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**Discotic liquid crystalline star-shaped hetero
heptamers for organic photovoltaic devices**

By
Anupama Jale

A Thesis

Submitted to the Faculty of Graduate Studies and Research
through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for
the degree of Master of Science at the
University of Windsor.

Windsor, Ontario, Canada

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Approved By:

Dr. Holger Eichhorn
Chemistry and Biochemistry

Dr. J.R. Green
Chemistry and Biochemistry

Dr. David Fowle
Earth Sciences

Abstract

Discotic liquid crystals (DLC's) have gained substantial attention due to their possible application as charge conducting material. A charge carrier mobility along the columnar π,π -stacks of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, close to mobility values found in single crystals of organic compounds, have been obtained for discotic mesophases of high stacking order. Processability and self-alignment on surfaces need to be combined with high packing order of the mesophase to make them ideal materials for organic electronic devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), and photovoltaic devices.

It has been shown that incorporation of discotic mesogens into linear polymers widens the temperature range of the columnar mesophase and fully suppresses crystallization (anisotropic glass formation). Linear main-chain polymers of discotic mesogens, however, do not form monodomains of macroscopic dimension and also make a homeotropic alignment of the columns very difficult. We chose a star-shaped structure for the oligomers presented here because we expect them to combine the advantages of linear oligomers with the formation of large monodomains as well as a homeotropic self-alignment on surfaces.

This thesis describes synthetic approaches to heteroheptamers of discotic liquid crystals, which should be ideal building blocks for organic photovoltaic devices. Hexaazatriphenylene-hexacarboxylic acid [$\text{HAT}(\text{CO}_2\text{H})_6$] and its derivatives were chosen as n-type semi-conducting central discotic monomer that has six p-type semi-conducting hexaalkoxytriphenylene discogens covalently attached to it. HAT derivatives were successfully synthesized and their conversions with alkyl alcohols and amines to hexa-esters and hexa-amides are discussed.

A complete conversion of all acid or ester groups with low molecular weight alcohols and amines was not achieved but transesterification of the hexa-methylester with alkyl alcohols catalyzed by titanium (IV) isopropoxide gave 80-90 % conversion. Optimization of the reaction conditions should result in a 100 % conversion.

Monofunctionalized hexaalkoxytriphenylene derivatives were chosen as p-type semi-conducting ligands and several different synthetic pathways towards these triphenylene derivatives are presented. Several approaches based on statistical cyclization to the triphenylene or statistical cleavage of one alkoxy group have been reported in literature. We, however, could not reproduce the reported yields and found the Suzuki cross-coupling pathway to be the most reliable and highest yielding synthetic approach.

The preparation of heteroheptamers containing [HAT(CO₂H)₆] as central core and hexaalkoxytriphenylene derivatives as ligands should be straightforward based on the synthetic approaches that have been developed in this thesis. The final assembly of heteroheptamers, however was not attempted within this thesis because of insufficient remaining time.

Dedication

I dedicate this thesis to my loving husband Mr. Dayakar R. Jale
and my parents.

Acknowledgements

I would like to thank my supervisor, Dr. S. H. Eichhorn for his constant support and guidance during this project in the past two years. I would also like to thank Dr. Green and Dr. David Fowle for being in my committee and Dr. P.H.J. Kouwer, whose PhD thesis, was really helpful while writing this thesis. I also wish to acknowledge the Department of Chemistry and Biochemistry, University of Windsor, for providing financial support.

It also gives me pleasure to thank all of my friends and colleagues whom I have worked with over the past two years, and the staff who have made it such an enjoyable place to study in.

And I would like to say a big thank you to my husband and parents for their constant encouragement and understanding, without which I would not have achieved all that I have. And finally special thanks to my cousin, Dr. Jaya and brother-in-law, Dr. Bhaskar Guntoori for interesting scientific discussions we have every time.

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Abbreviations

Ar	aromatic
br	broad
BuLi	butyllithium
δ	chemical shift in ppm
Col	columnar phase
Col _h	hexagonal columnar phase
°C	degrees of Celsius
d	doublet
dd	doublet of doublet
DLC	discotic liquid crystal
DMSO	dimethyl sulfoxide
DCM	dichloromethane
DSC	differential scanning calorimetry
DEE	diethyl ether
eq	equivalent
EtAc	ethyl acetate
Et ₃ N	triethylamine
FET	field effect transistor

HPLC	high performance liquid chromatography
HAT	hexaazatriphenylene
h	hours
IR	infrared spectroscopy
LC	liquid crystals
LED	light emitting diode
LCD	liquid crystal display
m	multiplet
mol.sieve	molecular sieve
MeOH	methanol
MeCN	acetonitrile
NMR	nuclear magnetic resonance
N _D	nematic discotic
N _{Col}	nematic columnar
N _L	nematic lateral phase
N*	chiral nematic
OPM	optical polarizing microscopy
OLED	organic light emitting diode
ppm	parts per million

q	quartet
refl.	reflux
RT	room temperature
SmA	smectic A phase
SmB	smectic B phase
SmC	smectic C phase
SmF	smectic F phase
SmI	smectic I phase
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
tt	triplet of triplets
temp	temperature
XRD	x-ray diffraction

1. INTRODUCTION

1.1 Liquid Crystals

1.1.1 Definition

The term liquid crystal, or mesogen, refers to compounds or materials that exhibit intermediate phases between the isotropic liquid and the crystalline solid states. Liquid crystals (LCs) have been reported and investigated since their discovery in the late 19th century.^{1,2,3} Historically, the discovery of liquid crystals is attributed to the work of Reinitzer (1888) and Lehman (1889), who both investigated the unusual *double melting* behaviour of cholesteryl benzoate. At a temperature of 145.5 °C, cholesteryl benzoate melts into an opaque, turbid liquid, *i.e.* an intermediate state of matter (mesophase), which clears into a transparent isotropic liquid at a much higher temperature of 178.5 °C. The notion of *double melting* refers to the melting point (transition from crystalline solid to mesophase) and the clearing point (transition from mesophase to isotropic liquid).⁴

Usually, matter is considered either fully ordered (crystalline) or fully disordered (liquid, gas, glass). In crystalline phases, molecules possess orientational order and three-dimensional positional order, while in isotropic liquid and isotropic amorphous phases the molecules lack (long range) order. In the various liquid crystalline phases, the molecules are in-between the two extremes, *i.e.* they possess orientational order and up to 2-dimensional long-range positional order.⁵

Liquid crystals are further categorized into thermotropic and lyotropic phases. Thermotropic LCs form different mesophases at different temperatures, whereas lyotropic LCs do so by changes in concentration of a solvent and temperature.⁶ Thermotropic mesophases have been found to be exhibited by two distinct types of anisotropic molecular shapes, rod-shaped molecules and disc-shaped molecules.⁷ Mesophases formed by rod-shaped molecules are called calamitic LCs and are subdivided into nematic phases (only orientational order) and smectic (layered) phases (orientational and one- or two-dimensional positional order). Discotic liquid crystal

phases displayed by disc-shaped molecules display nematic and columnar phases (the later has orientational and two dimensional positional order).⁵

1.2 Classification of Mesophases⁸

In the beginning of this century George Friedel conducted many experiments on liquid crystals and it was he who first explained the orienting effect of electric fields and the presence of defects in liquid crystals. In 1922 he proposed a classification of liquid crystals based upon the different molecular orderings of each substance such as nematic, smectic, and cholesteric phases.⁴

1.2.1 Calamitic Liquid Crystals⁹

Calamitic, or rod-shaped, molecules show a large difference in length and breadth, thus delivering the shape anisotropy required for the formation of these mesophases. Until 1977, the discovery of discotic LCs, all known thermotropic mesogens belonged to this class of mesophases. Consequently, most applications such as liquid crystal displays (LCDs) are based on the properties of calamitic mesophases.

A typical calamitic mesogen consists of a rigid core unit, ensuring the anisotropic character, together with flexible side chains, which reduce the melting temperature and also induce layer-formation when of sufficient length (microphase segregation). The rigid core is usually aromatic, but can also be alicyclic. Two examples of typical calamitic LCs are shown below.

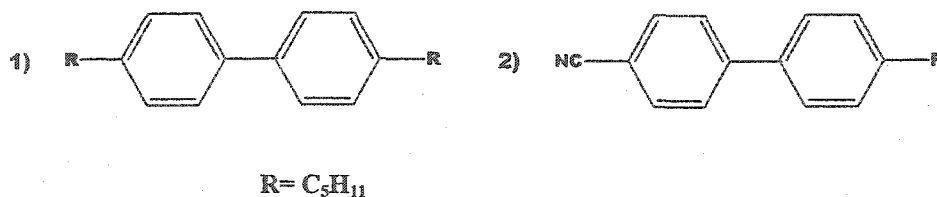


Fig 1.1: Examples of calamitic liquid crystals 1) dialkylbiphenyl; 2) cyanobiphenyl⁵

The physical properties cannot only be widely influenced by the nature of the core and of the side-chains but also by polar groups that are usually attached to the rigid core. Polar groups, especially the CN group, play an important role in the application of liquid crystals. In cyanobiphenyls, for example, the CN group introduces a strong longitudinal dipole that promotes anti-parallel dimerization and an increase in density due to intermolecular dipole-dipole interactions.⁵ The most important calamitic LC phases, although not main subject of this thesis, are briefly discussed in the following parts.

1.2.2 Nematic Calamitic Liquid Crystals

The nematic phase is the least ordered liquid crystal phase, with molecules only possessing orientational order, but no positional order. The lack of positional order results in a very fluid LC phase that quickly responds to external fields. This fast response made it the most common mesophase of today's LCDs.

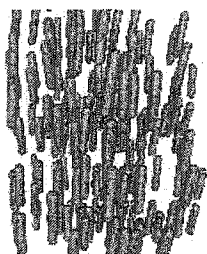


Fig 1.2: The nematic calamitic phase.⁴

1.2.3 Chiral Nematic or Cholesteric phases

The term cholesteric is used for historical reasons since this phase type was first observed in derivatives of cholesterol, a chiral natural product. Molecules are arranged in a helical super-structure without exhibiting long-range positional order. An N^* phase is either displayed by a non-racemic chiral liquid crystal or by a mixture of a non-chiral nematic LC and a chiral dopant.

1.2.4 Smectic Calamitic Liquid Crystals

Smectic phases show orientational order and also up to 2D positional order as molecules form layered structures. About ten different smectic mesophases have been characterized with Smectic-A (SmA, see Figure 1.3) and Smectic-C (SmC, see Figure 1.3) being the most common ones. The director n is perpendicular to the planes of the layers in a SmA phase and tilted with respect to the layer plane in a SmC phase.¹⁰

SmC can, therefore, be distinguished from SmA by the tilt of the molecules with respect to the layer plane that causes the formation of distinctly different optical defect textures. Their other characteristics are rather similar. Both phases represent the least ordered and most fluid smectic mesophases with no in-plane long-range positional order. All other smectic phases show some degree of in-plane positional order. In the SmB phase, for example, the constituent molecules adopt a hexagonal order within the layers. The hexagonal nature of SmB phase generates two tilted analogues called the SmF and SmI where the molecules are tilted towards the side and apex of the hexagonal lattice respectively.¹¹

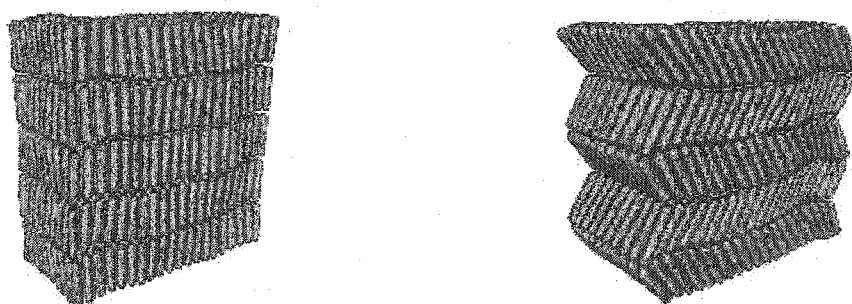


Fig 1.3: Structure of the SmA (left) and SmC (right) phases.⁴

1.3 Discotic Liquid Crystals

1.3.1 Introduction

Although many applications have been suggested for discotic liquid crystal phases,^{12,13} such as semi-conducting materials in photovoltaic cells¹⁴ and OLEDs,¹⁵ as well as electrically tuneable cholesteric mirrors,¹⁶ the only industrial application so far has been the production of optical compensating films.^{17,18} These are used to increase the viewing angle of modern LCDs.

The most important future competing technology for LCDs are organic light emitting diodes (OLED's) because of their higher contrast for superb readability in most lighting conditions, thinner design for better ergonomics, and compatibility with flexible plastic substrates.¹⁹ Columnar discotic mesophases could become the new generation of semi-conducting materials for OLEDs because of their high and anisotropic charge carrier mobility along the columnar stacks, their excellent processability due to high solubility and good surface wetting, and their self-alignment and self-healing properties.

While LEDs convert electricity into light, photovoltaic devices (photodiodes) convert light into electricity. Thus, both technologies are closely related and discotic LCs developed for the OLED technology will also benefit the advancement of photovoltaic devices.²⁰

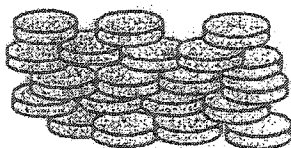
1.3.2 Classification of Discotic Mesogens

The discovery of discotic liquid crystals generally dates back to the work of Chandrasekhar in 1977, although DeGennes and others had already recognized that not only rod-shaped but also disc-shaped molecules should form liquid crystal phases.²¹ During the past seventeen years an enormous amount of research has been invested in the synthesis of new disc-shaped LCs and the structural characterization of discotic mesophases.²²

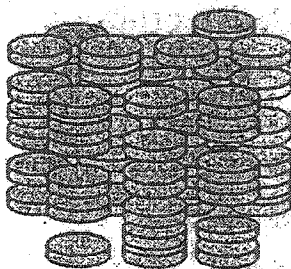
Two basic types of discotic mesophases have been widely recognized; these are columnar and nematic. The least ordered (usually highest temperature) mesophase formed by disc-shaped molecules is the N_D phase. The N_D phase is analogous to the nematic phase formed by rod shaped molecules and is characterized by the presence of only orientational order.²³

Two other nematic phases have been reported, the nematic columnar (N_{col}) and the nematic lateral (N_L) phase. However, the most common phases exhibited by disc shaped molecules are those in which molecules π,π -stack into columns. These show orientational and positional order in two dimensions. Columnar phases show a rich polymorphism and are generally classified according to their symmetry (the orientation of the molecules with respect to the columnar axis) and the degree of ordering within the columns.²³ The intercolumnar order (hexagonal, oblique, rectangular, *etc.*) and the intracolumnar order (ordered, disordered) are variables that are indicated in suffixes. In addition, chiral forms of N_D and Col mesophases have also been published.¹⁰

Nematic Phase N_D



Disordered Columnar Hexagonal Phase D_{hd}



Common variations in stacking within the columns



Ordered (o)



Disordered (d)



Tilted (t)

Common variations in stacking of the columns



Hexagonal (h)



Rectangular (r)



Oblique (ob)

*Fig 1.4: Cartoons of most common thermotropic discotic mesophase.*²⁴

Many different combinations of cores and side chains have been shown to produce discotic liquid crystalline phases (Fig. 1.5), but phthalocyanines and triphenylenes have been by far the most studied disc-shaped cores.²²

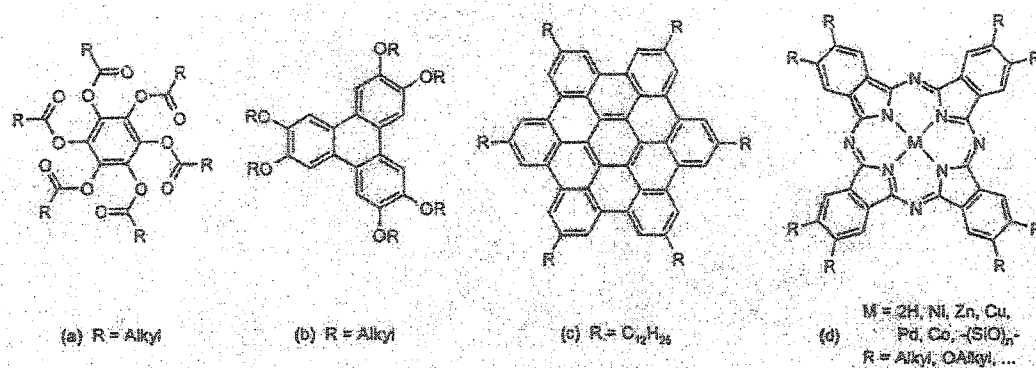


Fig 1.5: Structures of some well known DLC's (a) benzene hexa-*n*-alkanoate, (b) hexaalkoxy triphenylene (c) hexa-*peri*-hexabenzocoronene and (d) phthalocyanines.^{9-b}

Examples of N_D phases are still rather scarce in comparison to the plethora of columnar materials. Molecules that exhibit N_D phase are hexa-*n*-alkyl and hexa-*n*-alkoxybenzoates of triphenylene and hexakis (4-octylphenylethynyl) benzene.⁵ Columnar mesomorphism is exhibited by most triphenylene-, phthalocyanine-, and tetraazaporphyrin- derivatives.

The different core sizes of the discotic molecular building blocks influence the type and order of the formed columnar mesophase. Hexabenzocoronene derivatives, for example, show Col_{ho} phase of high intracolumnar stacking order due to their large aromatic cores while triphenylene derivatives usually display Col_h phases with low intracolumnar stacking order. Increasing the size of the discotic cores also benefits the temperature range of the columnar mesophase. Large disc-shaped compounds, such as substituted phthalocyanines and hexabenzocoronens, display very viscous mesophases,²⁴ that are difficult to align, and monodomain formation is difficult to obtain if possible at all. (Charge carrier mobility and alignment is discussed in section 1.3.6)

1.3.3 Characterization of Discotic Liquid Crystals

To prove the existence of previously discussed mesophases, principally three techniques are employed: optical polarized microscopy (OPM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). OPM involves the analysis of defect textures of liquid crystals with plane-polarized light under crossed polarized conditions.²⁵ Each LCs phase displays characteristic textures and each phase transition is accompanied by a

distinct texture change. DSC measures the transition temperatures and heats involved in phase transitions while XRD elucidates the molecular packing of each phase.

By using these three techniques, one can easily distinguish between the different discotic mesophases. For example, nematic mesophases are easily identified by their characteristic defect textures (*e.g.* Schlieren texture) when viewed by polarized light microscopy, their low N to isotropic transition enthalpy (DSC), as well as the absence of sharp peaks in the X-ray diffraction pattern. Col_h phase can be identified by OPM experiments because of its uniaxial nature since all other columnar mesophases are biaxial. The variety of tilted (biaxial) columnar mesophases can only be distinguished by X-ray diffraction. The common Col_h phase gives a simple and characteristic diffraction pattern that is described by the formula $d_{hk} = a/4/3(h^2+k^2+hk)$.

1.3.4 Synthetic Routes to Discotic Mesogens

Most of the (organic) disc shaped liquid crystals described in literature are built up from an aromatic core, substituted with alkyl or alkoxy tails. Hexasubstituted benzenes were the first discotic liquid crystals to be reported⁵, followed by discotic liquid crystals that contain triphenylene and phthalocyanine cores. However, many other core structures for discotic liquid crystals have been discovered that include hexaethynylbenzene, perylene, porphyrin, triazine, hexabenzocoronene, trisoxadiazolylbenzene, and tristyrilpyridine derivatives. They all have in common the ability to stack due to intermolecular π,π -interactions.

In the following, I will focus on the synthesis of hexaazatriphenylene (HAT) and triphenylene derivatives, the two systems studied in this thesis.

