hz, 2H), 7.20 (dd, *J* = 2.5, 9.0 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 4H), 4.17 (t, *J* = 6.6 Hz, 4H), 1.97-1.87 (m, 8H), 1.60-1.53 (m, 8H), 1.43-1.37 (m, 16H), 0.95-0.92 (m, 12H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 157.8, 149.7, 130.1, 124.6, 124.5, 123.5, 114.7, 107.4, 107.1, 69.6, 68.5, 31.8, 31.8, 29.6, 29.5, 26.0, 26.0, 22.8, 14.2, 14.2 ppm.

2,11-Dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene 94[3]



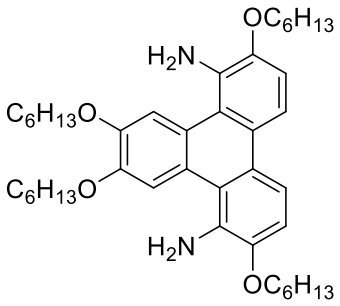
2,3,6,11-Tetrakis(hexyloxy)triphenylene **31** (9.0 g, 0.0143 mol) was stirred in dichloromethane (250 mL) at 0°C. Bromine (4.60 g, 1.48 mL, 0.0288 mol) was added dropwise *via* pipette, and the mixture stirred for 30 minutes. Sodium metabisulphite solution (20%, 100 mL) was added to the mixture, and the crude product extracted with dichloromethane. The combined organic phases were dried over magnesium sulphate, and the solvents were removed *in vacuo*. The crude product was loaded onto a silica gel column (pore size 40-63µ) and eluted using a 1:4 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **94** was obtained as a light yellow powder (7.88 g, 70%). IR (thin film) ν 2930, 2859, 1600 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.67 (s, 2H), 7.46 (s, 2H), 4.25 (t, *J* = 6.5 Hz, 4H), 4.17 (t, *J* = 6.5 Hz, 4H), 2.0-1.93 (m, 8H), 1.65-1.59 (m, 8H), 1.46-1.40 (m, 16H), 0.98-0.95 (m, 12H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 153.9, 149.8, 129.0, 127.3, 123.8, 122.8, 112.3, 107.0, 105.0, 69.6, 69.4, 31.9, 31.8, 29.6, 29.4, 26.1, 26.0, 22.8, 22.8, 14.5, 14.2 ppm.

2,7,10,11-Tetrakis(hexyloxy)-1,8-dinitrotriphenylene 103



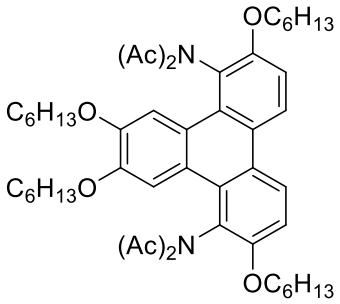
2,3,6,11-Tetrakis(hexyloxy)triphenylene **31** (2.00 g, 3.18 mmol) was crushed to a fine powder in a pestle and mortar, then dissolved in diethyl ether (100 mL) and acetic acid (30 mL). Nitric acid (3 mL) was added slowly and the reaction heated at reflux for 16 hours. Upon completion, the reaction mixture was washed with water (2x100 mL) and sat. potassium carbonate solution (2x100 mL). The organics were collected and dried over magnesium sulphate, before being concentrated *in vacuo*. The crude product was loaded onto a silica gel column (pore size 40-63µ) and eluted with a 3:7 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **103** was obtained as a yellow oil (1.51 g, 66%). IR (thin film) ν 2932, 2860, 1532, 1284 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 9.2 Hz, 2H), 7.56 (s, 2H), 7.28 (d, *J* = 9.2 Hz, 2H), 4.19 (t, *J* = 6.4 Hz, 4H), 4.09 (t, *J* = 6.4 Hz, 4H), 1.90 - 1.80 (m, 8H), 1.54 - 1.47 (m, 8H), 1.40 - 1.33 (m, 16H), 0.94 - 0.90 (m, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.5, 137.6, 125.1, 122.1, 121.3, 120.9, 112.1, 107.7, 69.9, 68.9, 31.7, 31.6, 29.1, 29.0, 25.8, 25.5, 22.7, 22.6, 14.0, 14.0 ppm; HRMS (ASAP (Solid)) *m/z* calculated for $C_{42}H_{58}N_2O_8$ $[M+H]^+$: 719.4266; found: 719.4262.