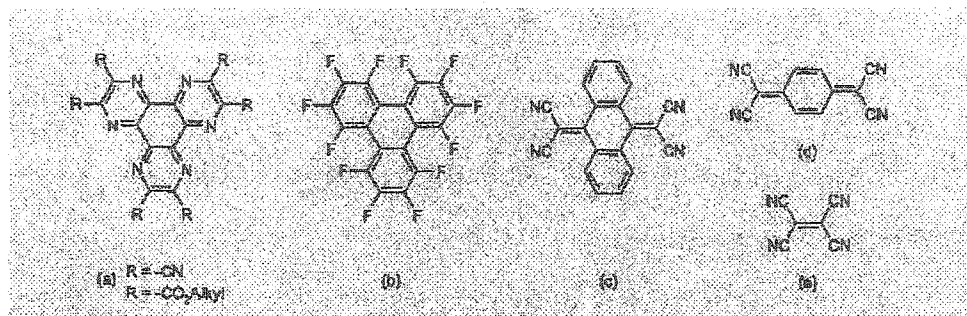
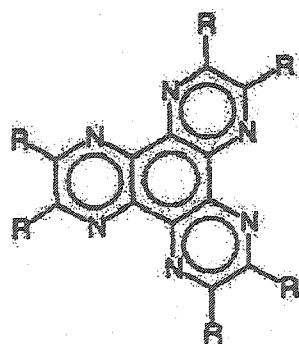


Fig 1.6: Examples of electron acceptors based on (a) 1, 4, 5, 9, 10, 12-hexaazatriphenylene; (b) Perfluorotriphenylene; (c) 11, 11, 12, 12-tetracyananthraquinodimethane (TCAQ); (d) 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ); (e) Tetracyanoethylene.^{9-b}

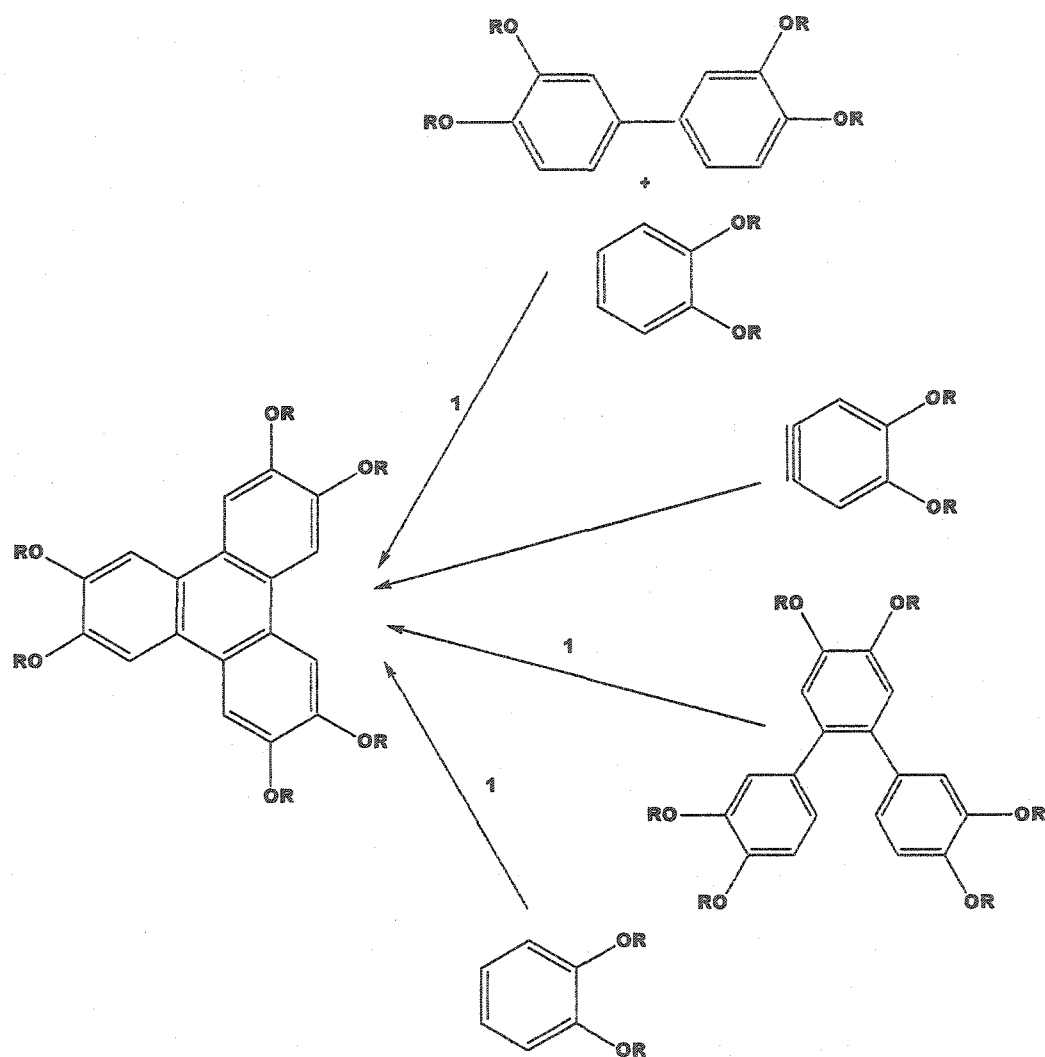
HAT is a potential n-type semiconductor with high electron affinity and examples of organic electron acceptor molecules are shown in Fig: 1.6. Hexasubstituted HAT moieties were first reported by Praefcke *et al.*²⁶ who condensed the very unstable hexaaminobenzene with three equivalents of α -diketones. Kanakarajan²⁷ and Czarnik²⁸ later showed that HAT derivatives can be prepared from the commercially available hexaoxocyclohexane octahydrate and α -diamines such as diaminomaleonitrile in 1994. Czarnik also developed the synthesis of different HAT derivatives that were substituted with peripheral electron withdrawing carboxylic ester, amide, and acid groups (Fig. 1.7).



a) R = H, CH₃, C₇H₁₅, C₉H₁₉; b) R= CN, CONH₂, COOCH₃, COOH

Fig 1.7: HAT derivatives reported by a) Praefcke *et al.*; b) Czarnik *et al.*²⁶

Scheme 1.1:



Scheme 1.1: Synthesis of triphenylenes.

1.3.5 Specific Interactions in Discotic Liquid Crystals¹⁰

Supramolecular chemistry—the chemistry beyond the molecular structure deals with non-covalent interactions. These interactions include forces like (i) electrostatic interactions (ion-ion, ion-dipole, and dipole-dipole), (ii) hydrogen bonding, (iii) π - π stacking, and (iv) van der Waals forces (dispersion and induction forces). A combination of these non-covalent interactions is used in nature to build complex structures that can show multiple levels of organization.³¹ Some examples of liquid crystals, wherein specific interactions play a major role, are displayed in Fig. 1.9.

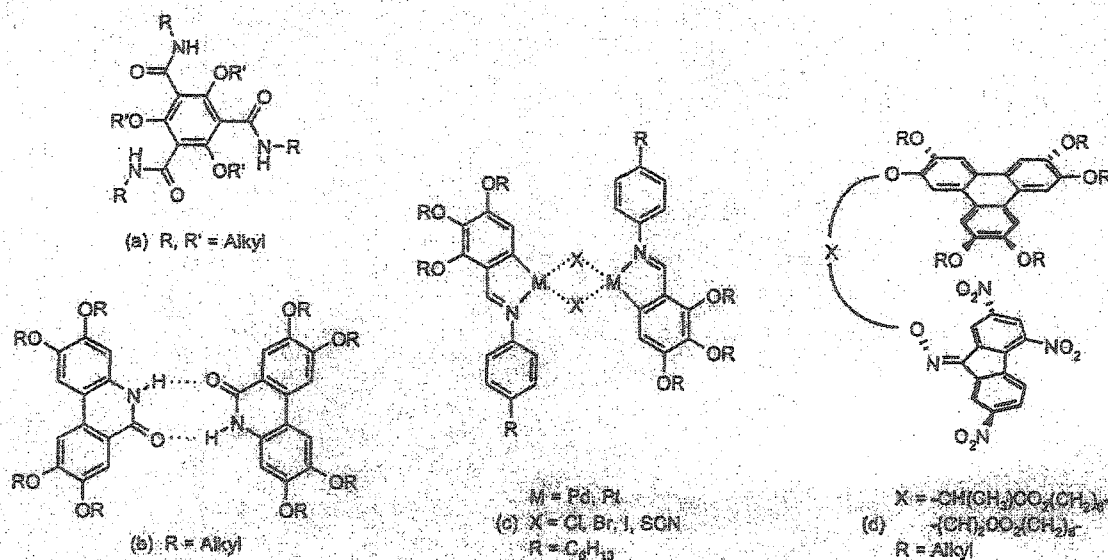


Fig 1.9: Examples of specific interactions in discotic liquid crystals: (a, b) hydrogen bonding (c) ion dipole interaction (d) charge transfer interaction (stacks of alternating donor and acceptor groups). Note that in (a) the H-bonds are directed perpendicular to the plane of the disk and in (b) directed in the plane of disk.¹⁰

Of all these interactions intermolecular π - π interactions are the most important in columnar stacks of DLCs. The overlap of adjacent π -systems within the columns facilitates one-dimensional charge-carrier conduction along the columns.

1.3.6 Discotic LCs as Charge Conducting Materials³²

Organic compounds have been discussed as potential candidates for active materials in electronic device for over a decade.³³ Solution-processable conjugated organic materials combine the electronic properties of inorganic semi-conductors and the processability of polymeric materials. This makes them suitable for commercial applications in opto-electronic technologies, in which the adaptability, simplicity, and low cost of manufacture make them extremely attractive.³²

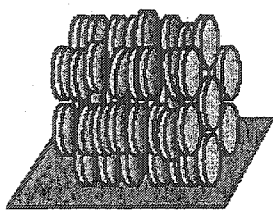
Recently, discotic liquid crystals have been discussed as new semi-conducting materials in photo-conducting systems and photovoltaic devices.³⁴ Their one-dimensional semi-conducting properties³⁵ combined with self-organizing properties make them particularly interesting as active electronic component. Discotic LCs also self-assemble at the interface with the (inorganic) electrodes, which should also optimize the performance of the devices.³⁶ Due to this unique combination of properties discotic liquid crystalline organics have shown high performance in several opto-electronic applications.³⁷

Typical charge carrier mobility values along the columnar stacks of discotic compounds are in the range of $0.3\text{--}0.001 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas their crystalline and (isotropic) liquid phases display values of about $0.6\text{--}0.3 \times 10^{-4}$ and $10^{-8}\text{--}10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.³⁸ These values are close to $1 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ which has been found in single crystals of aromatic molecules and was, remarkably, of the same order of magnitude for all investigated organic materials. This value can therefore be considered to be the maximum achievable mobility in conventional organic materials.

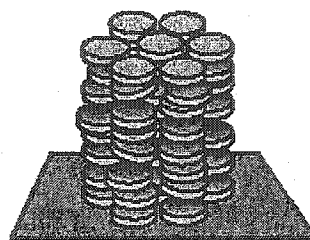
The anisotropic charge conduction of discotic materials can guide the charge carriers to the active interfaces of electronic devices. This, however, requires a perfect alignment of the self-organizing material which is usually obtained by utilizing interfacial forces or by applying external fields.²³ Alignment techniques for calamitic liquid crystals are well developed and play a crucial role in liquid crystal devices such as LCDs. Comparably little attention has been paid to the alignment of discotic liquid crystals. Only recently the

integration of discotic liquid crystals into optical and electronic devices stimulated the development of new alignment techniques for discotic nematic and columnar phases.²⁴

A homogeneous alignment (Fig.1.10) of the columnar mesophase is required for devices such as organic field effect transistors (OFETs), while organic light emitting diodes (OLEDs) and photovoltaic cells dictate a homeotropic alignment (Fig.1.10). A homeotropic alignment is most easily obtainable with the uniaxial hexagonal columnar mesophases (Col_h) and always results in the formation of a monodomain (Fig.1.11). Homogeneous alignment does not necessarily result in a macroscopic in-plane alignment (unidirectional) of the columns, which is essential for the formation of a monodomain.



Homogeneous alignment



Homeotropic alignment

Fig 1.10: *Alignment of discotic liquid crystals.*

Low molecular weight DLCs have been shown to align in simple mechanical, electric, and magnetic fields. The negative magnetic susceptibility makes the disc shaped cores align parallel to the magnetic field while the orientation of the director is confined to the plane perpendicular to the magnetic field. Thus, a monodomain can only be obtained if the sample is spun in a magnetic field to control the in-plane orientation of the director.

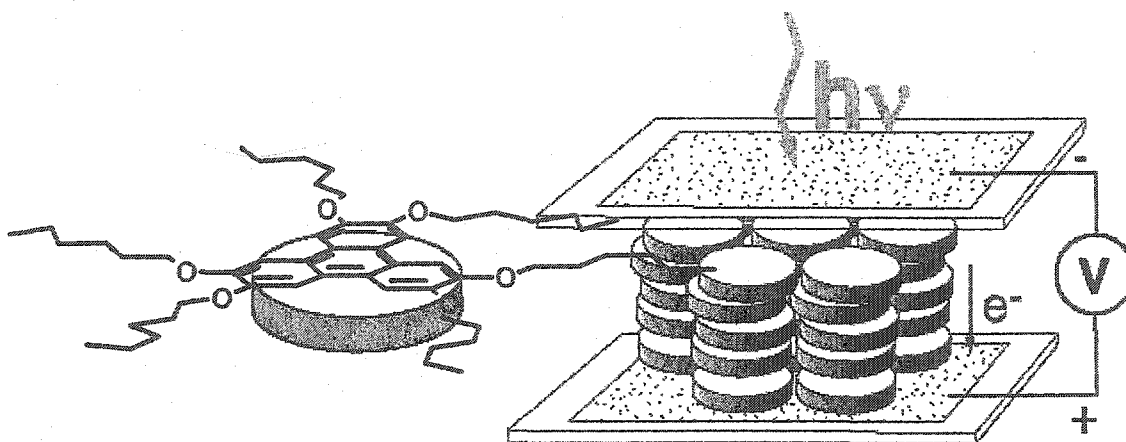


Fig 1.11: Homeotropic alignment of a hexagonal columnar mesophase (hexa-hexyloxy triphenylene) in a photovoltaic cell.³⁹

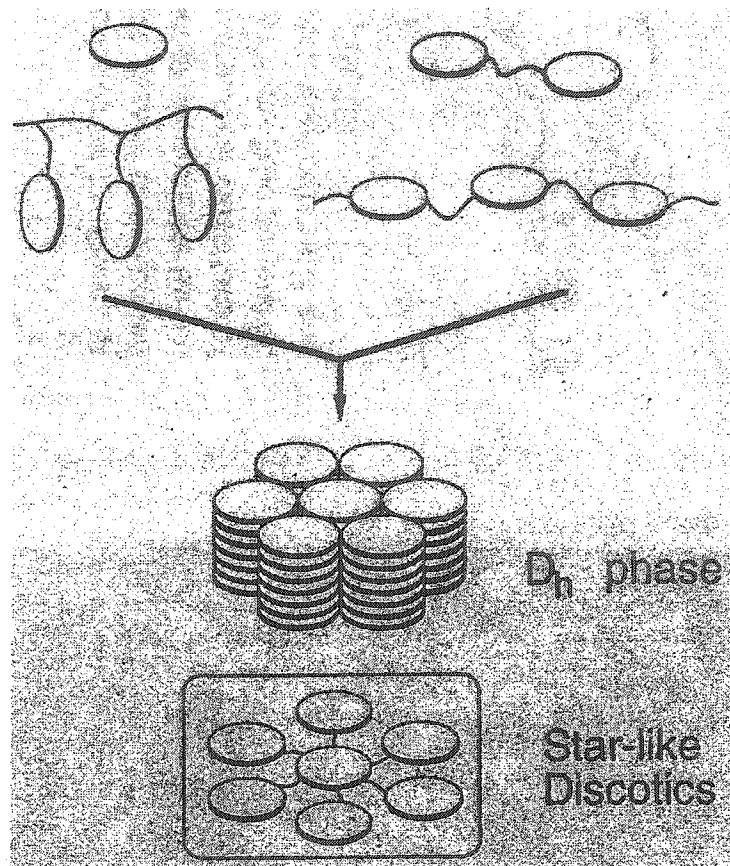
These techniques, however, are difficult to integrate into a production process and the homeotropic self-alignment that has been found for some fluid DLCs is much more attractive. In general, DLCs that gradually change from a very fluid columnar mesophase to a highly ordered solid-like mesophase, such as hexaalkylthiotriphenylenes and alkoxytriphenylene derivatives containing one group that sterically and/or electronically interact with neighboring molecules in the same column, self-align homeotropically in their fluid mesophase and remain aligned upon cooling into the solid like discotic columnar mesophase. The higher ordered mesophases were obtained mainly because crystallization occurred at much lower temperature or was fully suppressed.²⁴ A change from a fluid to solid-like mesophase with tight π , π -stacks is also favorable for the charge transport as a better π - π overlap is obtained.

Devices such as OLEDs and photovoltaic cells require hole and electron semi-conducting organic materials. Most organic materials, however, are hole conductors with low ionization potential, such as hexaalkoxytriphenylenes, while electron conductors with high electron affinity are rare. Few discotic n-type cores have been described⁴⁰ and among them is the HAT-hexacarbonitrile that features a first reduction potential of -0.01 V, indicating the n-type character of the HAT moiety.⁴¹ HAT derivatives have been used in thermally stable polymers,³⁸ liquid crystals,⁴² and charge transfer complexes.⁴³

1.3.7 Oligomeric Discotic Liquid Crystals

An oligomer can be a defined structure that can be treated and purified as a single molecule but also has polymer-like properties. Main chain polymer liquid crystals are formed when the mesogens are themselves part of the main chain of a polymer. The stiff regions along the main chain allow the polymer to orient in a manner similar ordinary liquid crystals, hence producing characteristics of liquid crystals. Side chain polymer liquid crystals are formed when the mesogens are connected as side chains to the polymer by a flexible “bridge”. They have three major structural components: the backbone, the spacer, and the mesogen.

Linear main-chain oligomeric discotic materials stabilize the columnar LC phase (wider temperature range) and suppress crystallization (formation of anisotropic glasses) but do not form monodomains. Also, they align with their column axis parallel to the substrate. In 1995, Ringsdorf and coworkers observed that a liquid crystalline star-shaped oligomer of triphenylene molecules shows the same properties as a linear main-chain oligomer but also aligns homeotropically and forms monodomains.⁴⁴ This unexpected behavior might be explained with the molecular structure of the star-shaped oligomer that matches the symmetry of its hexagonal columnar supramolecular structure while a linear oligomer does not (Fig. 1.12).



*Fig 1.12: Arrangements of discs in hexagonal columnar mesophase.*⁴⁴

1.4 Scope of Thesis⁴⁵

We propose star-branched oligomers of DLCs as superior molecular building blocks organic semi-conducting materials in OLEDs and photovoltaic devices. They stabilize the columnar mesophase, so that polymerizable groups, such as acrylic acid esters, could be attached to the side-chains without losing the liquid crystallinity. Also, disc shaped aromatic molecules that do not form columnar mesophases on their own are likely to display columnar liquid crystalline phases, when linked together to an oligomer. These oligomers do not crystallize on cooling but form an anisotropic glass of the preceding mesophase structure. Crystallization needs to be suppressed because it goes along with grain boundary formation and structural rearrangements. The formation of anisotropic glasses is also beneficial to the columnar stacking order and, therefore, to the charge

carrier mobility along the columnar π,π -stacks. Finally, the oligomeric approach gives us wide flexibility in molecular design.

By synthesizing a star-shaped heteroheptamer containing an electron withdrawing aromatic core such as hexaazatriphenylene coupled with electron rich ligands such as triphenylene, a columnar mesophase containing a p-n junction is obtained. A sketch of the envisaged supramolecular design for a single layer photovoltaic device is shown in (Fig.1.13). Here, the star-shaped heteroheptamer contains a hole conducting discotic as central core and six electron conducting discotics as ligands. Nanophase separation into hole- and electron conducting π,π -stacks will allow the photo-generated excitation to dissipate into two free charge carriers on two separated columns. The two charge carriers can now quickly move along the semi-isolated columns to the electrodes. This way recombination of hole and electrons should be greatly diminished.

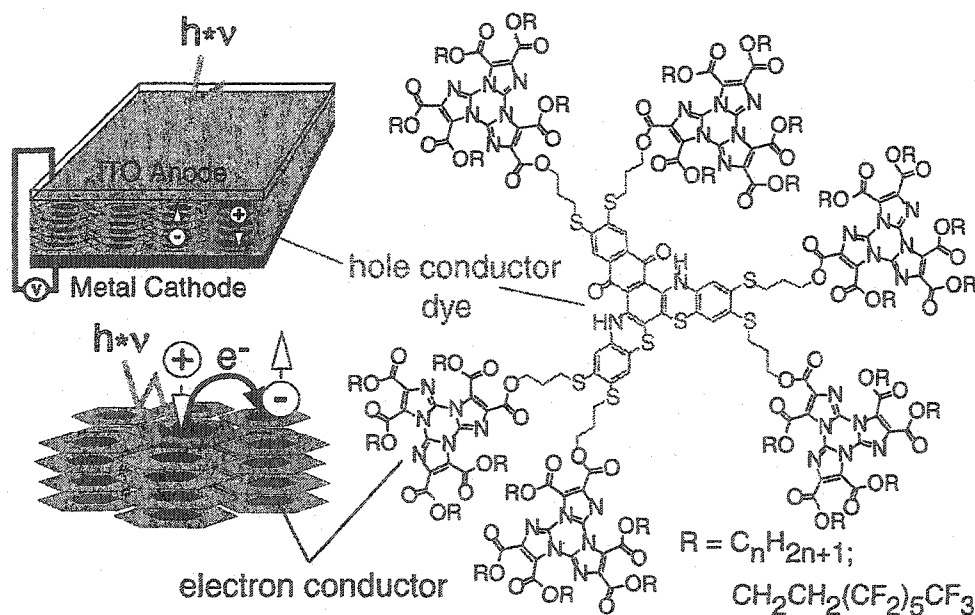
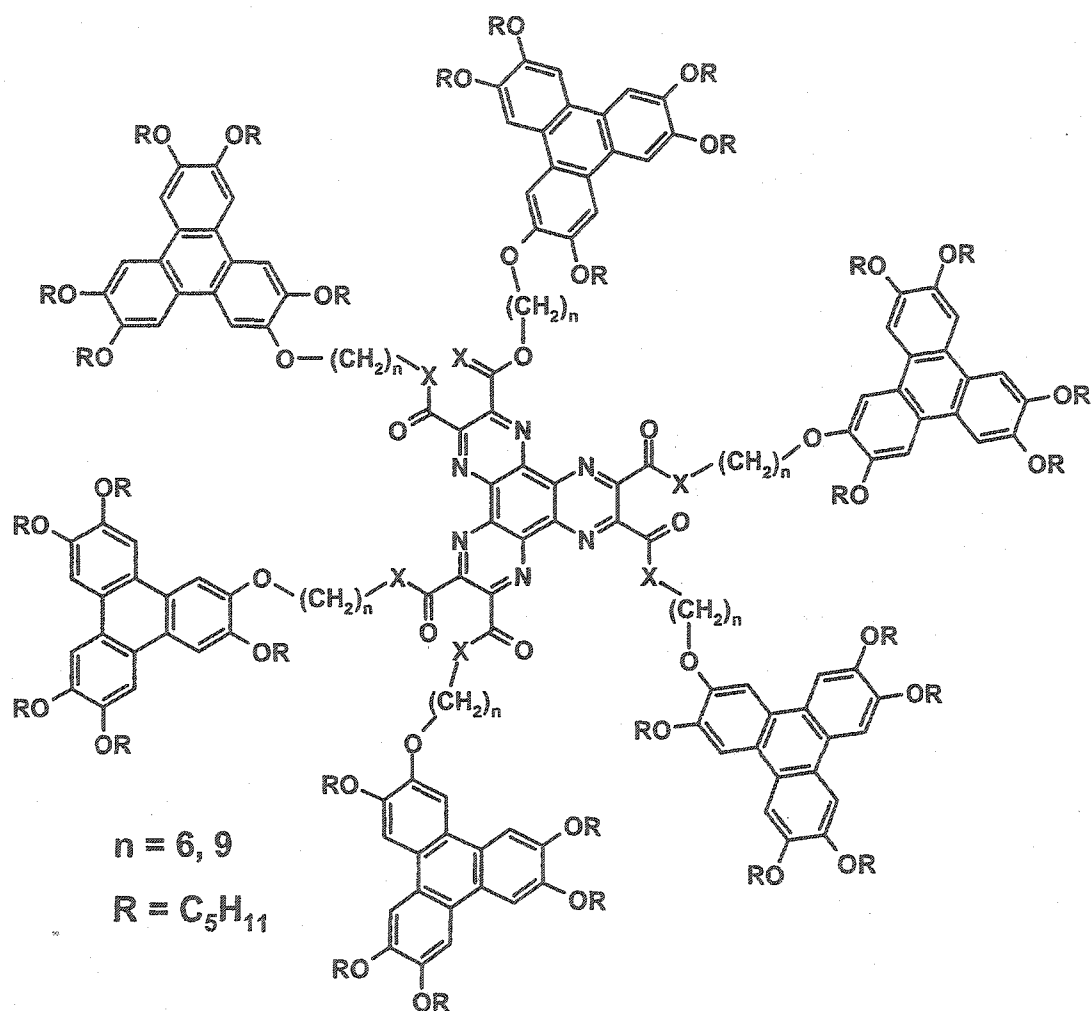


Fig 1.13: Simplified cartoon of a photovoltaic device containing a star shaped hetero heptamer self-organized and self-aligned into nano separated columns of the same discotic entity.⁴⁵

This thesis targets the synthesis of a model star-shaped heteroheptamer based on known discotic liquid crystals. The structure is shown in (Fig. 1.14) and requires the preparation of monofunctionalized triphenylenes (as peripheral ligands) and hexaazatriphenylene derivatives (as central core).



$X = O \text{ or } N$

Fig 1.14: Targeted hetero heptamer containing six triphenylene derivatives attached to a central hexaazatriphenylene moiety.

2. RESULTS AND DISCUSSION

2.1 HAT chemistry

Hexazatriphenylene (HAT) derivatives are electron deficient heterocycles.²⁸ HAT derivatives (promising central n-type core) were synthesized in fair to excellent yields following a procedure that was previously described by Kanakarajan.²⁷ The hexacyanohexaazatriphenylene **1** was prepared by the acid catalyzed condensation of the hexacarbonyl and the diamine as shown in Scheme 2.1. Hexaamide **2** was obtained from **1** by acid catalyzed hydration of all six nitrile groups. **2**, was prepared in good yields only when **1** was purified prior to use. Preparation of **3** was achieved by acid catalyzed conversion of the amides to methyl esters. The complete conversion took as long as 10 days, which might be one reason for the moderate yield of 51 %. **4** was obtained by ester cleavage of **3** under mild conditions using Et₃N. The use of Et₃N as a mild base gives the hexaacid that is free of counter ions because the resulting non-complexing counter ion is easily removed upon acidification.

Earlier synthetic approaches of **4** were based on a direct conversion of **2** through a perdiazotization of the amides using NaNO₂ in trifluoroacetic acid and subsequent quenching with water. The complete protonation of all acid groups, however, was proven to be difficult and remaining trace amounts of Na⁺ interfered with the complete conversion of the acid groups to esters, amides, or imides.²⁷ ¹³C-NMR was the spectroscopic method of choice for the verification of structures **1-4** and Figure 2.1 and 2.2 show the spectra of compounds **3** and **4**.

Scheme 2.1:

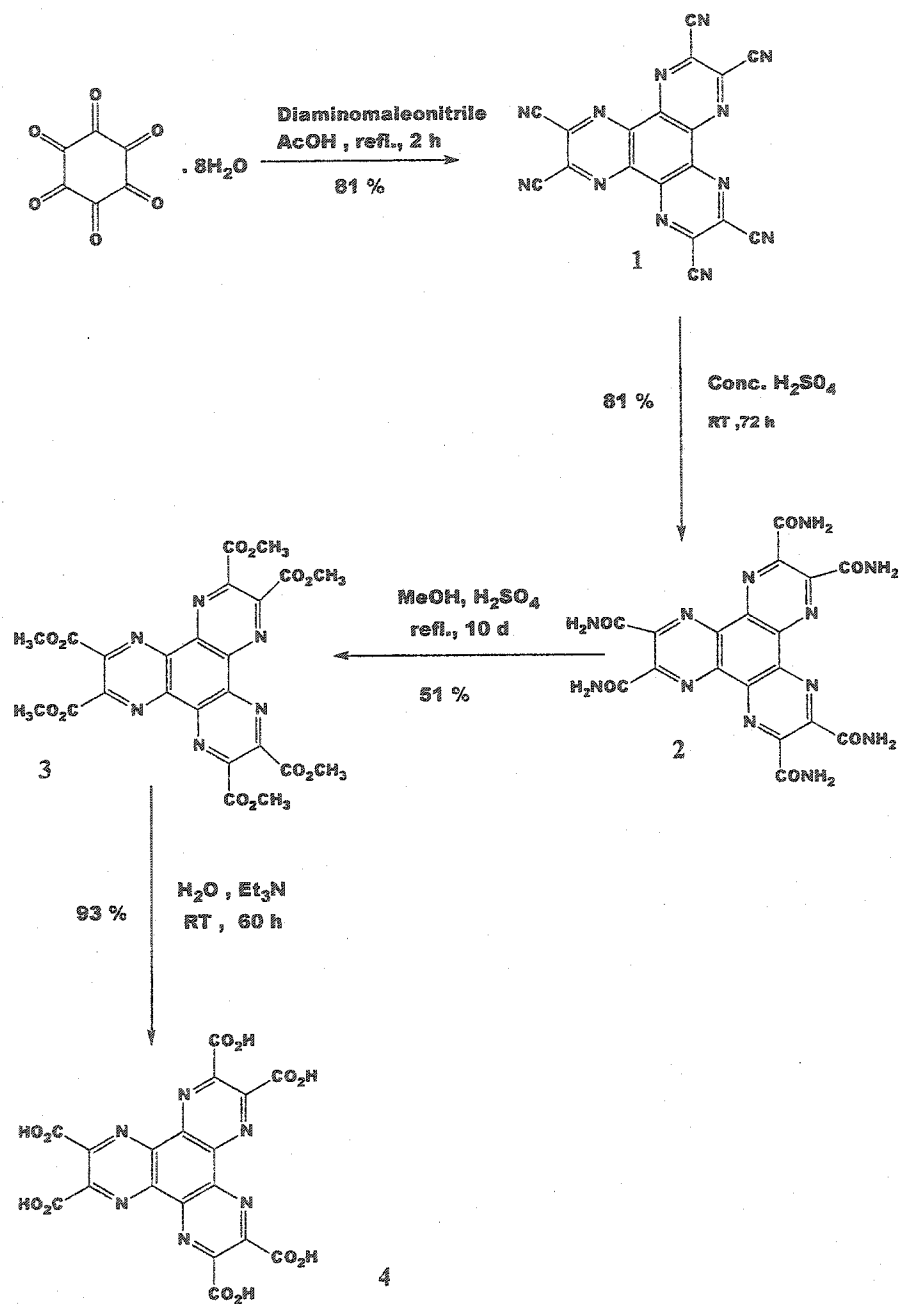


Fig 2.1: ^{13}C -NMR spectrum of [4, HAT (CO_2H)₆]

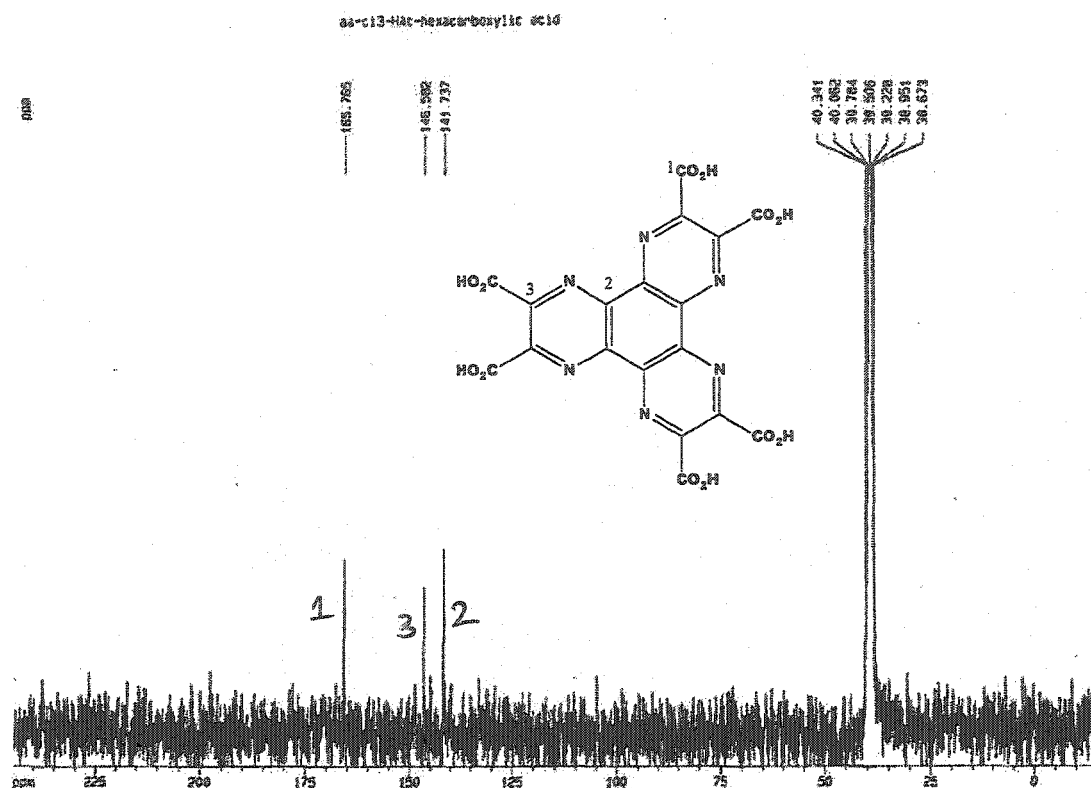
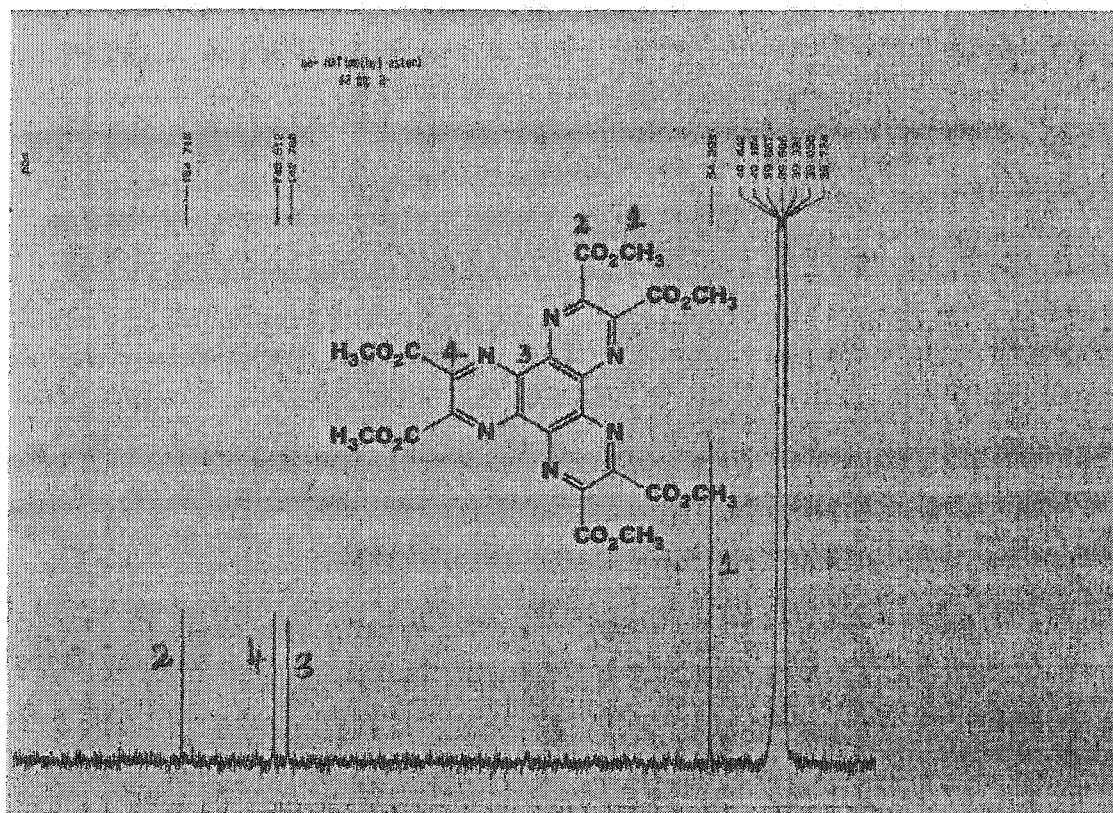


Fig 2.2: ^{13}C -NMR spectrum of [3, HAT (CO_2Me) $_6$]

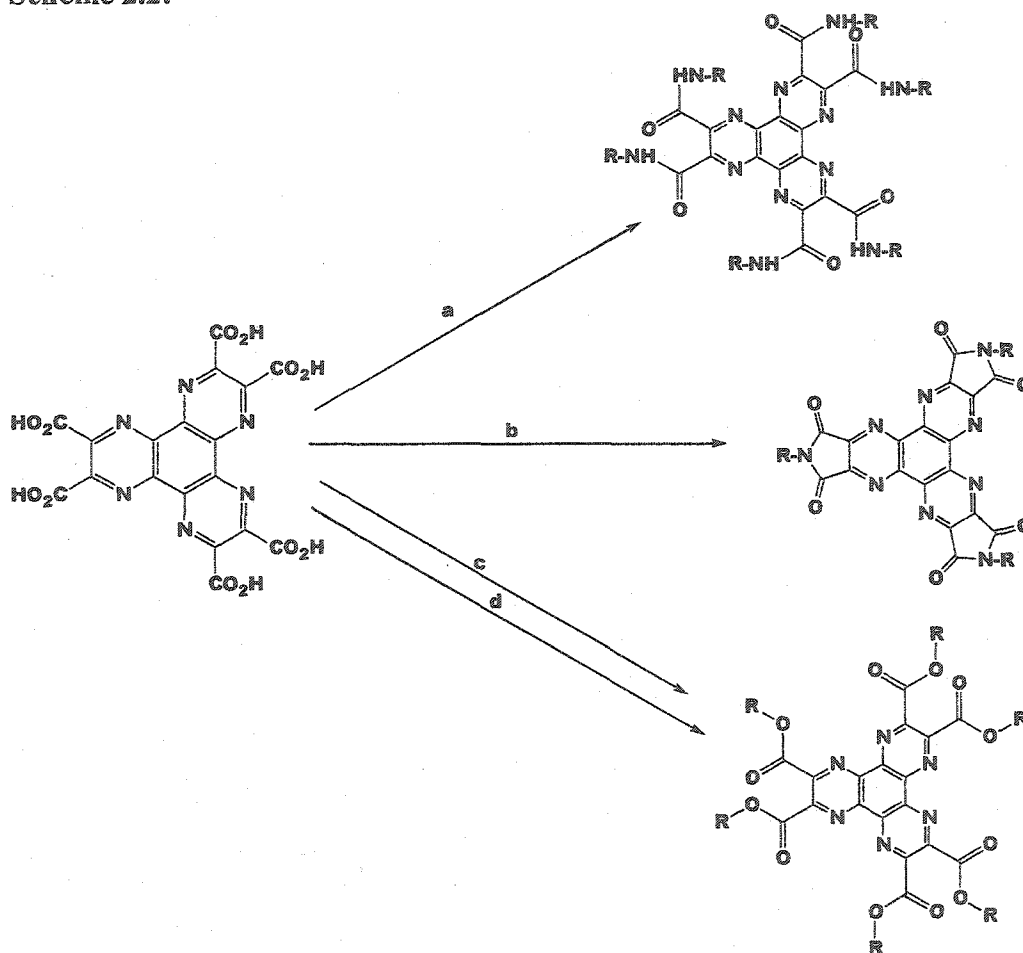


In order to convert the HAT derivatives into potential discotic liquid crystals or use them as the central building block of a heteroheptamer, all six carboxylic acid or ester groups need to be converted. Acid groups of 4 could be converted to esters, amides, or imides as shown in Scheme 2.2.

Esterification of a carboxylic acid with alcohols proceeds in the presence of an acid catalyst (Fischer esterification) or, in general, a dehydrating agent such as DCC. Alternatively, the acid could first be converted to acid chlorides or anhydrides and then reacted with an alcohol, or better an amine, to give the corresponding esters or amides, respectively. Less common is the reaction of a cesium carboxylate salt with an alkyl halide in an $\text{S}_{\text{N}}2$ reaction.

Esters can also be prepared from esters by transesterification with an alcohol of usually much higher boiling point. The transesterification can be catalyzed by acid or base (usually alkoxide ion) and is driven to completion when the exchanged alcohol is removed in vacuum. The mechanism of transesterification in the presence of a Lewis acid catalyst is discussed in section 2.1.2.

Scheme 2.2:



R= alkyl

- a) SOCl₂, excess primary amine
- b) SOCl₂, primary amine (4eq)
- c) DIPC, ROH
- d) Cs₂CO₃, R-Br

A trisdiimide (Scheme 2.2) has been prepared before and displayed discotic LC phases.⁴⁶ The hexaamides are less likely to give LC phases because of the expected strong intermolecular H-bonding, which will probably increase their melting points to too high temperatures. We, therefore, focused on the preparation of hexaesters for the small molecule derivatives. For the formation of the heptamers both, hexaesters and hexaamides could be useful building blocks.

The following two parts, 2.1.1 and 2.1.2, will discuss the hexaesterification and hexaamidation of **4** as well as the transesterification of **3**, respectively. For all attempts, methods were those that usually result high yielding conversions since we have to convert six groups per molecule. Most of these esterification methods have been developed for polyester formation as polymers of high molecular weights can only be achieved at very high turn over numbers (>99.9 %).

2.1.1 Esterification and Amidation of Hexaazatriphenylene-hexacarboxylic acid **4**

Esterification of **4** was first attempted with pentanol (dried over 4 Å mol. sieves), 1,3-diisopropylcarbodiimide (DIPC), THF and dimethyl aminopyridine (DMAP),⁴⁷ (Scheme 2.3). DMAP is widely used synthetically as a nucleophilic catalyst in acylation reactions of amines and alcohols. DMF was added to the reaction mixture after few hours, as **4** did not fully dissolve in THF. IR spectra of the product mixtures confirmed the presence of free acid groups, resulting from incomplete conversion. Upon repeating the reaction with di (ethylene glycol) methyl ether as alcohol, the same results were obtained.

High conversions have been reported when a salt 4-(dimethylamino) pyridinium 4-toluenesulfonate (DPTS)⁴⁸ was used as the catalyst for the carbodiimide method. These conditions resulted in a partial conversion of the acid groups but no ester formation. The carbonyl stretching vibration in IR spectra suggests the formation of amide-like groups, which could be N-acylureas, a typical side product of the carbodiimide-mediated esterification. DPTS has been shown to fully suppress this side-reaction in the polycondensation of benzoic acid and phenol derivatives. We assume that the two acid

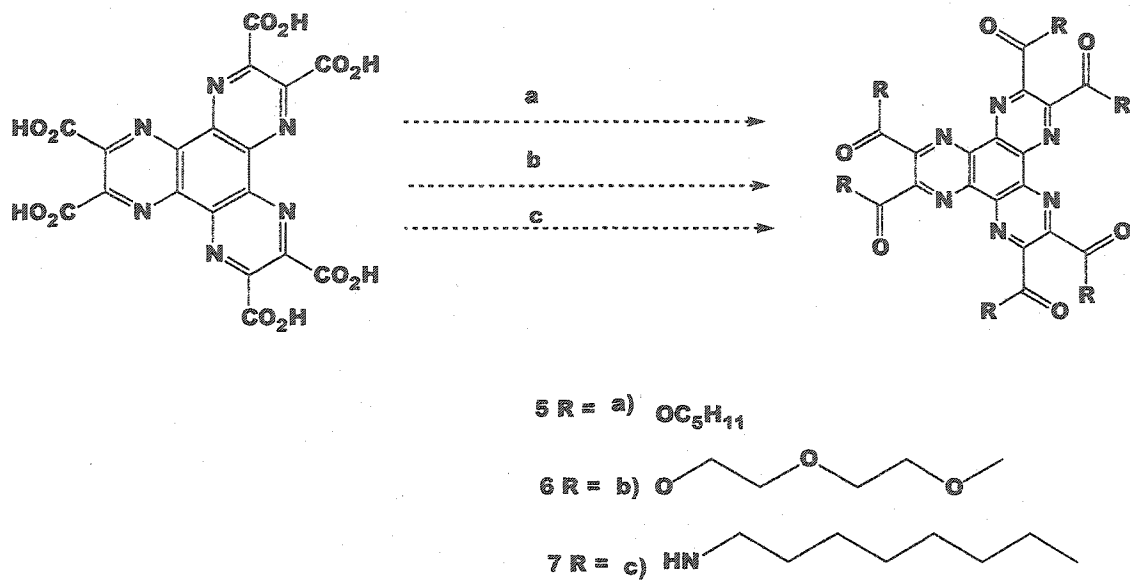
groups in *ortho* position might be the main reason why the formation of N-acylureas seems to be favoured in our case. Another interesting observation is that the observed side-product became insoluble in DMF/THF and precipitated out.