2,7,10,11-Tetrakis(hexyloxy)triphenylene-1,8-diamine 104



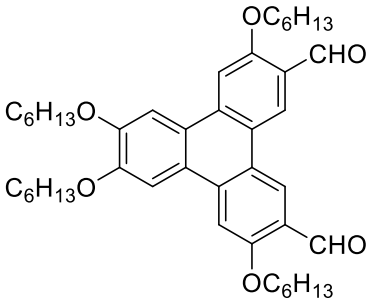
2,7,10,11-Tetrakis(hexyloxy)-1,8-dinitrotriphenylene **103** (1.00 g, 1.39 mmol) and tin powder (2.31 g, 0.0195 mol) were stirred in acetic acid (100 mL), and the mixture heated at reflux for 2 hours. Upon completion, the hot solution was poured into water (300 mL) and extracted with dichloromethane (3x100 mL). The organics were collected and dried over magnesium sulphate, before being concentrated *in vacuo*. The crude product was filtered through a pad of silica and used immediately (550 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 4.42 (s, 4H), 4.14-4.09 (m, 8H), 1.94 – 1.85 (m, 8H), 1.58 – 1.49 (m, 8H), 1.42 – 1.34 (m, 16H), 0.94 (m, 12H) ppm.

***N,N'*-(2,7,10,11-tetrakis(hexyloxy)triphenylene-1,8-diyl)bis(*N*-acetylamide) 105**



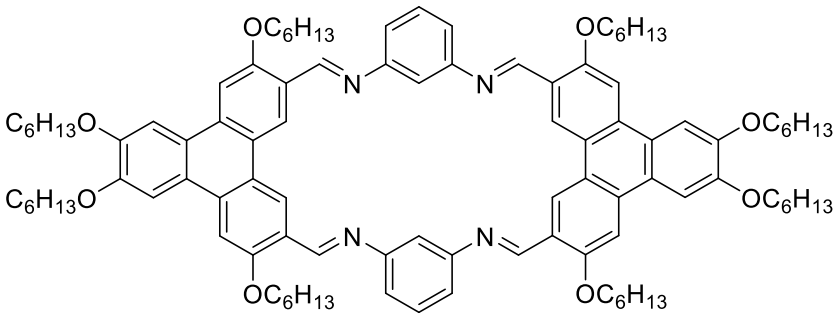
2,7,10,11-Tetrakis(hexyloxy)triphenylene-1,8-diamine **104** (203 mg, 0.308 mmol) was stirred in chloroform (30 mL) with pyridine (0.348 mL, 341 mg, 4.32 mmol). Acetyl chloride (0.154 mL, 169 mg, 2.16 mmol) was added and the reaction mixture stirred for 16 hours. Upon completion, the reaction mixture was washed with sat. copper sulphate solution (2x50 mL) and water (2x50 mL) and the organics were extracted with dichloromethane. The organics were combined and dried over magnesium sulphate, before being concentrated *in vacuo*. The crude product was loaded onto a silica column and eluted with a 1:4 mixture of ethyl acetate/petroleum ether. Removal of solvents and recrystallisation from ethanol gave **105** as pale yellow crystals (102 mg, 40%). Mp. 99-101 ^{o}C; IR (thin film) ν 2933, 2860, 1713 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.3 Hz, 2H), 8.03 (s, 2H), 7.24 (d (hidden by $CHCl_3$), 2H), 4.10 (t, *J* = 6.6 Hz, 4H), 4.05 (t, *J* = 6.6 Hz, 4H), 2.17 (s, 12H), 1.90 – 1.77 (m, 8H), 1.54 – 1.43 (m, 8H), 1.40 – 1.32 (m, 16H), 0.92 (m, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 153.2, 148.8, 128.5, 125.0, 124.7, 124.1, 123.9, 111.9, 109.1, 69.1, 68.8, 31.7, 31.6, 29.4, 29.3, 26.1, 25.8, 25.8, 22.8, 22.7, 14.2, 14.2; HRMS (ASAP (Solid)) *m/z* calculated for $C_{50}H_{70}N_2O_8$ $[M+H]^+$: 827.5205; found: 827.5209.