The next attempted conversion of the acid groups was based on the prior conversion of the hexaacid to the hexaacid chloride. Acid chlorides were prepared from the corresponding acids by the reaction with thionyl chloride. This reaction needed DMSO as co-solvent and did not proceed at room temperature but at 70 °C over 3 days.

The hexaacid chloride was reacted in situ with octylamine in the presence of triethylamine since amines react more easily with acid chlorides than alcohols. The reaction was quenched after 3-4 days and resulted in an incomplete conversion of the acid groups according to proton NMR and IR spectra.

Since the acid chloride was reacted in situ it is unclear whether the conversion to the acid chloride or the amide formation was incomplete. The method, however, seems to work in principle and optimized reaction conditions should allow for the formation of the hexaamide.

Scheme 2.3:



a) Pentanol, DMAP, DIPC, DMF, RT

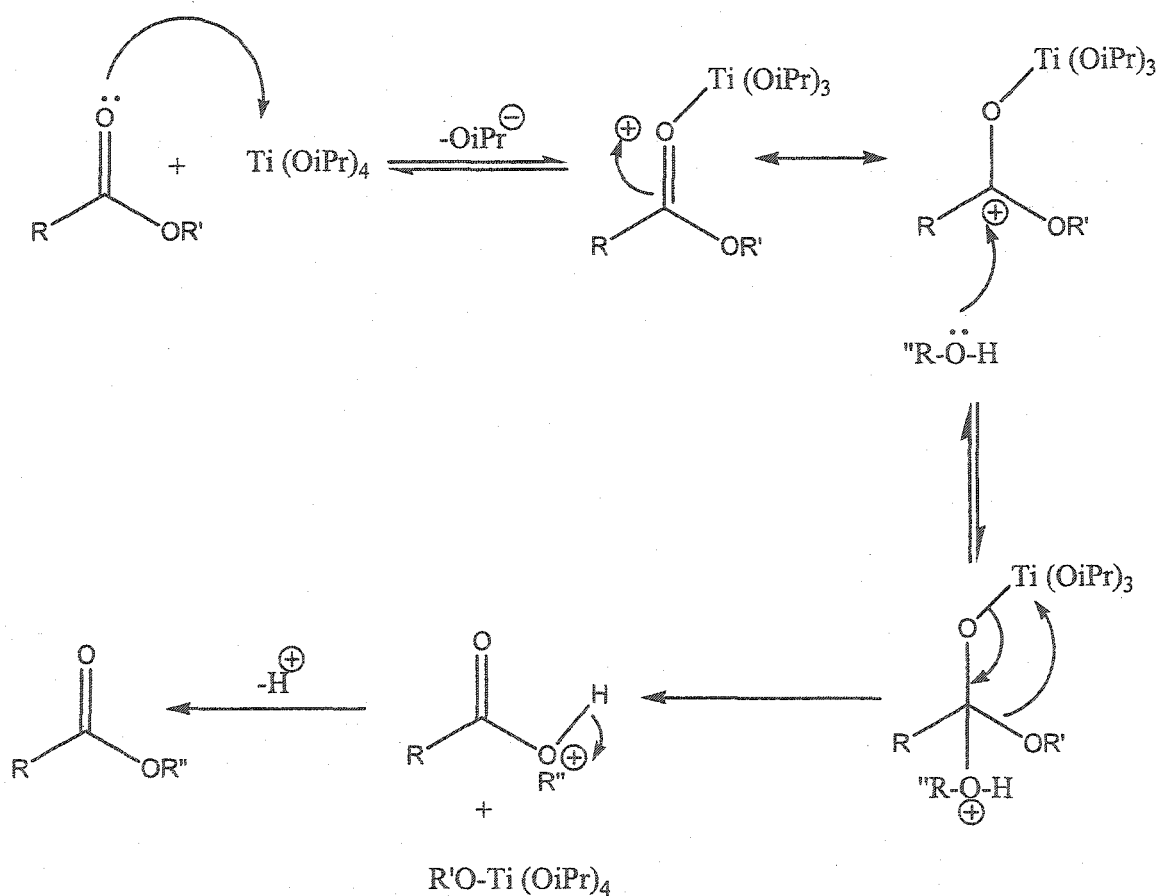
b) Di (ethyleneglycol) methyl ether, DMAP, DIPC

c) SOCl_2 , 70 °C, Octylamine, Et_3N

2.1.2 Transesterification of Hexamethyl hexaazatriphenylene hexacarboxylate 3

Transesterification of esters is usually acid catalyzed, as base catalysis could cause side-reactions due to α -deprotonation (though not in our case). We employed titanium (IV) isopropoxide as a Lewis acid catalyst that has been successfully used for polycondensations.⁴⁹ The mechanism of this transesterification is shown in Scheme 2.4.

Scheme 2.4:

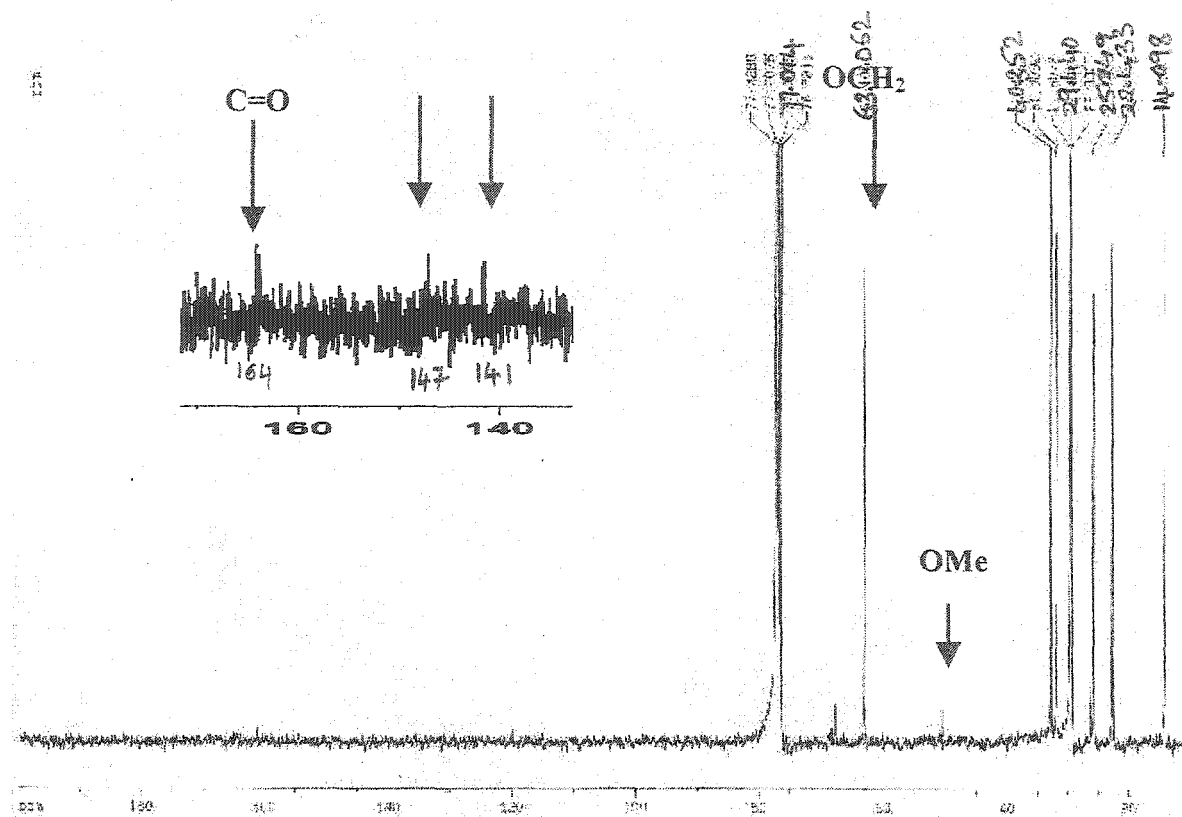


Transesterification of 3 was attempted with different alcohols under different conditions. Pentanol, undecanol, and bromononanol were reacted at temperatures between 120 °C and 150 °C under vacuum for 1 to 8 days and gave incomplete conversions according to ^1H - and ^{13}C -NMR (Scheme 2.5 and Fig. 2.3). DMF and DMSO were added as co-solvents without changing the course of the reaction.

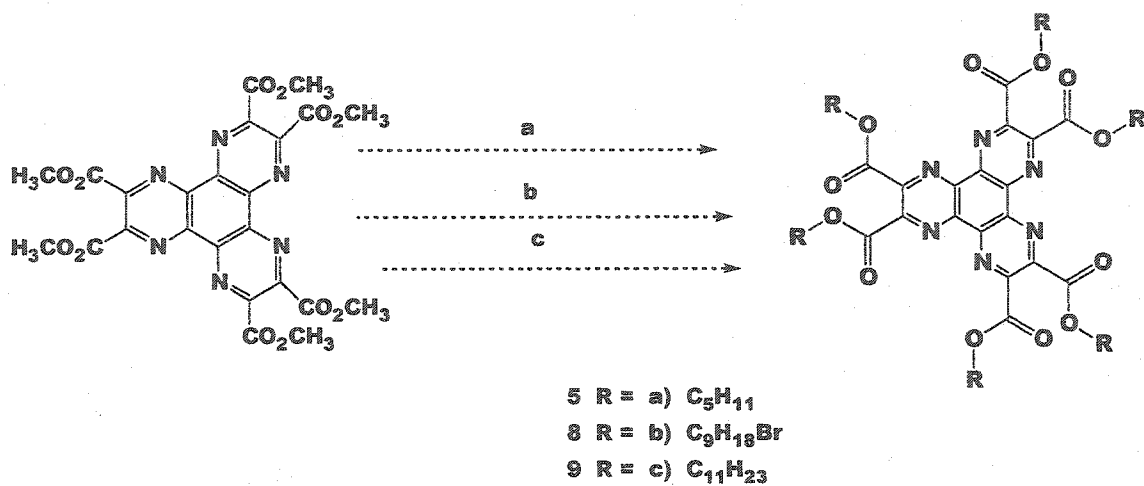
Conversions of 82 %, determined by integration of the ^1H -NMR spectrum were achieved with higher boiling alcohols such as undecanol. A complete conversion apparently needs higher temperatures as prolonged reaction times or repeated treatment did not change the ratio between methyl ester and transesterified ester. We later found that complete conversion for similar polyacids was only obtained if the residue, that is left over after the alcohols were evaporated in vacuum, was heated to 200 °C for several hours.⁴⁹

Bromononanol also gave incomplete conversions although the bromine functionality was inert to the applied conditions. Difficult, however, was the removal of excess bromononanol from the product mixture. Di(ethylene glycol)monomethylether, on the other hand, was not stable to the reaction conditions and resulted in the formation of a dark insoluble solid that was not further characterized.

Fig 2.3: ^{13}C -NMR of Transesterification of Hexaazatriphenylene hexamethylester



Scheme 2.5:



- a) Pentanol, 120 °C, titanium (IV) isopropoxide.
 b) Bromononanol, DMF, 120 °C, titanium (IV) isopropoxide.
 c) DMSO, 1-undecanol, 110 °C, titanium (IV) isopropoxide.

2.2 Making monofunctionalized hexaalkoxy triphenylenes

Hexasubstituted triphenylenes (electron rich, p-type conductivity) are the most widely synthesized and studied discotic mesogens, due to their pronounced photoconductivity, self-organization and high charge carrier mobility. We tried two methods for the preparation of monofunctionalized triphenylene as ligands (Scheme 2.11 and Scheme 2.23). Both approaches follow procedures that have already been presented by others.^{50, 51}

The statistical approaches are based on the oxidative trimerization of alkylated catechols and require a chromatographic separation of product mixtures. The other approach is based on Suzuki cross couplings and is more versatile. It, however, requires the synthesis of several intermediates but would avoid the chromatographic separation of triphenylene product mixtures.

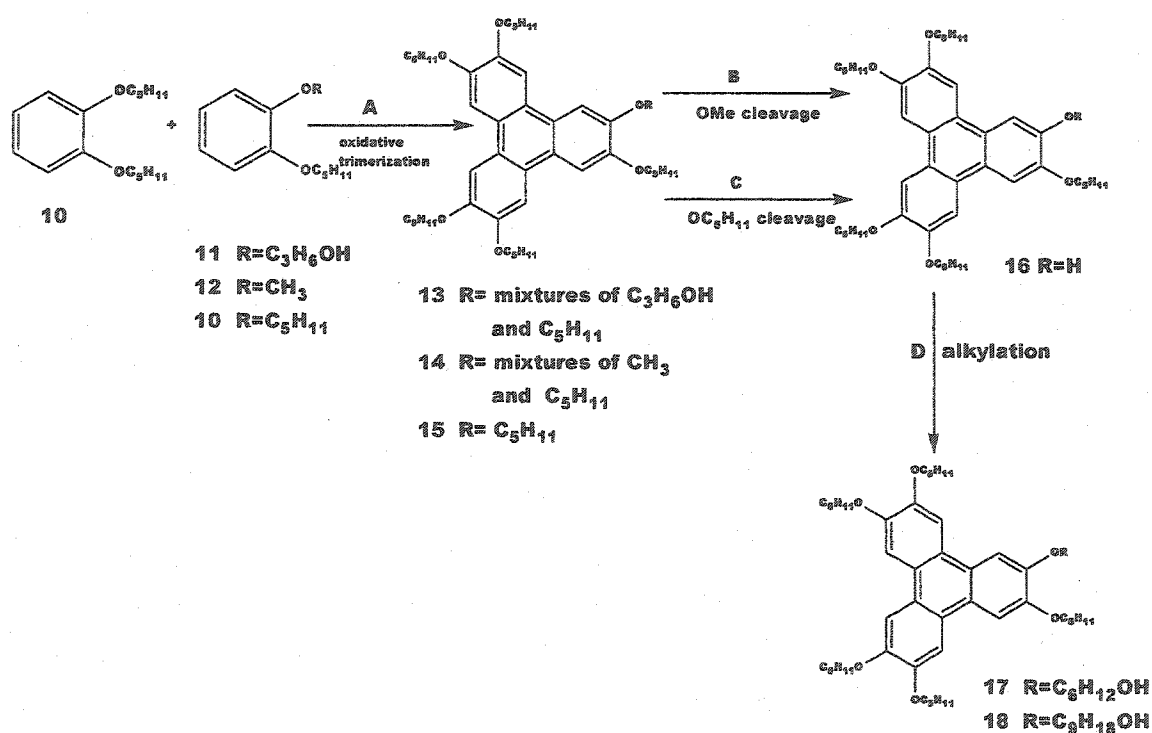
2.2.1 Approach 1: Oxidative trimerization of dialkoxy benzenes to hexaalkoxytriphenylenes

The oxidative trimerization of electron rich catechol derivatives with FeCl_3 and other inorganic oxidizing agents are old reactions but their mechanisms are still not fully understood. An oxophilic Lewis acid oxidizing agent such as molybdenum pentachloride might coordinate to the dialkoxy moiety. The subsequent electron transfer from the π -system to the molybdenum fragment forms a radical cationic species. Subsequent electrophilic intermolecular attack on another electron rich arene results in the initial step for C-C coupling. Loss of a proton and oxidation of the resulting radical with another equivalent of molybdenum pentachloride is succeeded by extrusion of the second proton. During this rapid conversion the evolution of HCl can be observed.⁵²

The synthesis of monofunctionalized triphenylene by oxidative trimerization was attempted by three different methods: 1) The trimerization of mixtures of dialkoxybenzene derivatives that already contain a functionalized side chain for subsequent coupling reactions to form the heptamer; 2) The trimerization of dialkoxy benzene followed by a statistical cleavage of alkoxy groups with bromocatecholborane to generate a high percentage of the monophenol; 3) The trimerization of mixtures of

dialkoxybenzene and alkoxyethoxy-benzene to form the monomethoxy-pentaalkoxy-triphenylene. The methoxy group can be cleaved selectively to generate the phenol, which can then be alkylating with alkyl bromides or iodides; Scheme 2.6 summarizes the three different synthetic approaches.

Scheme 2.6:



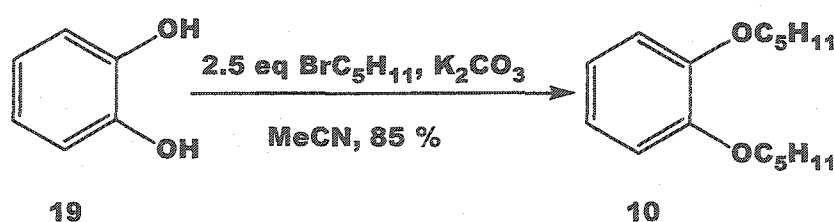
Method A) is only one step if we can separate the product mixture and OH does not interfere with the oxidative trimerization. Method B) has been reported in literature but requires an extra step for the selective cleavage; 12 can be made selectively in one step by alkylation of the commercially available guaiacol. Method C) requires the separation of several products after the ether cleavage of OC₅H₁₁.

2.2.1.1 Preparation of dialkoxy benzene derivatives and their oxidative trimerization

As we were interested in finding the best approach to synthesize monofunctionalized triphenylenes, we attempted many synthetic reactions using different reagents and conditions.

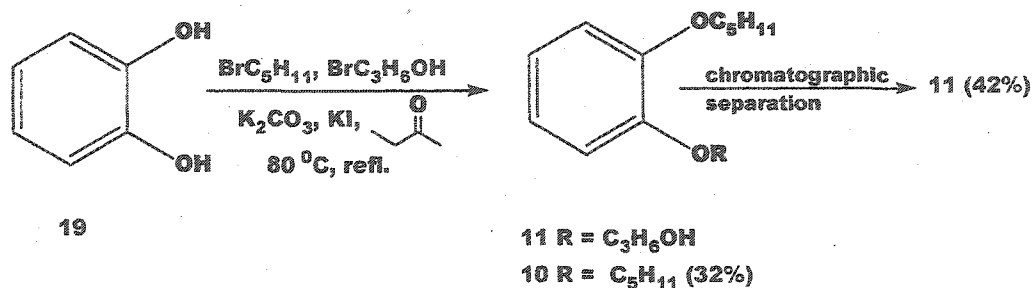
The substituted 1,2-dialkoxybenzene derivatives ⁵³ needed for the synthesis of monofunctionalized triphenylenes via oxidative trimerization were prepared as shown in Scheme 2.7

Scheme 2.7:



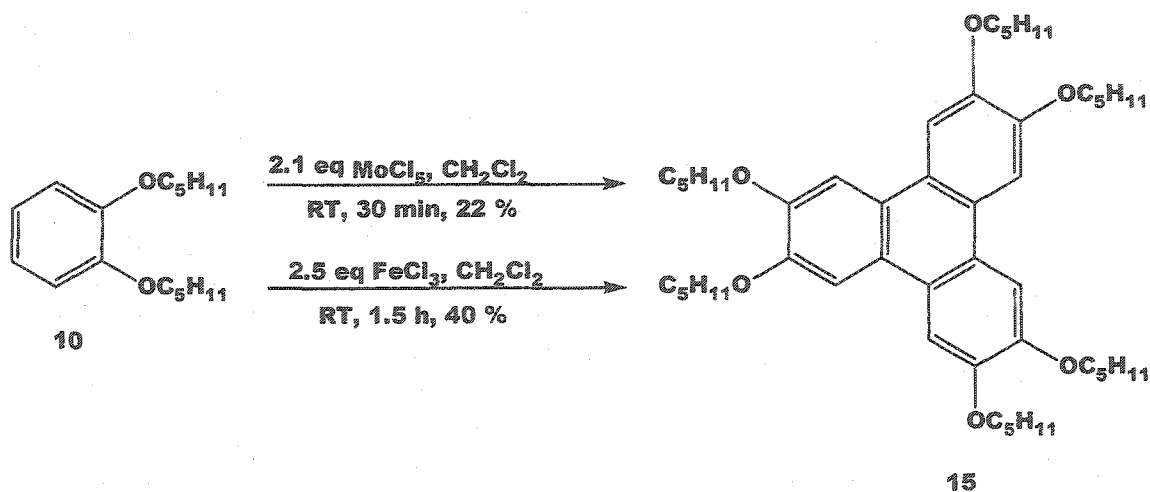
3-(2-pentyloxy phenoxy) propan-1-ol (11) was synthesized from catechol, 1-bromopentane and bromopropanol as seen in Scheme 2.8. The yield was only 42 % because of the side products 1,2-dipentyloxybenzene and 3-[2-(3-hydroxy propoxy)phenoxy] propan-1-ol, which were separated by flash chromatography on silica gel using DCM/hexanes 3:2 as solvent mixture for 1,2-dipentyloxy-benzene, and DCM/EtAc 4:1 for 3-[2-(3-hydroxy propoxy) phenoxy] propan-1-ol.

Scheme 2.8:



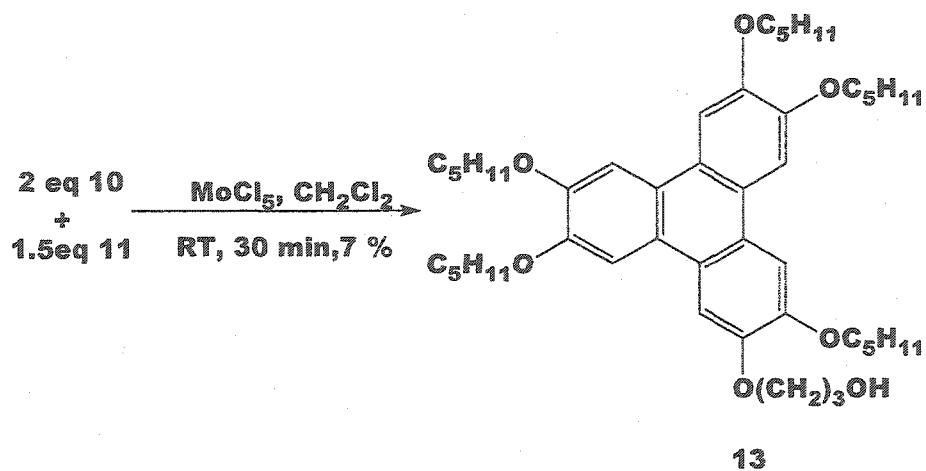
Oxidative trimerization of 10 (Scheme 2.9) has been achieved with different oxidizing agents such as FeCl₃, MoCl₅ and VOCl₃, of which MoCl₅ was reported to give the highest yields of 92 % and purest products.⁵⁰ We did not obtain yields above 22 % despite several test reactions at slightly different conditions (Table 1) and the highest yields of 40 % were obtained with FeCl₃. Main side products of all these reactions are phenols that were generated by HCl catalyzed ether cleavage. Optimum results were obtained for FeCl₃ when the reaction was run at room temperature for 1.5 h and the generated HCl was removed continuously by purging the reaction with N₂.

Scheme 2.9:



Oxidative mixed trimerization of **10** and **11** to the monofunctionalized triphenylene shown in Scheme 2.10 was conducted with MoCl_5 . The reaction is completed in 30 min at room temperature and yielded the product in 7 % after tedious chromatographic separations. The use of FeCl_3 for MoCl_5 did not significantly improve the final yields and this approach was dismissed altogether.

Scheme 2.10:

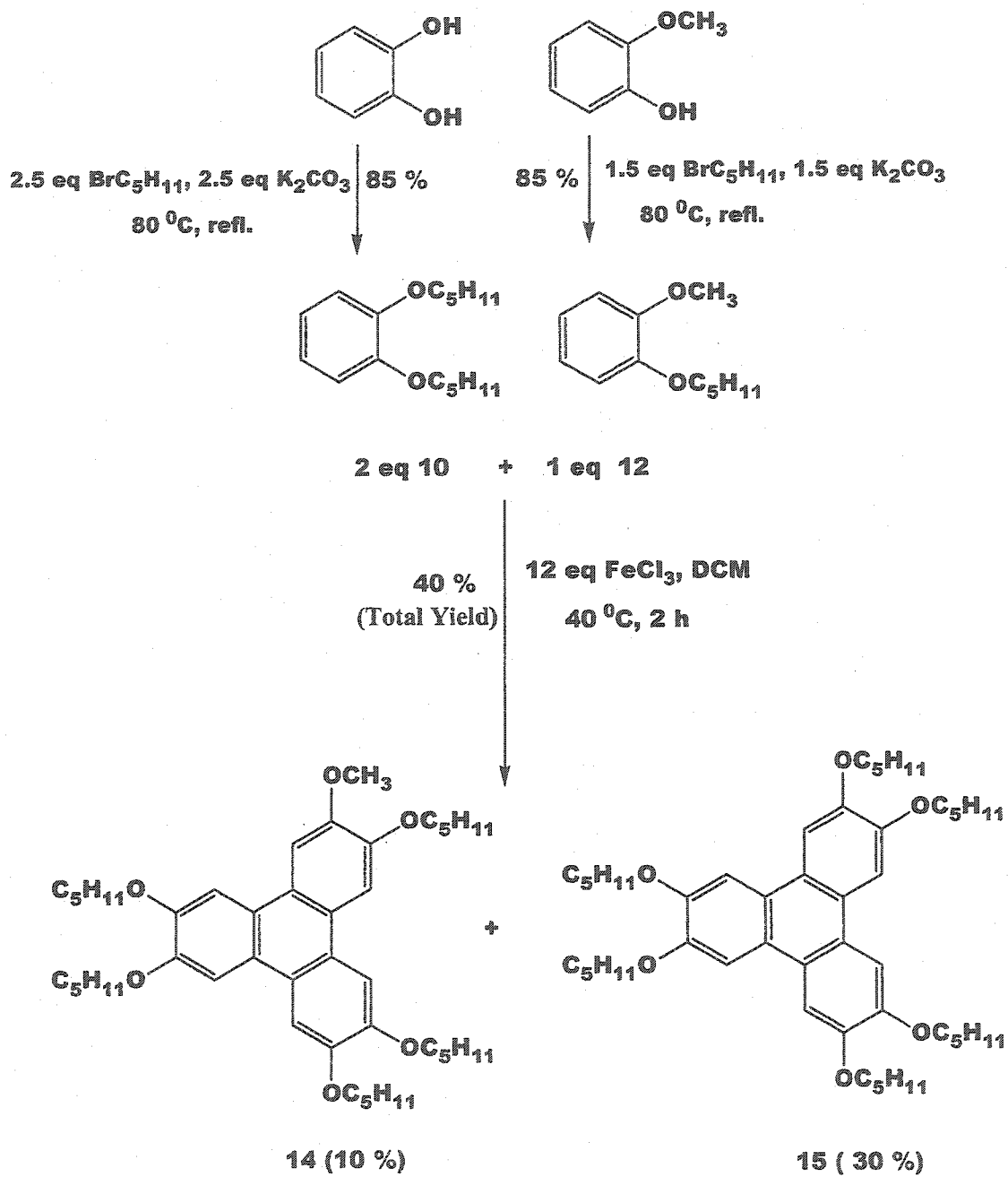


Oxidative mixed trimerization of 10 and 12 (Scheme 2.11) to 14 has been achieved by using FeCl_3 . The reaction is completed in 2 h at about 40 °C and yielded the product triphenylenes in 40 % yield. The workup of the reaction mixture is straightforward but only gives a crude product. The product contained small amounts of derivatives that had lost alkylchains (not methyl) and were observed as purple solids (probably due to oxidation of the generated phenolic intermediate).

Purging the solution with argon in order to remove excess of HCl gas could reduce the amount of cleavage products. Trapping of the generated HCl by K_2CO_3 resulted in the formation of dialkoxy benzoic acids (29 % yield) and only about 7 % triphenylene. It should be mentioned here that a catalytic amount of strong acid is required for the oxidative trimerization of dialkoxy benzenes.

Selective cleavage of the methoxyether in compound 14 (Scheme 2.11) using LiPPh_2 ⁵⁴ was accomplished successfully with 70 % yield. Unsuccessful was the separation of 16 from the side product 15. Thus, 16 was converted to 20 using NaH and acetic anhydride in THF at room temperature. The chromatographic separation of 15 was now straightforward and the pure 20 was alkylated with bromononanol to give 18 in 46 % yield.

Scheme 2.11:



Scheme 2.11 cont'd

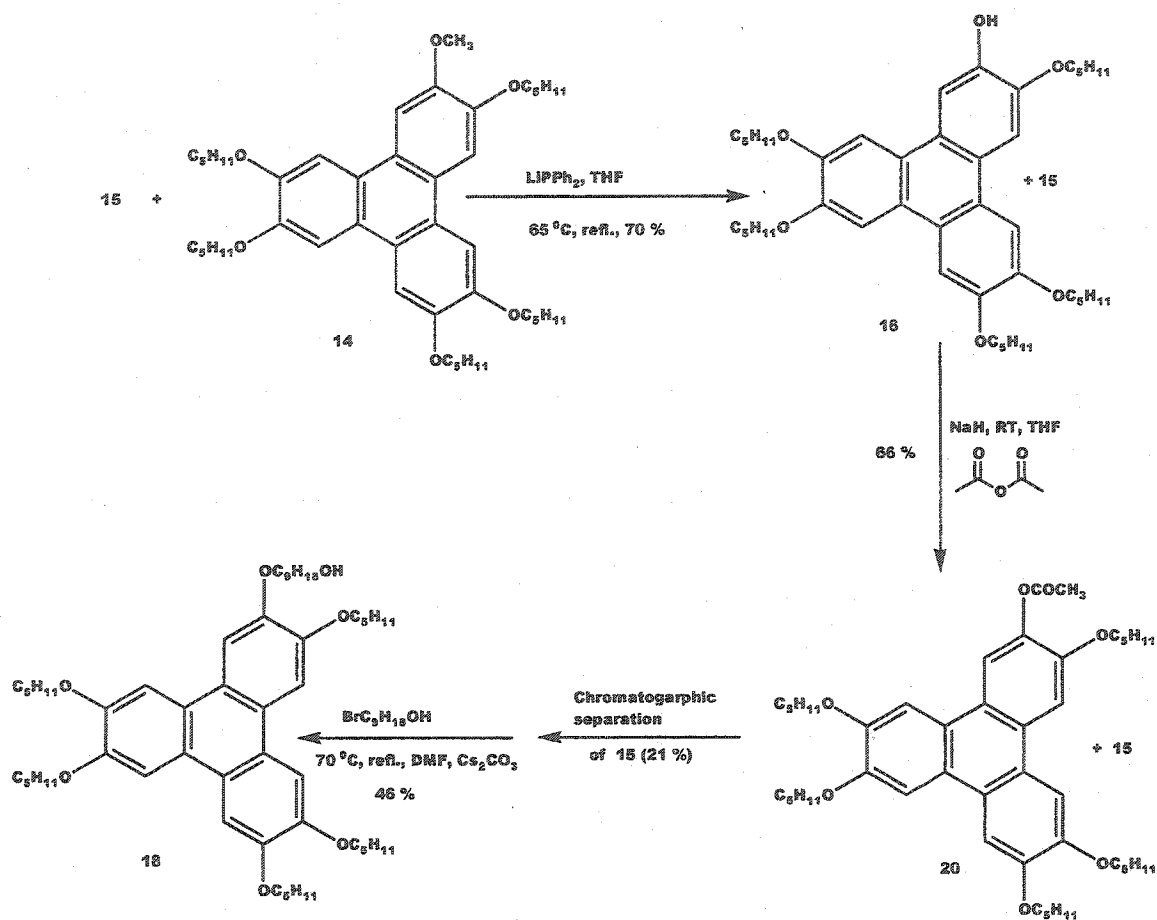
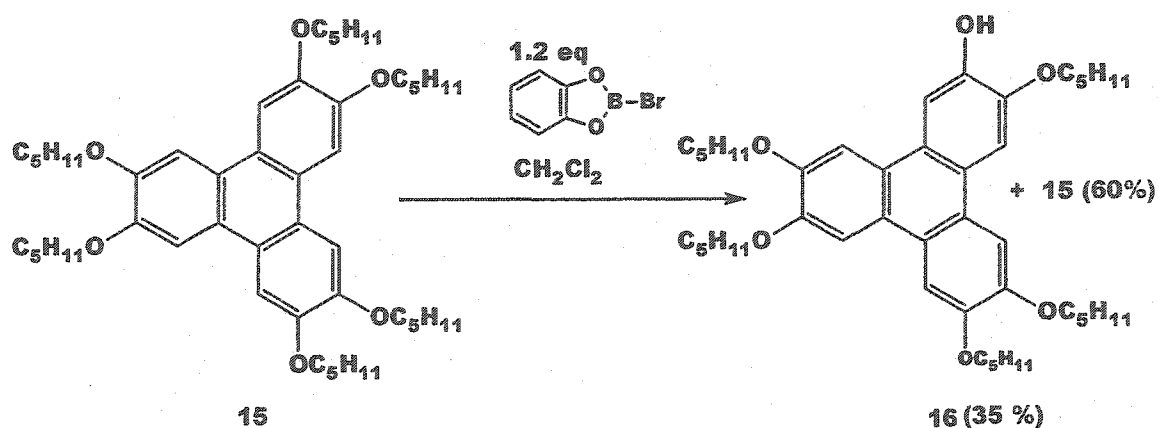


Table 1: Results for MoCl_5 trimerization reactions of 10 using different conditions

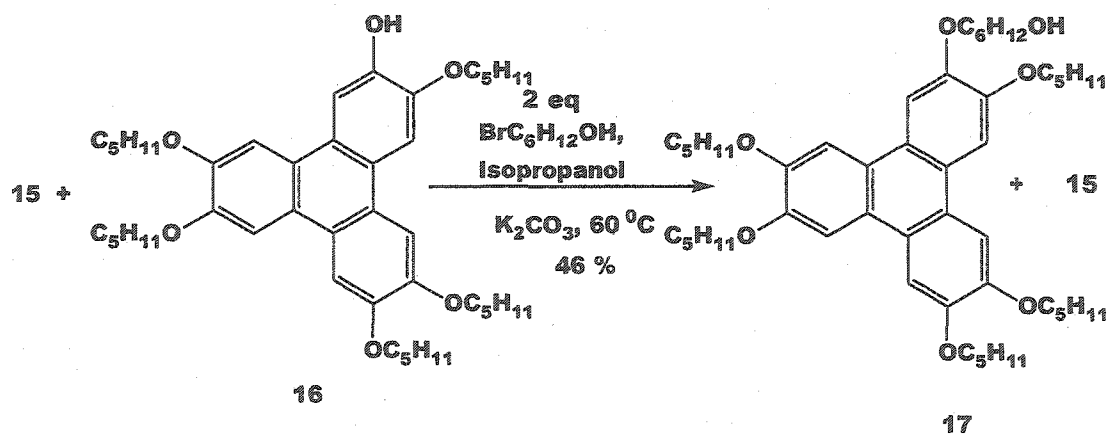
REACTIONS	TIME & TEMP	Eq	NMR	YIELD
T# 1	RT/30 min	1.5	Okay	22 %
T# 2	RT/30 min	1	Okay	20 %
T# 3	RT/30 min	1 + K_2CO_3	Not Okay (Dialkoxy benzene derivative peaks)	29 % substituted dialkoxy benzene derivatives and 7 % triphenylene
T# 4	35° C/1.5 h	1	Okay	14 %
T# 5	35° C/1 day	2	Not Okay (Phenolic peak)	16 % pure triphenylene
T# 6	35° C/4.5 h	1.5	Not Okay (Phenolic peak)	7 % pure triphenylene
T# 7	35° C/30 min	1.5	Not Okay (Phenolic peak)	10 % pure triphenylene

Scheme 2.12:



Method C (page: 39) was the last approach we tested (Scheme 2.12) and followed a literature procedure.⁵⁵ 3,6,7,10,11-pentakis-pentyloxy-triphenylen-2-ol (**16**), the intended product, was obtained in 35 % yield, and 60 % of **15** was recovered. An increase in reaction time and temperature (from RT to 45°C) did not change the ratio of **16**:**15** significantly. We, unfortunately, did not succeed in separating **16** from **15** by flash chromatography on silica gel (Al_2O_3 would have been a better choice) and, therefore, used the mixture for the following alkylation with bromohexanol to yield **17** in 46 % (before purification) as shown in Scheme 2.13.

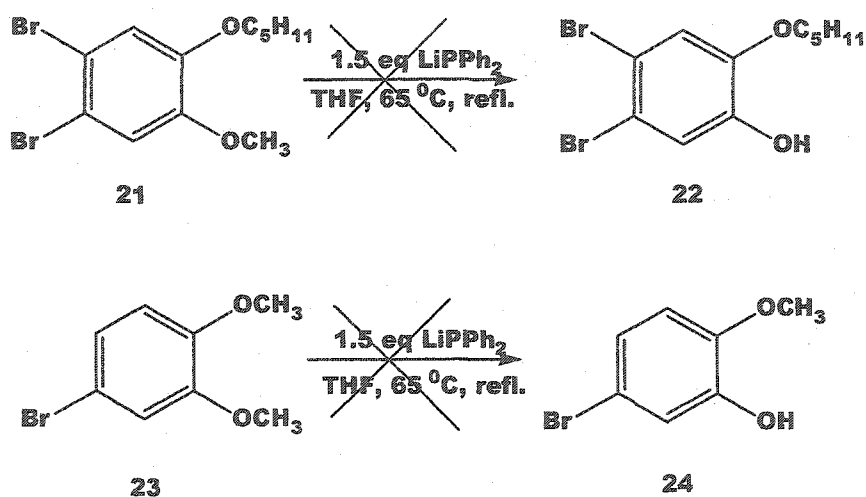
Scheme 2.13:



Chromatographic separation of **17** and **15** on a pre-packed silica gel column only yielded **15** as pure product but no **17** was recovered. It is possible that most of **17** was oxidized overtime as phenols of alkoxy triphenylenes are known to be readily oxidized by air. Discouraged by the low initial yield of **17** and a difficult separation we decided not to repeat and optimize this approach as method B) gave better results.

We also attempted to employ the methyl ether cleavage by LiPh_2P for the selective MeO cleavage of dialkoxy bromo benzene derivatives **21** and **24** as shown in Scheme 2.14. To our surprise neither of the two derivatives reacted under the employed conditions and the starting materials were fully recovered. An increase of the amount of LiPh_2P (from 1.5 eq to 3 eq) also did not result in any methyl cleavage.

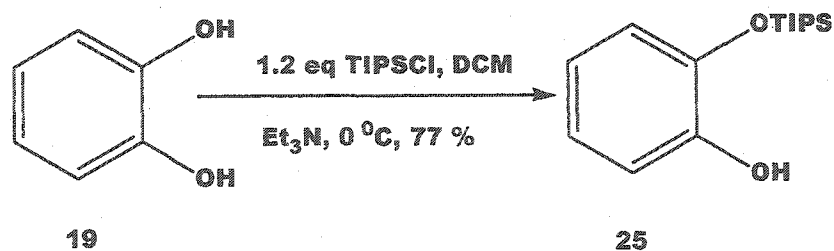
Scheme 2.14:



2.2.1.2 Mixed oxidative trimerization with TIPS instead of methyl as phenolic protecting group

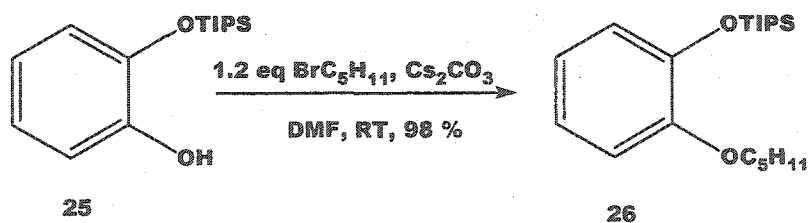
Although the methyl ether approach above worked, it is tedious and we tried TIPS as an alternative to the methyl protecting group. The TIPS protected phenol could be deprotected and alkylated in one step by using CsF in DMF. This would also circumvent stability problems caused by the easily oxidized phenols of triphenylenes. 2-Triisopropylsiloxy-phenol (**25**) was selectively formed from catechol as seen in Scheme 2.15 due to the bulky nature of the TIPS group.⁵⁶

Scheme 2.15:



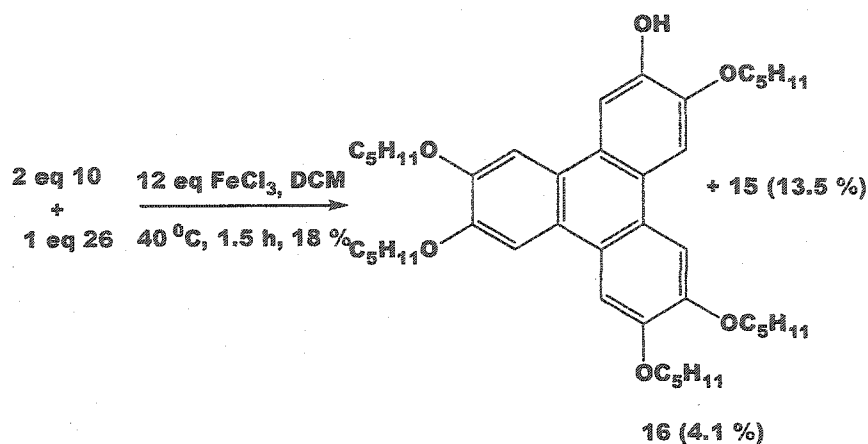
The alkylation of **25** with bromopentane in ethanol at 80 °C surprisingly resulted in a partial cleavage of the TIPS group but alkylation in DMF at RT with Cs₂CO₃ as base gave **26** in 98 % yield. No TIPS cleavage was observed by NMR spectra.

Scheme 2.16:



The optimized FeCl₃ method was employed for the oxidative trimerization of **10** and **26** to yield triisopropyl-(3,6,7,10,11-pentakis-pentyloxy-triphenylen-2-yloxy)-silane but resulted in **16** as seen in Scheme 2.17.

Scheme 2.17:



According to the ^1H -NMR spectra the TIPS group was completely cleaved off during the reaction. It is known that TIPS can be cleaved (from a phenol) by acids. So, it is not surprising but we wanted to test how much is cleaved and whether this effects the yield. If the phenol was generated early in the trimerization a low yield is expected, as phenolic groups are known to interfere with the oxidative cyclization. The resultant product mixture included 15 and 16 in a ratio of 3:1 with an overall yield of 18 %. Due to the limited amounts of material available, separation of 15 was not attempted.