3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-dicarbaldehyde 109



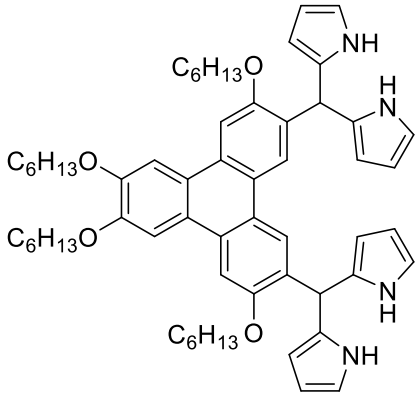
2,11-Dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene **94** (3 g, 3.81 mmol) was stirred in anhydrous tetrahydrofuran (50 mL) under nitrogen at -78°C. n-BuLi (2.5 M in hexanes, 9.23 mL, 23.1 mmol) was added *via* syringe and the mixture stirred for 3 hours, monitored by TLC. Anhydrous DMF (1.78 mL, 1.69 g, 23.1 mmol) was added *via* syringe and the reaction left to warm to room temperature overnight. Upon completion the reaction was quenched with water and extracted with dichloromethane. The organics were combined and dried over magnesium sulphate, before being concentrated *in vacuo*. The crude product was recrystallized from dichloromethane and ethanol giving the desired product **109** as a yellow solid (1.89 g, 73%). Mp. 208-210 °C; IR (thin film) ν 2932, 2859, 1683 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 10.61 (s, 2H), 8.93 (s, 2H), 7.71 (s, 2H), 7.63 (s, 2H), 4.26-4.21 (m, 8H), 1.99-1.93 (m, 8H), 1.63-1.57 (d, 8H), 1.45-1.38 (m, 16H), 0.97-0.94 (m, 12H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 189.6, 159.3, 150.9, 134.8, 124.9, 124.5, 124.3, 122.8, 107.8, 104.6, 69.7, 68.8, 31.8, 31.8, 29.5, 29.3, 26.1, 26.0, 22.8, 22.8, 14.2 ppm; HRMS (ESI^+) *m/z* calculated for $C_{44}H_{60}O_6$ $[M+H]^+$: 685.4463; found: 685.4463.

Diaminetriphenylene Twin 143



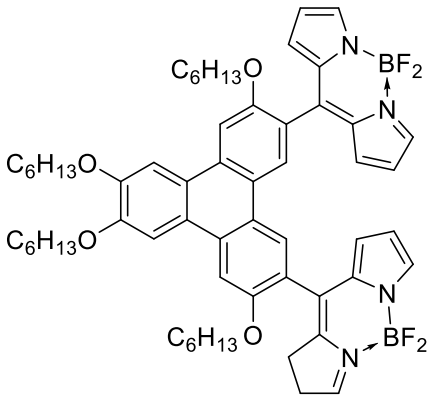
3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-dicarbaldehyde **109** (100 mg, 0.146 mmol) and 1,3-diaminobenzene (15.79 mg, 0.146 mmol) in degassed toluene (20 mL) were heated at reflux under Dean-Stark conditions in a nitrogen atmosphere. After 4 days, the reaction mixture was allowed to cool to room temperature, and the resulting precipitate collected by filtration. The precipitate was washed with methanol then hexane, giving the desired product **143** as a yellow solid (42 mg, 19%). Mp. Cr 276^{o}C N_D > 300^{o}C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 4H), 9.34 (s, 4H), 7.91 (t, *J* = 2.1 Hz, 2H), 7.89 (s, 4H), 7.79 (s, 4H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.31 (dd, *J* = 2.1, 7.9 Hz, 4H), 4.32 (t, *J* = 6.4 Hz, 8H), 4.28 (t, *J* = 6.4 Hz, 8H), 2.03-1.96 (m, 16H), 1.69-1.59 (m, 16H), 1.47-1.40 (m, 32H), 0.98-0.94 (m, 24H) ppm.