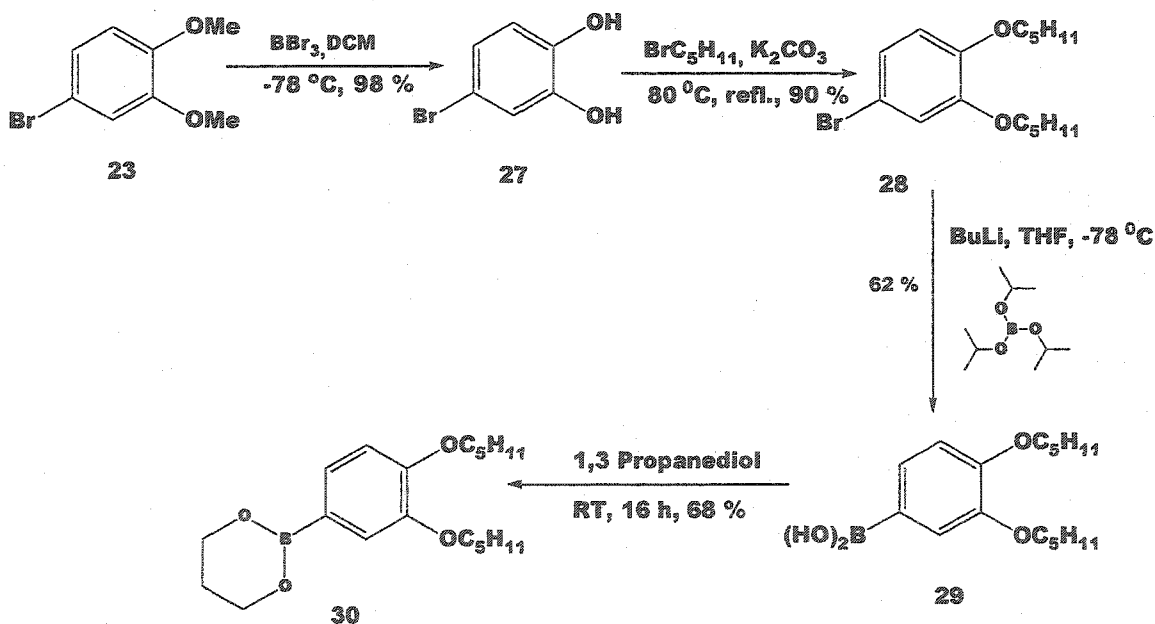
2.2.2 Approach 2: Preparation of a mono-functionalized triphenylenes via Suzuki cross coupling reactions

Approach 1 requires the chromatographic separation of product mixtures, which is tedious when gram quantities are required. A selective method that can be easily scaled up was based on the Pd (0) catalyzed cross coupling of benzene derivatives to terphenyls.⁵¹ Another advantage of this method is that we can also couple arenes containing electron withdrawing groups, which can not be used for the oxidative coupling, and it can also tolerate many more functional groups.

2.2.2.1 Synthesis of aryl halides and boronic esters

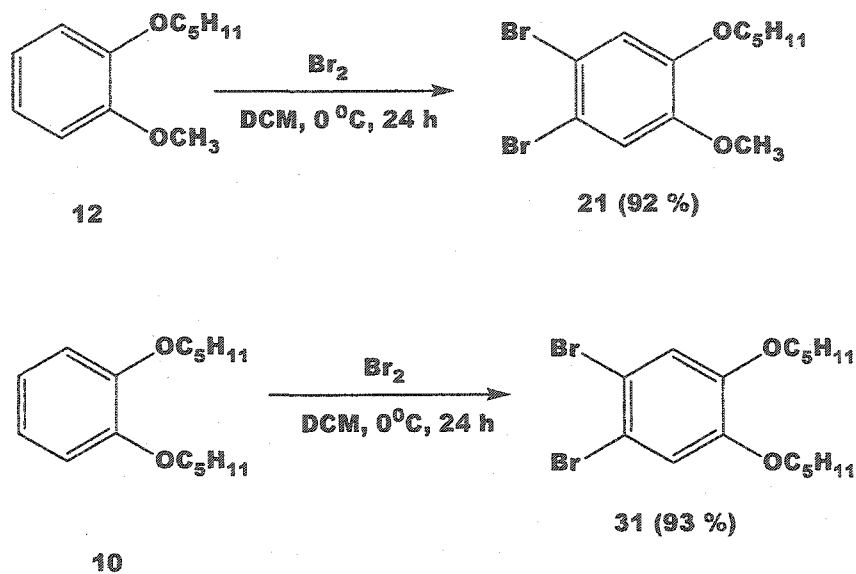
Starting materials for the Suzuki cross coupling are aryl halides and aryl boronic acids/esters and their synthesis is described below (Scheme 2.18). Compound **27** was synthesized via demethylation of **23** by boron tribromide with a yield of 98 %.⁵⁷ **27** was successfully alkylated to **28** with pentyl bromide, and subsequently converted in 62 % yield to the boronic acid **29**. The boronic acid was finally converted to the boronic ester **30**.⁵⁸ During the conversion to **29** we observed the side product **10** in a ratio of 2:1 that could be removed by extraction with hexanes. However, we later completely eliminated the formation of **10** by using distilled triisopropyl borate.

Scheme 2.18:



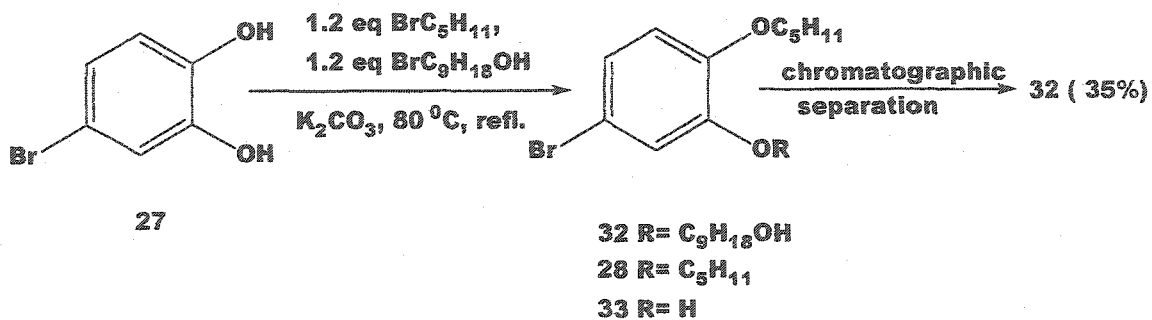
Compounds **21** and **31** (Scheme 2.19) were prepared from dibromination of **12** and **10** respectively; at 0°C for 24 h in more than 90 % yields.⁵⁹

Scheme 2.19:



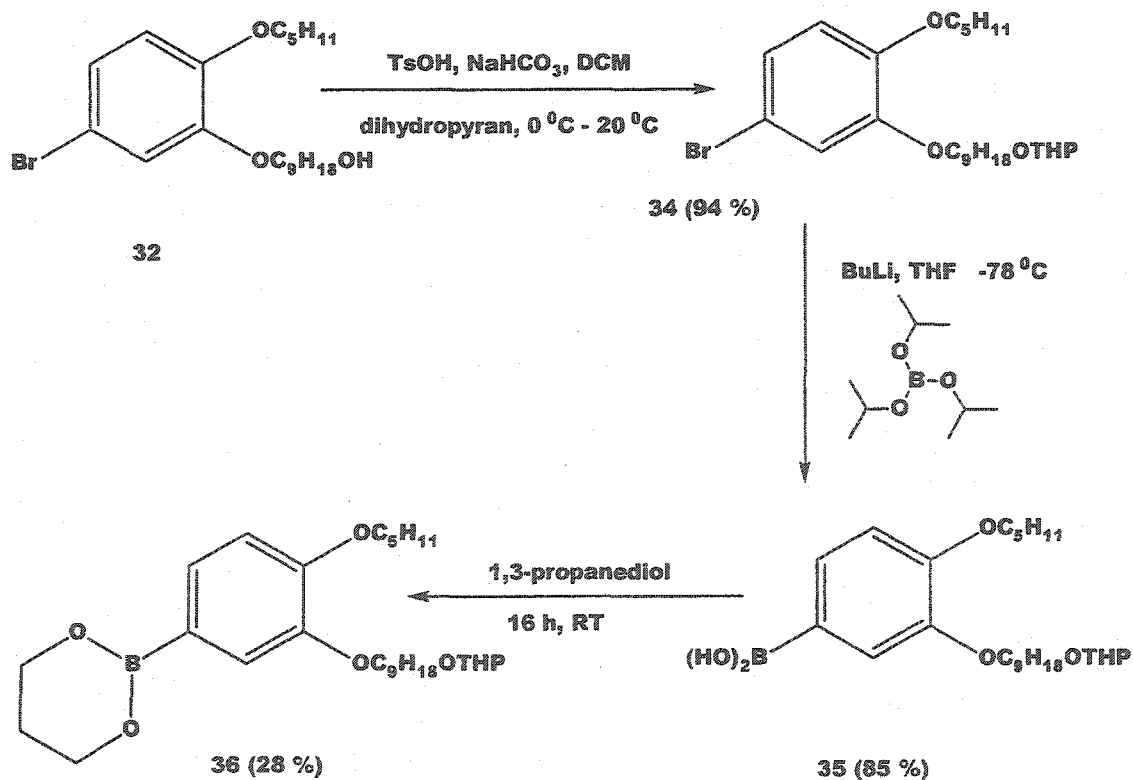
Compound **32** was prepared by simple alkylation using appropriate alkyl bromides as seen in Scheme 2.20. The problems with the attempted synthesis have been attributed with the side products produced during the reaction time, which resulted in low yield of 35 %. The side products encountered during the reaction are 4-bromo-1, 2-dipentyloxybenzene (**28**) and 4-bromo-2-pentyloxyphenol (**33**). The mixture can be separated by column chromatography, which resulted in a 35 % yield of **32**.

Scheme 2.20:



The next stage of the synthesis involved the protection of the hydroxyl group in 32 using dihydropyran⁶⁰ to yield 34 in 94 % (Scheme 2.21). The hydroxyl group in compound 32 was protected as it interferes the formation of boronic acids (it would react with BuLi). 34 was successfully converted to 35 in a yield of 85 % (crude product) and subsequently to 36 in an overall yield of only 28 %. The THP protecting group, however, appeared to be stable to all applied conditions.

Scheme 2.21:

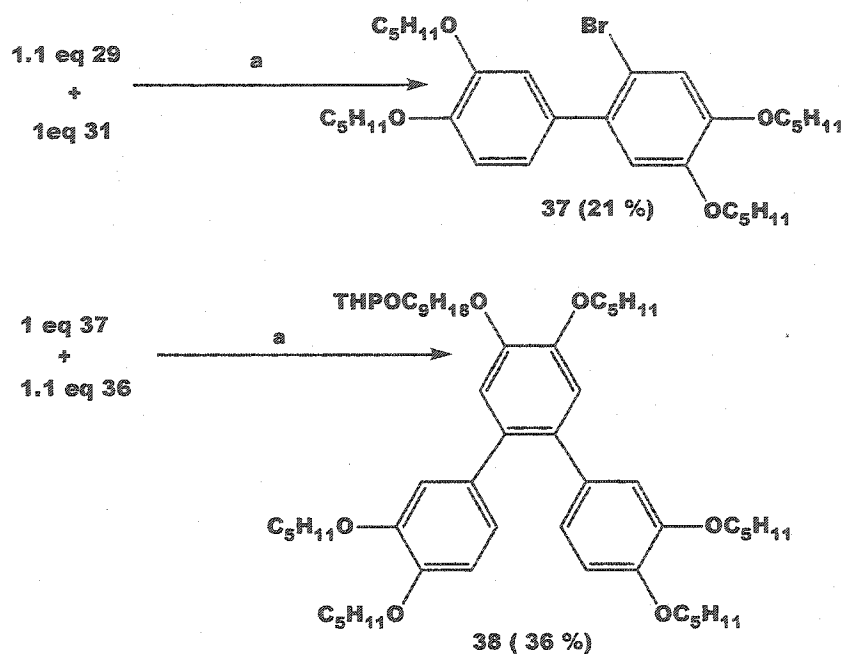


2.2.2.2 Synthesis of *ortho*-terphenyl and triphenylene derivatives

Two different approaches to the terphenyl derivatives were tested; a) a stepwise cross coupling via biphenyl as shown in Scheme 2.22 and b) a one-pot dual Suzuki reaction as shown in Scheme 2.23.

Approach a) started with the synthesis of the biphenyl **37** via the cross coupling of **31** and **29** using tetrakis-triphenylphosphine palladium (0) as catalyst in only 21 % yield. The yield was only 21 % because of the side product 1,2-dipentyloxybenzene, which was separated by flash chromatography on silica gel. **36** was subsequently cross-coupled with **37** using Pd (0) to give terphenyl **38** in 36 % yield. The yield was low because of the side product 3,4,3',4'-tetrakis-pentyloxy-biphenyl which might have formed during hydrolysis and was separated by flash chromatography on silica gel. **38** did not crystallize probably due to the racemic THP group and the non-planar *ortho*-terphenyl core and, therefore, was difficult to purify.

Scheme 2.22:



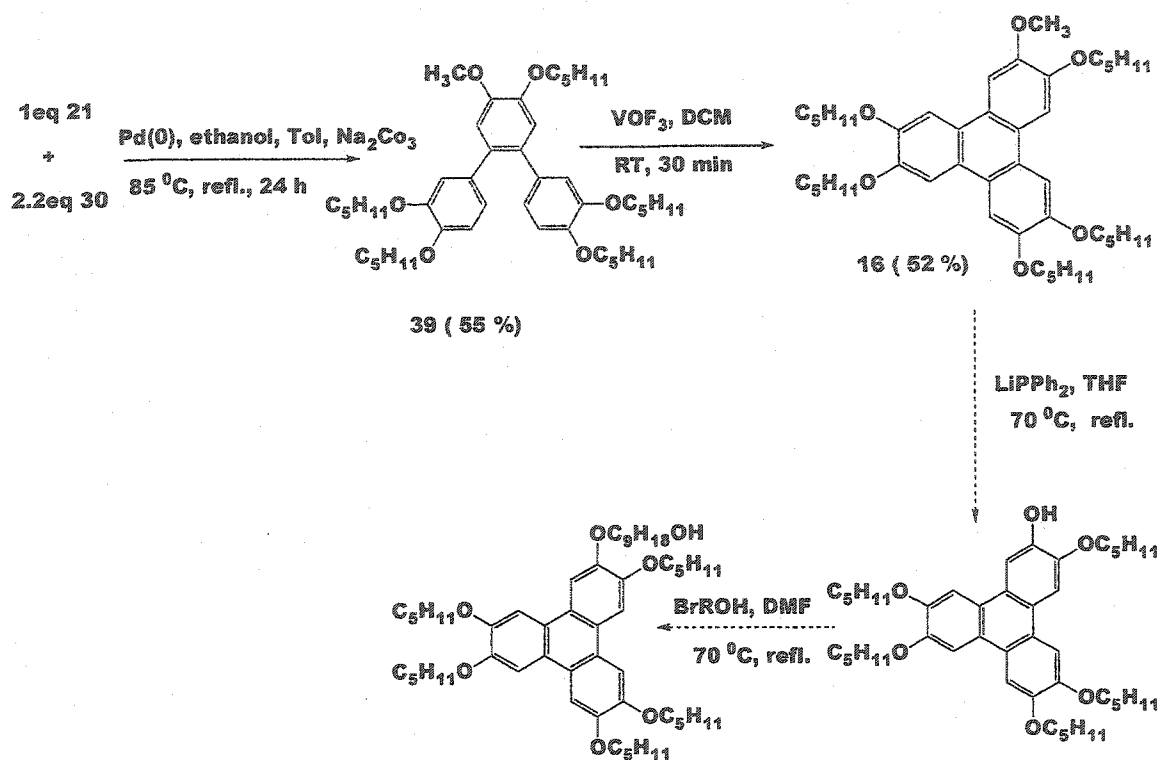
a) Pd(0), Tol, Ethanol, Na₂CO₃

85 °C, refl., 24 h

Approach b) as seen in scheme 2.23, is a one-pot dual Suzuki reaction to yield terphenyl, **39** from compounds **21** and **30** using Pd(PPh₃)₄ catalyst at 85 °C for 24 h. **39** was synthesized successfully in a yield of 55 %. We again observed 3,4,3',4'-tetrakis-pentyloxy-biphenyl as side product (32 %), which was separated by chromatography on silica gel. Trimerization of **39** with VOF₃ at room temperature yielded **16** in 52 %. The trimerization of **39** was previously attempted with FeCl₃, which resulted in small amounts of derivatives that had lost alkylchains and were observed as purple solids.

Through this Suzuki cross coupling approach we could successfully synthesize monofunctionalized triphenylene and also avoid the side product **15**, which we encountered in the oxidative trimerization approach. (Scheme 2.23 next page)

Scheme 2.23:



3. CONCLUSIONS AND OUT LOOK

We were successful in synthesizing the n-type conducting discogenic (not discotic yet) hexaazatriphenylene-hexacarboxylic acid, **4** and its methyl ester, **3**. Both hexaazatriphenylenes **3** and **4** could function as central building blocks for the preparation of the targeted hetero-heptamer and, consequently, different methods for the attachment of six side-groups were investigated.

Our efforts focused on the hexaesterification and hexaamidation of **3** and **4**, as we wanted electron-withdrawing groups to be attached to the hexaazatriphenylene ring. A complete conversion of all six carboxylic acid groups per molecule in good yields is required since mixtures of penta-, hexa-, and heptamers would be very difficult to separate. Thus, esterification and amidation methods that have been successfully used for the preparation of polyesters and polyamides by polycondensation reactions were expected to be most promising.

Of all the esterification methods that have been tested, hexa-esterification by titanium (IV) isopropoxide catalyzed transesterification of the methyl ester **3** gave the best results. Test reactions with aliphatic alcohols resulted in incomplete transesterification of up to 85 %. These reactions were all run at temperatures between 110 °C and 150 °C, which are not sufficient according to a published investigation, we found later.⁴⁹ Final reaction temperatures of up to 250 °C were reported to be required for a complete conversion. Nick Fox, who continues this project, will carry out these reactions. He will not only use simple aliphatic alcohols but also the monohydroxy hexaalkoxytriphenylene which is also stable to temperatures above 250 °C but does not evaporate or sublime to a considerable degree.

Amidation of **4** was attempted *via* the hexaacid chloride intermediate but again gave only incomplete conversion. The incomplete amidation might either be the result of an incomplete formation of the acid chloride or an incomplete reaction with the primary aliphatic amine. An optimization of the reaction conditions, however, should allow for a successful hexaamidation. The formation of a hetero-heptamer also requires the

preparation of an 9-(3,6,7,10,11-pentakis-pentyloxy-triphenylen-2-yloxy)-nonan-1-amine ligand, in analogy to the alcohol (18).

The synthesis of mono-functionalized triphenylenes as ligand discotics for the hetero-heptamers was based on chemistry that has been described in literature but caused more problems than expected. Two principally different approaches have been investigated in this thesis.

Approach 1 was based on the statistical formation of mono-functionalized hexaalkoxytriphenylenes. In all these cases, the triphenylene core was assembled *via* an oxidative trimerization of 1,2-dialkoxybenzenes, which appeared to be the problematic step. The acidic reaction conditions resulted in a partial cleavage of pentyloxy ether groups and the generated phenols were then oxidized to pinkish quinone type structures. Although the amounts of these side-products are relatively small (< 10 %) they complicated the already difficult chromatographic separation of the statistical product mixture. Consequently, the overall yields for all pathways based on approach 1 were low and the purification was time consuming.

Approach 2 was based on the preparation of mono-functionalized *ortho*-terphenyls by Suzuki cross-coupling. On paper, this approach appears to be more tedious than approach 1 as several more synthetic steps are involved in the preparation of the *ortho*-terphenyl. All steps to the terphenyl, however, gave good to excellent yields of easily purified products and the final oxidative ring closure of the terphenyl to the triphenylene was achieved with VOF_3 . $\text{VOF}_3 \cdot \text{BF}_3$ etherate, in contrast to FeCl_3 , did not cause any ether cleavage and an off-white crude product was obtained.

In summary, successful routes to two starting materials for hetero-heptamers have been developed in this thesis. Nick Fox, who continues the work on hetero-heptamers, presently studies the final attachment of six p-type semi-conducting monohydroxy hexaalkoxy triphenylenes to the n-type semi-conducting hexaazatriphenylene 3 by transesterification.

4. EXPERIMENTAL SECTION

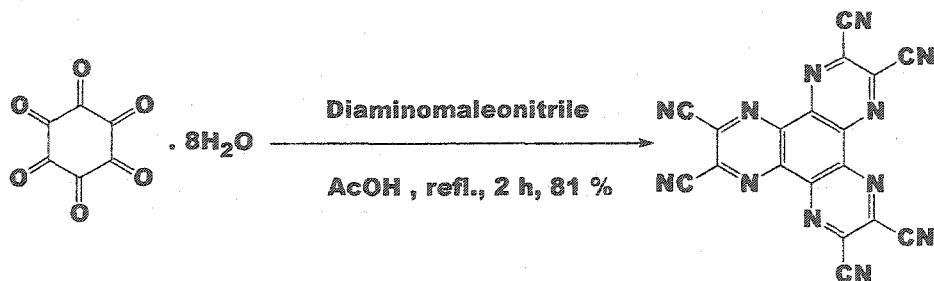
4.1 General methods

Reagents used in this thesis were purchased from Aldrich Chemical Company. Chemicals were used without further purification unless noted otherwise. Solvents were dried over magnesium sulphate prior to use and THF was freshly distilled from sodium. Preparative thin layer chromatography was performed using Silica gel GF* 1000 micron plates. Analytical thin layer chromatography was performed using 60 F₂₅₄ aluminum sheets from VWR. Silica gel 60 (Merck, 200 to 240 mesh) was used for flash chromatography.

Infrared spectra were run on a Bruker Vector 22. Liquid samples were performed as neat films on potassium bromide plates, and solid samples were run as potassium bromide pellets. NMR spectra were recorded on a Bruker Avance 500 Spectrometer at 500 MHz for ¹H-NMR and 75 MHz for ¹³C-NMR in chloroform if not stated otherwise. Chemical shifts are given in ppm relative to TMS and the multiplicities are described using the following notations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). The *J* coupling values are given in Hz. Fractional distillations were performed using a Buchi GKR-51 Kugelrohr set-up. All reactions were performed under nitrogen or argon if not stated otherwise.

4.2 Synthesis of hexaazatriphenylene derivatives

Hexaazatriphenylene hexacarbonitrile [1, HAT-(CN)₆]

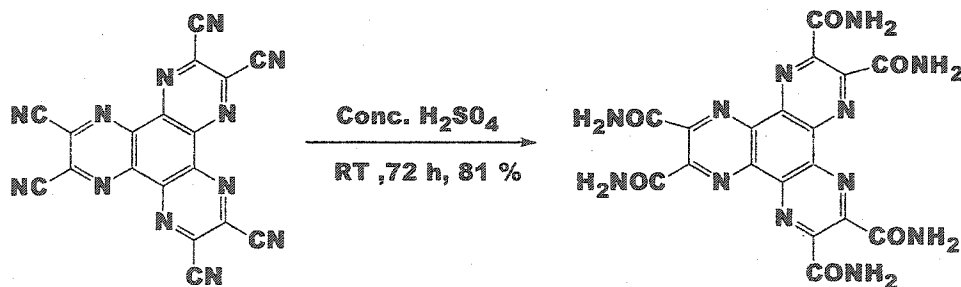


Glacial AcOH (1.2 L), hexaoxocyclohexane octahydrate (10.0 g, 32 mmol), and diaminomaleonitrile (26.0 g, 240 mmol) was added to a 2 L round bottom flask and

heated to reflux for 2 h. The resulting black mixture was filtered hot, washing with hot AcOH (3*200 mL) to give a black solid. The solid was suspended into 30 % HNO₃ (150 mL) in a 250 mL round bottom flask and was heated to 100 °C for 3 h. The resulting brown suspension was cooled, poured into ice H₂O (100 mL) and filtered to give crude HAT(CN)₆ as a dark brown solid. Purification was done using a 1 L round bottom flask equipped with a magnetic stirring bar was added MeCN (500 mL). Soxhlet apparatus with a 43*123 cm thimble size was attached to this flask. The crude HAT(CN)₆ was placed in a cellulose thimble and the system was heated to high reflux for 72 h. The receiving flask was allowed to cool and the solvent was removed *in vacuo* to yield **1** as yellow orange solid. (10.2 g, 81 %).

¹³C NMR [(CD₃)₂SO]: δ = 141.6 (external C_{Ar}), 135.4 (internal C_{Ar}), 114.2 (CN). All spectroscopic data agree with the values reported in literature.²⁷

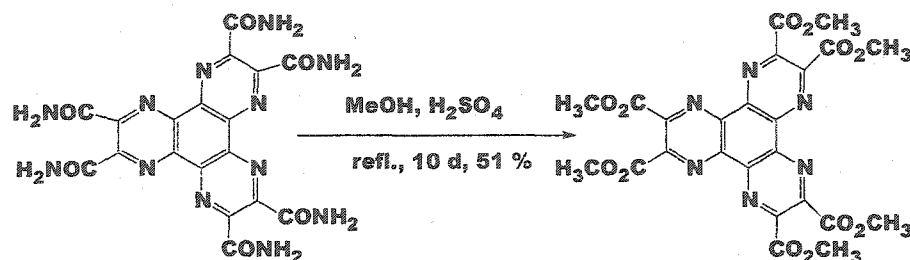
Hexaazatriphenylene hexacarboxamide [2, HAT-(CONH₂)₆]



Compound **1** (10.2 g, 26 mmol) and concentrated H₂SO₄ (300 mL) were added to a 1 L round bottom flask equipped with a magnetic stirring bar. The mixture was left to stir for 72 h. The solid slowly dissolved to give a red orange solution. The solution was then added drop wise into stirring ice water (3 L), adding extra ice as it melted. The yellow suspension was filtered, washed with water (3*300 mL) and acetone (3*300 mL), and dried overnight *in vacuo* to yield **2** as yellow solid (10 g, 81 %).

^{13}C NMR $[(\text{CD}_3)_2\text{SO}]$: $\delta = 166.2$ (CONH_2), 148.3 (external C_{Ar}), 140.5 (internal C_{Ar}). All spectroscopic data agree with the values reported in literature.²⁷

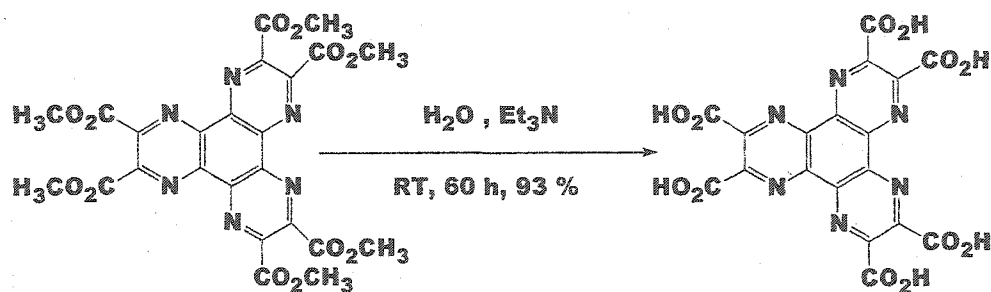
Hexamethyl Hexaazatriphenylene hexacarboxylate [3, HAT-(CO_2Me)₆]



To a 1 L round-bottom flask equipped with a magnetic stirring bar were added **2** (10 g, 20.3 mmol), anhydrous MeOH (500 mL), and concentrated H_2SO_4 (24 mL, 20 eq) and heated at reflux for 10-15 d. The resulting gray-yellow suspension was cooled, filtered, washed with MeOH (3*100 mL), and dried *in vacuo* giving a gray solid. The crude product was dissolved into freshly distilled MeCN (1.3 L) and filtered through Celite (60 g) using a fine frit (10-20 μ) 140 mL funnel; the plug was then washed with additional MeCN (300 mL) to ensure complete elution of the hexaester. The resulting yellow powder after removing the solvent *in vacuo* was recrystallized from MeCN/MeOH. The small crystals were filtered and washed with MeOH to yield **3** as tan solid (7.6 g, 51 %).

^{13}C NMR $[(\text{CD}_3)_2\text{SO}]$: $\delta = 167.2$ (CO_2), 148.8 (external C_{Ar}), 143.8 (internal C_{Ar}), 56.4 (OMe); IR (KBr): $\nu_{\text{max}} = 2957$ (CH_3 , s), 1729 ($\text{C}=\text{O}$), 1564, 1442 ($\text{CO}-\text{O}$), 1298, 1031 ($\text{O}-\text{CH}_3$) cm^{-1} ; ^1H NMR $[(\text{CD}_3)_2\text{SO}]$: $\delta = 4.28$ (s, OMe). All spectroscopic data agree with the values reported in literature.²⁷

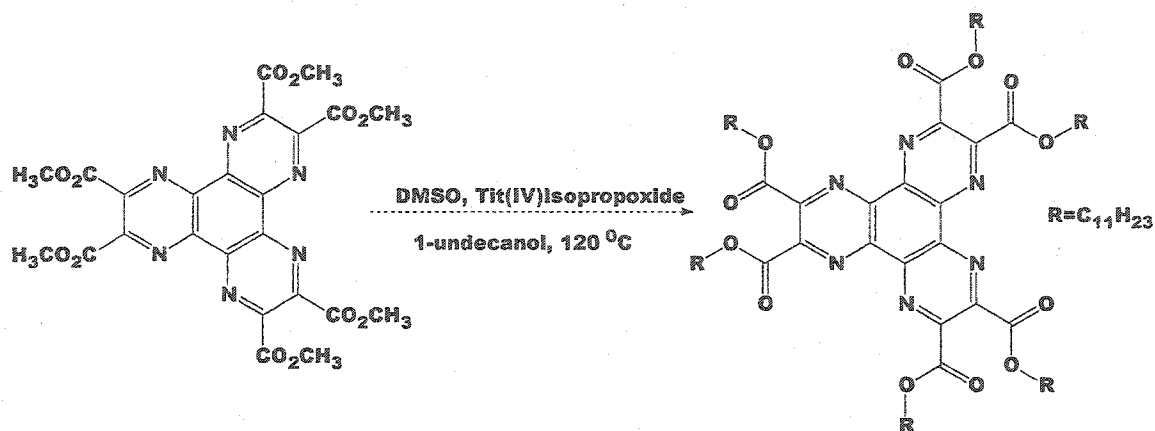
Hexaazatriphenylene hexacarboxylic acid [4, HAT- (CO₂H)₆]



Compound 3 (6.5 g, 11.16 mmol) was placed in a 1 L round bottom flask equipped with a magnetic stirring bar. To the solid were added distilled H₂O (300 mL) and Et₃N (30 mL). The mixture was left to stir for 60 h until complete dissolution occurred. The yellow solution was filtered to remove any undissolved particles; the filtrate was then acidified by drop wise addition of concentrated HCl (ca.25 mL) until initial precipitation. After stirring for 30 min, an additional 50 mL of conc. HCl was added and the suspension was filtered and dried *in vacuo* to yield 4 as beige-yellow solid (5.2 g, 93 %).

¹³C NMR [(CD₃)₂SO]: δ =165.9 (CO₂H), 146.8 (external C_{Ar}), 141.9 (internal C_{Ar}); IR (KBr): ν_{max} = 3200-2400 (OH), 1740-1600 (broad, C=O), 1212 (CO-O), 1107 cm⁻¹. All spectroscopic data agree with the values reported in literature.²⁷

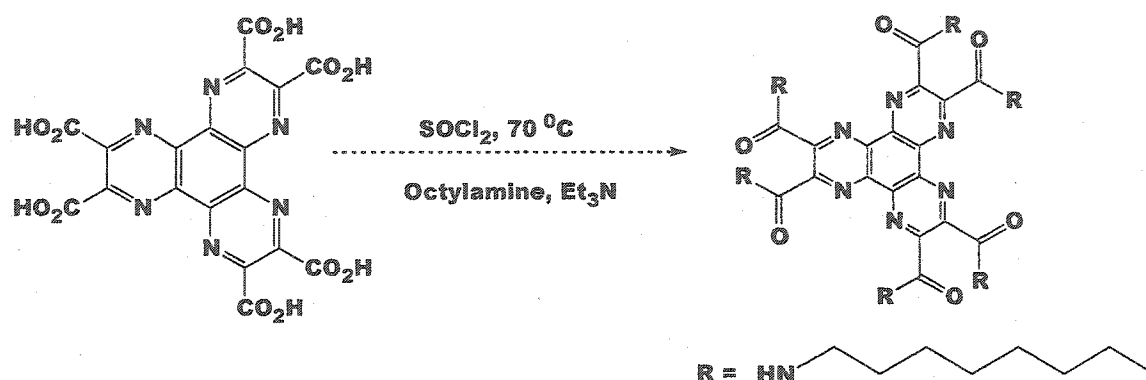
Attempted transesterification of Hexamethyl Hexaazatriphenylene hexacarboxylate
[3, HAT-(CO₂Me)₆]



To a 250 mL round bottom flask equipped with a magnetic stirring bar was placed 3 (100 mg, 0.171 mmol), 1-undecanol (8 eq, 1.368 mmol, 235 mg) and Titanium (IV) isopropoxide (50 mol %, 24.3 mg), DMSO (10 mL) and was attached a drying tube. The suspension was then left to stir for 4 days at 120 °C. After 4 days cooled the reaction mixture, added 1M HCl (50 mL) and extracted with diethyl ether. The ether layer was washed with aqueous sodium bicarbonate solution and dried over magnesium sulphate. The resultant brown oil was recrystallized from methanol. Crystals were not observed even after 5-6 days. ¹H-NMR and ¹³C- NMR spectra indicated the presence of partial conversion.

¹³C NMR [(CD₃)₂SO]: δ = 167.2 (CO₂), 148.8 (external C_{Ar}), 143.8 (internal C_{Ar}), 63.0 (OCH₂), 56.4 (OMe, starting material), 40.3 (CH₂), 29.6 (CH₂), 28.4, 22.6, 14.0 (CH₃).

Attempted amidification of Hexaazatriphenylene hexacarboxylic acid [4, HAT-(CO₂H)₆]



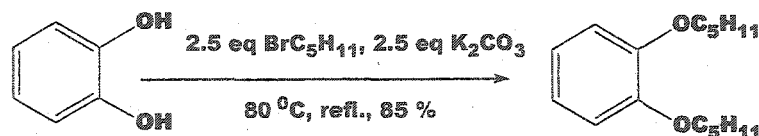
To a 250 mL round bottom flask equipped with a magnetic stirring bar was placed 4 (100 mg, 0.200 mmol), thionyl chloride (12 eq, 2.4 mmol, 286 mg) and DMSO (10 mL) and attached a drying tube. The suspension was then left to stir for 3 days at 70 °C. After 3 days removed the excess of thionyl chloride and DMSO using vacuum and added Et₃N (10eq, 202 mg) and octylamine (9 eq, 1.8 mmol, 232 mg) at 0 °C under argon and stirred for three days at RT. After 3 days ethyl acetate (50 mL) was added to the reaction mixture and extracted with 1M HCl and then with H₂O. The ether layer was washed with aqueous sodium bicarbonate solution and dried over magnesium sulphate. The resultant brown oil was recrystallized from methanol to obtain brown solid. ¹H-NMR and ¹³C-NMR spectra indicated the partial conversion.

IR (KBR): $\nu_{\text{max}} = 2960\text{--}2856$ (CH₂ and CH₃), 1740 and 1631 (broad, mixtures of amide, acid and imide) cm⁻¹.

4.3 Approach 1: Synthesis of monofunctionalized hexaalkoxytriphenylenes

4.3.1 Starting materials (dialkoxy benzenes)

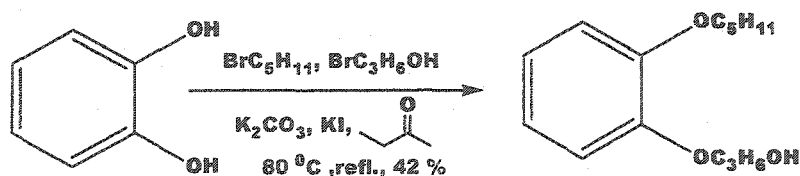
1, 2-dipentyloxy-benzene (10)



To a 500 mL round bottom flask was added catechol (13.2 g, 120 mmol), 1-bromopentane (2.5 eq, 42.2 g, 279 mmol), potassium carbonate (2.5 eq, 41 g, 296 mmol) and acetonitrile (400 mL). The reaction mixture was refluxed at 80°C . After 3 days the reaction mixture was filtered and the resulting brown solution was evaporated in vacuum to remove the solvent. The resulting brown oily residue was purified by flash chromatography on silica gel using toluene/hexane mixtures 1:1 as solvent to yield 10 as light yellow oil. This was further purified by fractional distillation at 225°C to yield 10 as colorless oil (12.5 g, 85 %).

TLC (silica; toluene/hexanes 1:1) R_f : 0.5; $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 6.9 (4H, m, Ar), 3.9 (4H, t, $J = 6.0$ Hz), 1.8 (4H, m), 1.4 (8H, m), 0.9 (6H, t, $J = 6.0$ Hz). All spectroscopic data agree with the values reported in literature.⁵³

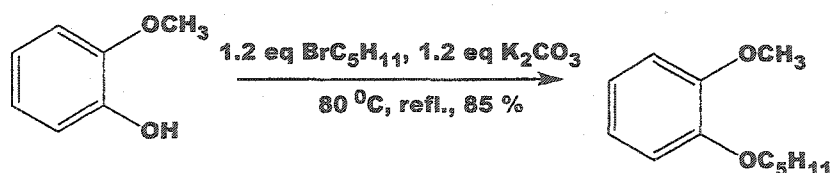
3-(2-Pentyloxy-phenoxy)-propan-1-ol (11)



To a 250 mL round bottom flask added was catechol (3 g, 27.2 mmol), 1-bromopentane (1.2 eq, 32.6 mmol, 4.5 g), bromopropanol (1.2 eq, 32.6 mmol, 4.5 g), potassium carbonate (3 eq, 81.6 mmol, 11.2 g), KI (20 mg) and 2-butanone (150 mL). The reaction mixture was refluxed at 80 °C. After 3 days filtered the reaction mixture and the resulting yellow solution was evaporated in vacuum to remove the solvent. The resulting yellow oily residue was purified by flash chromatography on silica gel using DCM as solvent to yield 11 as light yellow oil (2.6 g, 42 %). The side products were separated during the purification on flash chromatography using silica gel with DCM/hexanes 3:2 solvent mixture for 1,2-di-pentyloxy-benzene and DCM/EtAc 4:1 for 3-[2-(3-hydroxy-propoxy)-phenoxy]-propan-1-ol.

TLC (silica; toluene) R_f 0.4; $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 6.9 (4H, m, Ar), 4.0 (4H, t, OCH_2 , $J = 6.0$ Hz), 3.9 (3H, t, $J = 3.0$ Hz), 1.8 (4H, m), 1.5 (4H, m), 0.9 (3H, t, CH_3 , $J = 6.0$ Hz).

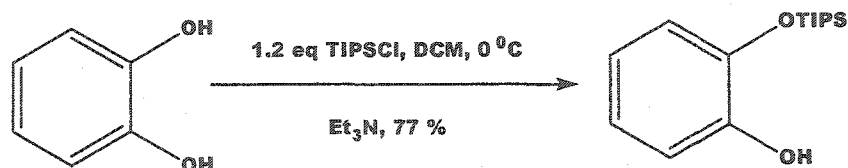
1-Methoxy-2-pentyloxy-benzene (12)



To a 250 mL round bottom flask was added 2-methoxyphenol (5 g, 40.2 mmol), 1-bromopentane (1.2 eq, 48.24 mmol, 7.2 g), potassium carbonate (1.2 eq, 48.2 mmol, 6.6 g) and ethanol (150 mL). The reaction mixture was refluxed at 80 °C. After 3 days filtered the reaction mixture and the resulting brown solution was evaporated in vacuum to remove the solvent. The resulting brown oily residue was purified by flash chromatography on silica gel using toluene as solvent to yield 12 as light yellow oil. Further purification by fractional distillation at 225 °C yielded 12 as colorless oil. (6.7 g, 85.5 %).

TLC (silica; toluene) R_f : 0.7; ^1H NMR (300 MHz, CDCl_3 , δ): 6.9 (4H, m, Ar), 4.0 (2H, t, J = 6.0 Hz), 3.8 (3H, s) 1.8 (2H, m), 1.4 (4H, m), 0.9 (3H, t, J = 6.0 Hz). All spectroscopic data agree with the values reported in literature.⁵³

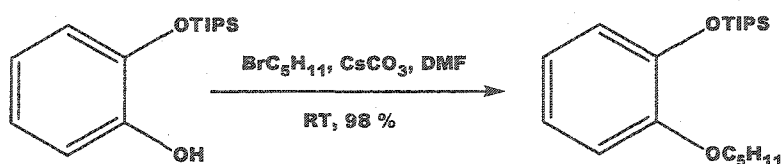
2-Triisopropylsiloxy-phenol (25)



To a 250 mL round bottom flask was added catechol (5 g, 45.4 mmol), TIPSCl (1.2 eq, 54.48 mmol, 10.4 g), triethylamine (2 eq, 90.8 mmol, 12.5 mL), and DCM (50 mL) and stirred at 0 °C. After one day the reaction mixture was filtered and the resulting orange solution was evaporated in vacuum to remove the solvent. The resulting orange oily residue was purified by flash chromatography on silica gel using DCM as solvent to yield **25** as light orange oil (9.3 g, 77 %).

TLC (silica; toluene) R_f : 0.5; ^1H NMR: δ (300MHz; CDCl_3) 6.9 - 6.7 (4H, m, Ar), 5.6 (1H, s, OH), 1.6 (3H, heptad, CH, J = 9.0 Hz), 1.1 (18H, d, CH_3 , J = 6.0 Hz).