2,2',2'',2'''-((3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-diyl)bis(methanetriyl))tetrakis(1*H*-pyrrole) 136



3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-dicarbaldehyde **109** (419 mg, 0.611 mmol) and freshly distilled pyrrole (20 mL) were degassed with argon for 10 minutes. TFA (5 μL, 6.96 mg, 0.061 mmol) was added *via* syringe and the mixture stirred at room temperature until TLC analysis showed full consumption of the aldehyde, 45 minutes. Upon completion, the crude mixture was diluted with dichloromethane and washed with aqueous NaOH solution. The organics were combined and dried over magnesium sulphate, before being concentrated *in vacuo*. The crude product was distilled under vacuum to remove the excess pyrrole, and the remaining residue recrystallized from dichloromethane and ethanol, yielding the desired product **136** as a light brown powder (262.5 mg, 47%). IR (thin film) ν 3381, 3108, 2929, 2858 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.27 (br s, 4H), 8.08 (s, 2H), 7.81 (s, 2H), 7.73 (s, 2H), 6.69 (td, *J* = 1.6, 2.6 Hz, 4H), 6.16 (dd, *J* = 2.6, 5.9 Hz, 4H), 5.99-5.97 (m, 4H), 5.92 (s, 2H), 4.21 (t, *J* = 6.4 Hz, 4H), 4.13 (t, *J* = 6.4 Hz, 4H), 1.96-1.90 (m, 4H), 1.79-1.73 (m, 4H), 1.61-1.55 (m, 8H), 1.44-1.32 (m, 16H), 0.96-0.91 (m, 12H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 155.4, 149.6, 132.5, 131.1, 128.9, 124.4, 124.3, 123.2, 116.9, 108.4, 107.5, 107.0, 104.9, 69.7, 67.0, 39.3, 31.8, 31.8, 29.5, 26.0, 25.9, 22.8, 22.7, 14.2, 14.2 ppm.

Bis-BODIPYtriphenylene 134



p-Chloranil (245.67 mg, 0.992 mmol) was stirred in anhydrous dichloromethane (35 mL) at -40°C under nitrogen. 2,2',2",2"'-((3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-diyl)bis(methanetriyl))tetrakis(1*H*-pyrrole) **136** (416.6 mg, 0.454 mmol) was added in anhydrous dichloromethane (50 mL) dropwise *via* an addition funnel over several minutes. The mixture was stirred at -40°C for 3 hours. Then DIPEA (0.95 mL, 704.35 mg, 5.45 mmol) was added, and the mixture stirred for a further 30 minutes. $BF_3.OEt_2$ (1.01 mL, 1.160 mg, 8.18 mmol) was added slowly and the reaction allowed to warm to room temperature overnight. Upon completion, the crude product was filtered through Celite, washed with aqueous $NaHCO_3$ solution and extracted with dichloromethane. The organics were combined and dried over magnesium sulphate, before being concentrated *in vacuo*. The crude product was recrystallised from dichloromethane and ethanol, giving the desired product **134** as a dark red solid (205 mg, 45%). Mp. 150-160°C (decomp.); IR (thin film) ν 2926, 2850, 1609 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 2H), 7.97 (s, 2H), 7.94 (s, 2H), 7.90 (s, 4H), 6.85 (d, *J* = 4.1 Hz, 4H), 6.48 (dd, *J* = 1.9, 4.1 Hz, 4H), 4.31 (t, *J* =6.4 Hz, 4H), 4.18 (t, *J* = 6.4 Hz, 4H), 2.02-1.97 (m, 8H), 1.71-1.67 (m, 8H), 1.45-1.39 (m, 16H), 0.97-0.94 (m, 12H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ 155.7, 150.7, 144.1, 135.9, 131.7, 131.3, 129.9, 127.0, 124.5, 123.3, 122.1, 118.4, 107.5, 105.2, 69.8, 69.2, 31.8, 31.5, 29.5, 29.1, 26.0, 25.8, 22.8, 22.6, 14.2, 14.1 ppm; HRMS (ESI^+) *m/z* calculated for $C_{60}H_{70}B_2F_4N_4O_4$ $[M+NH_4]^+$: 1026.5876; found: 1026.5853.

Chapter 4

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