Triisopropyl- (2-pentyloxy-phenoxy)-silane (26)



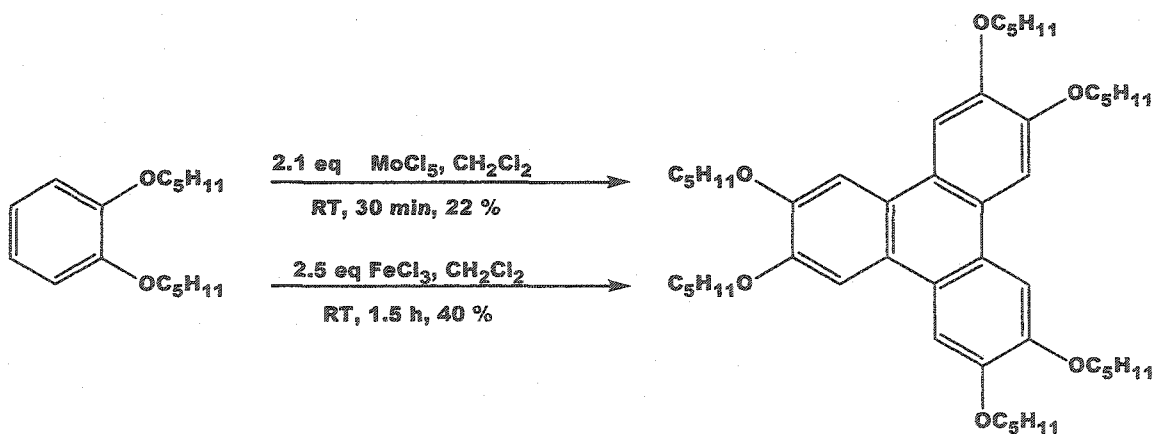
To a 250 mL round bottom flask was added **25** (9.3 g, 34.9 mmol), 1-bromopentane (1.5 eq, 52.3 mmol, 7.9 g), cesium carbonate (1.5 eq, 52.3 mmol, 18.4 g) and DMF (80 mL)

and the mixture was left to stir at room temperature. After 3 days the reaction mixture was dissolved in hexanes and extracted with water to remove DMF. The reaction mixture was filtered and the resulting yellow solution was evaporated in vacuum to remove the solvent. The resulting yellow oily residue was purified by flash chromatography on silica gel using toluene/hexane 1:2 as solvent to yield **26** as colorless oil (9.1 g, 98 %).

TLC (silica; toluene) R_f : 0.6; ^1H NMR: δ (300MHz; CDCl_3) 6.9- 6.7 (4H, m, Ar), 3.9 (2H, t, OCH_2 , J = 3.0 Hz), 1.8 (2H, m), 1.3 (3H, m, CH), 1.6 (4H, m), 1.1 (18H, d, CH_3 , J = 6.0 Hz), 0.9 (3H, septad, J = 6.0 Hz).

4.3.2 Oxidative trimerizations

2,3,6,7,10,11-hexakis-pentyloxy-triphenylene (**15**)

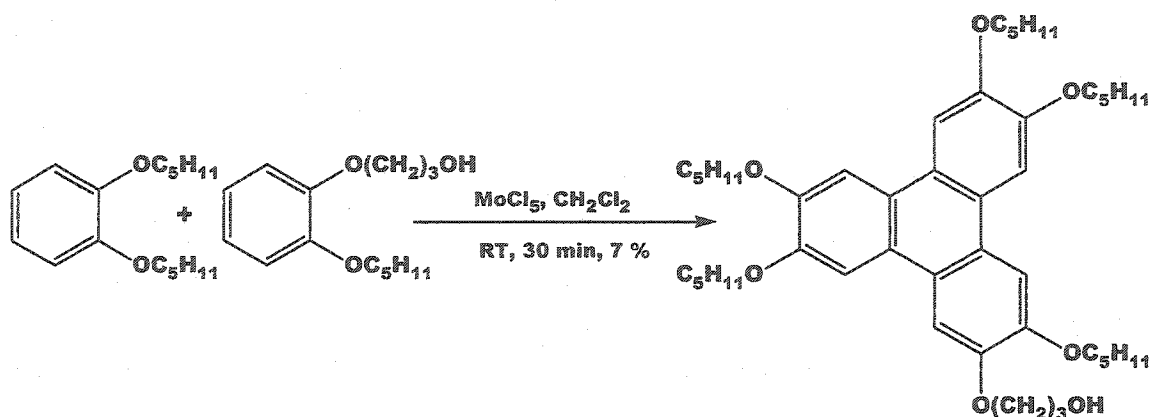


The compound, **10** (800 mg, 3.19 mmol), and dry dichloromethane (20 mL) were added to a 250 mL 3-neck flask and stirred under argon at RT for about 30 min. Then 2.1 eq MoCl_5 (1.5 g) was added while purging argon. After 30 min, the reaction mixture was added to cold MeOH (dried over MgSO_4). Greenish yellow precipitation was observed. The precipitate was filtered and the obtained crude solid was purified by flash chromatography on silica gel using EtAc; the obtained crude solid was recrystallized from methanol to yield **15** as white crystals (0.508 g, 22 %). Using the same procedure

repeated the reaction with 2.5 eq ferric chloride for about 1.5 h at room temperature resulted in 40 % yield.

TLC (silica; toluene) R_f 0.5; ^1H NMR (300 MHz, CDCl_3 , δ): 7.8 (6H, s, Ar), 4.2 (12H, t, OCH_2 , $J=6.0$ Hz), 1.9 (12H, m), 1.5 (24H, m), 0.9 (18H, t, CH_3 $J=6.0$ Hz).

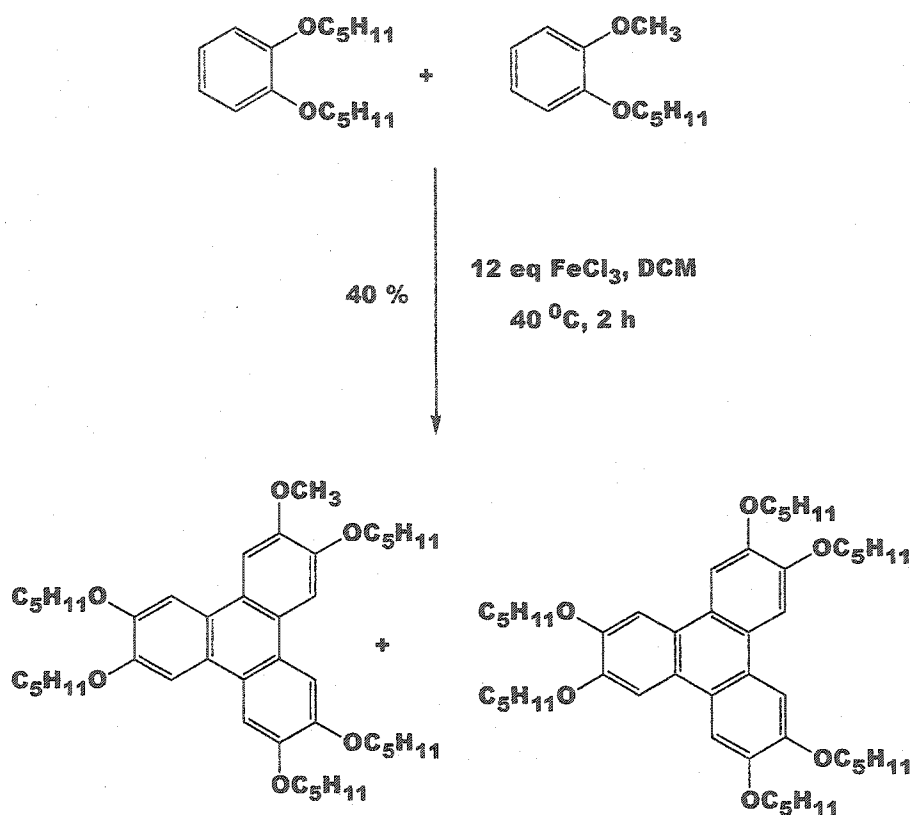
3-(3,6,7,10,11-Pentakis-pentyloxy-triphenylen-2-yloxy)-propan-1-ol (13)



10 (796 mg, 3.17 mmol), 11 (1.5 eq, 602 mg, 2.52 mmol) and dry dichloromethane (30 mL) were added to a 250 mL three-neck flask. Then 12 eq MoCl_5 (1303.2 mg, 4.76 mmol) was added under argon and stirred at RT for 30 min. After 30 min, the reaction mixture was added to cold MeOH (dried over MgSO_4), diluted with H_2O (20 mL) and extracted with DCM (80 mL) using separatory funnel. The organic layer was filtered and the obtained crude solid was recrystallized from hexanes to yield 13 as white crystals (0.160 g, 7 %).

TLC (silica; toluene) R_f 0.4; ^1H -NMR (300 MHz, CDCl_3 , δ): 7.8 (6H, s, Ar), 4.4 (12H, t, OCH_2 , $J=6.0$ Hz), 4.2 (3H, t, CH_2OH , $J=6.0$ Hz) 1.9 (12H, m), 1.5 (20H, m), 0.9 (15H, t, CH_3 , $J=6.0$ Hz).

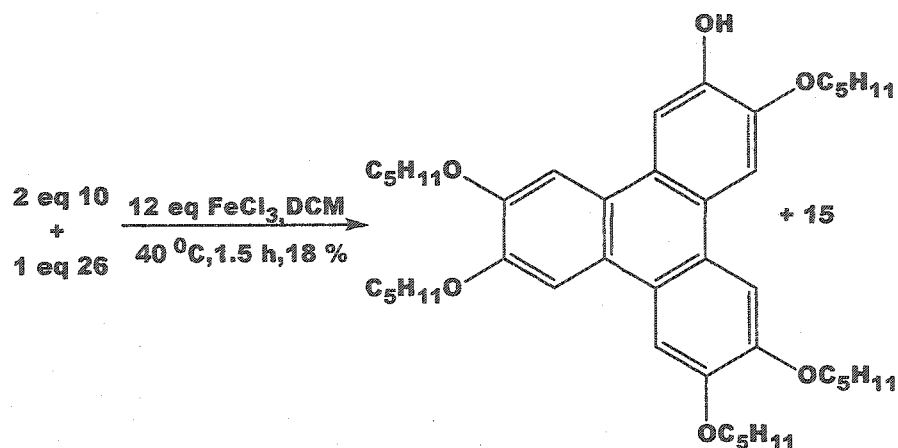
2-Methoxy-3,6,7,10,11-pentakis-pentyloxy-triphenylene (14)



The compounds, **10** (3 g, 15.4 mmol), **12** (2 eq, 7.7 g, 30.8 mmol) and dry dichloromethane (60 mL) were added to a 250 mL 3-neck flask and stirred under argon at 40°C . Then 12 eq ferric chloride (184.8 mmol, 29.9 g) was added. The reaction was run through continuous purging of nitrogen and trapping the liberated HCl using wash bottles for 1.5 h. After 1.5 h, the reaction mixture was added to cold MeOH (dried over MgSO_4). Greenish yellow precipitation was observed. The precipitate was filtered and the obtained crude solid was purified by flash chromatography on silica gel using toluene; the obtained crude solid was recrystallized from methanol to yield **14** as white crystals (1.7g, 40 %). The side product 2,3,6,7,10,11-hexakis-pentyloxy-triphenylene (**15**) in a ratio of 3:1 was observed during the reaction.

TLC (silica; toluene) R_f 0.6; ^1H NMR (300 MHz, CDCl_3 , δ): 7.7 (6H, s, Ar), 4.2 (10H, t, OCH_2 , $J = 6.0$ Hz), 4.1 (3H, s, OCH_3) 1.9 (10H, m), 1.5 (20H, m), 0.9 (15H, t, CH_3 , $J = 6.0$ Hz).

Attempted Triisopropyl- (3,6,7,10,11-pentakis-pentyloxy-triphenylen-2-yloxy)-silane

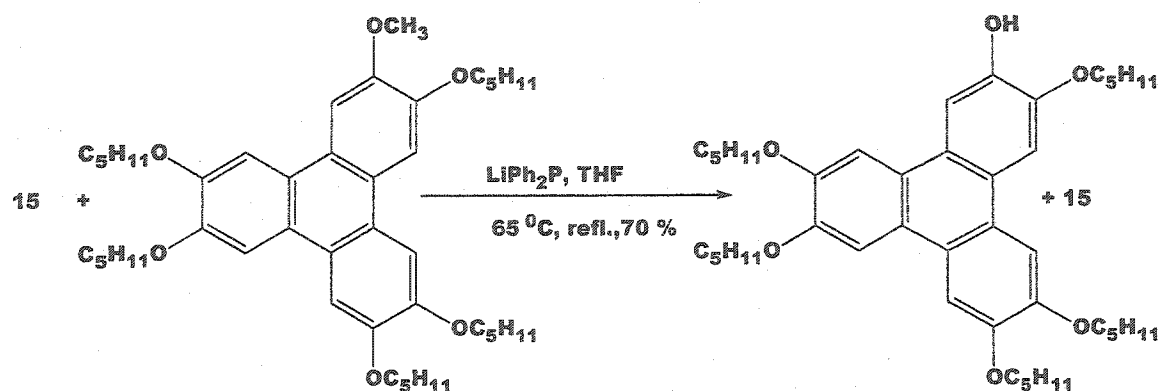


The compounds, 10 (2 eq, 13.6 mmol, 3.4 g), 26 (2.3 g, 6.8 mmol) and dry dichloromethane (50 mL) were added to a 250 mL 3-neck flask and stirred under argon at 40°C . Then 12eq ferric chloride (81.6 mmol, 13.8 g) was added. The reaction was run through continuous purging of nitrogen and trapping the liberated HCl using wash bottles for 1.5 h. After 1.5 h, the reaction mixture was added to cold MeOH (dried over MgSO_4). Greenish yellow precipitation was observed. The precipitate was filtered and the obtained crude solid was purified by flash chromatography on silica gel using toluene to yield Triisopropyl-(3,6,7,10,11-pentakis-pentyloxy-triphenylen-2-yloxy)-silane. According to the ^1H -NMR spectra the TIPS group was completely cleaved off during the reaction. The resultant product mixture included 16 and 15 in a ratio of 3:1 in an overall yield of 18 % (1.0 g).

Note: ^1H NMR spectral information for compound 16 was discussed on page 67.

4.3.3 Reactions with triphenylene derivatives

3, 6, 7, 10, 11-Pentakis-pentyloxy-triphenylene-2-ol (16)

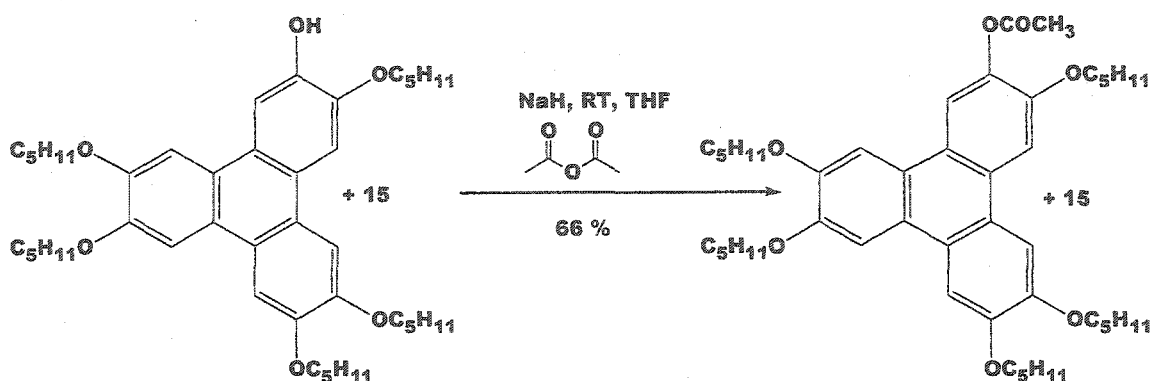


Lithium diphenylphosphine (0.1 M in THF) (1.5 eq, 1.26 mmol, 12.6 mL) was added to **14** (0.582 g, 0.84 mmol) in dry THF and refluxed at 65 °C for 2-3 days. After 3 days diethyl ether and water were added to the reaction mixture, which was extracted with water and then with 0.1M HCl. After evaporation of the ether *in vacuo*, the resulting brown oil was purified by flash chromatography on silica gel using toluene to yield **16** as light yellow oil (0.8 g, 70 %).

Note: Has the side product 2, 3, 6, 7, 10, 11-Hexakis-pentyloxy-triphenylene (**15**) in 2:1 (**16**:**15**) ratio from the previous reaction.

TLC (silica; toluene) R_f : 0.41, 0.5, 0.55 ; ^1H NMR (300 MHz, CDCl_3 , δ): 7.9 – 7.7 (6H, m, Ar), 5.9 (1H, b, OH) 4.3 (10H, t, OCH_2 , $J = 6.0$ Hz), 1.9 (10H, m), 1.5 (20H, m), 0.9 (15H, t, CH_3 , $J = 6.0$ Hz).

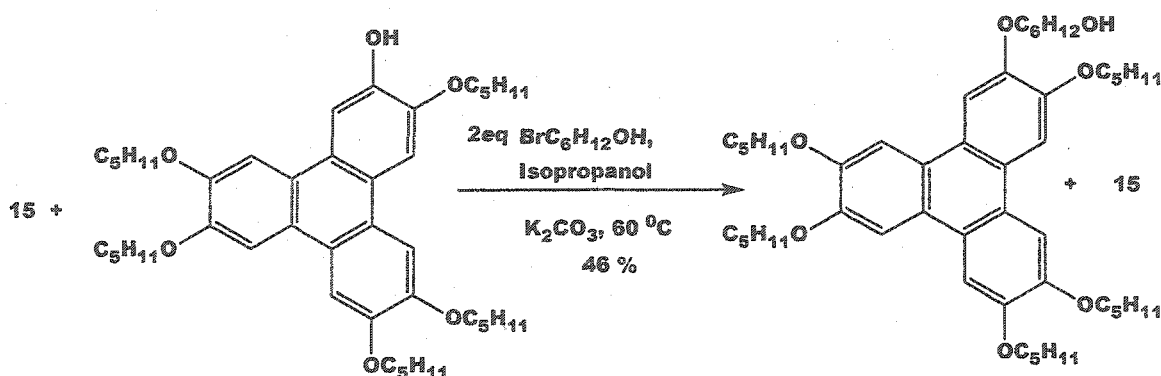
3,6,7,10,11-Pentakis-pentyloxy-triphenylene-2-carboxylic acid methyl ester (20)



THF (25 mL) was added to 16 (0.278 g, 0.412 mmol), and followed by added acetic anhydride (2 eq, 0.824 mmol, 0.084 g). While purging with nitrogen, NaH (2 eq, 0.824 mmol, 19.7 mg) was added and stirring was continued at room temperature. After 24 h *tert*-butanol was added to the reaction mixture and then the mixture was poured on to ice. The suspension was extracted with dichloromethane and washed with water. The solvent was evaporated under vacuum and the resulting yellow oily residue was purified by a pre-packed silica gel column using toluene/hexanes mixtures 3:1 and 2:1 as solvent for side product 2, 3, 6, 7, 10, 11-hexakis-pentyloxy-triphenylene, 15 and toluene to yield 20 as light yellow solid (0.445 g, 66 %).

TLC (silica; toluene) R_f : 0.4; ^1H NMR (300 MHz, CDCl_3 , δ): 7.9 – 7.7 (6H, m, Ar), 4.2 (10H, t, OCH_2 , $J = 6.0$ Hz), 2.3 (3H, s), 1.9 (10H, m), 1.5 (20H, m), 1.0 (15H, t, CH_3 , $J = 6.0$ Hz).

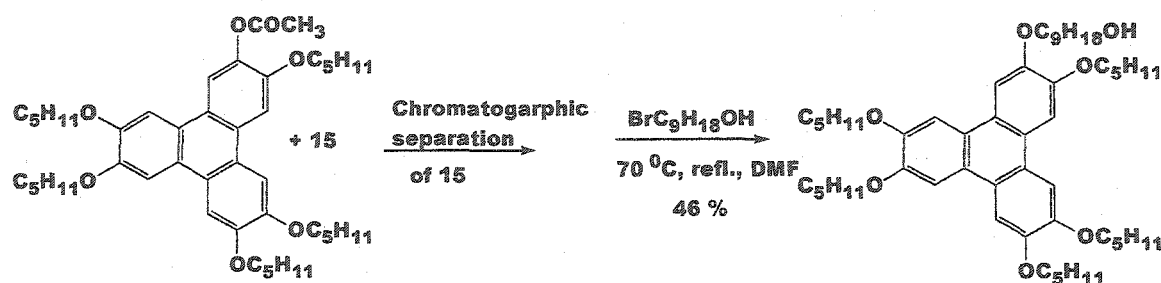
6-(3, 6, 7, 10, 11-Pentakis-pentyloxy-triphenylen-2-yloxy)-hexa-1, 3, 5-triyn-1 (17)



To compound, **16** (0.262 g, 0.388 mmol) in 15 mL dry isopropanol was added 2eq bromohexanol (140 mg, 0.776 mmol) and 2eq potassium carbonate (106 mg, 0.776 mmol). The mixture was refluxed at 60 °C. After three days the reaction mixture was filtered and the resulting brown solution was evaporated under vacuum to remove the solvent. Chromatographic separation of **15** and **17** in a pre-packed silica gel column only yielded **15** as pure product but no **17** was recovered (133 mg, 46 %, before purification).

Note: ^1H NMR spectral information for compound **15** was discussed on page 64.

9-(3,6,7,10,11-Pentakis-pentyloxy-triphenylen-2-yloxy)-nonan-1-ol (18**)**



To a solution of **20** (0.445 g, 0.620 mmol) in 10 mL DMF were added a few drops of MeOH, 1.5 eq 9-bromononanol (207 mg, 0.930 mmol) and 1.5 eq cesium carbonate (328 mg, 0.930 mmol) and the mixture was refluxed at 70 °C. After three days the reaction mixture was filtered and the resulting brown solution was evaporated under vacuum to remove the solvent. Further purification was done by flash chromatography on silica gel using toluene and the obtained crude solid was recrystallized from methanol to yield **18** (233 mg, 46 %).

TLC (silica; toluene) R_f : 0.4; ^1H NMR (300 MHz, CDCl_3 , δ): 7.9 – 7.8 (6H, m, Ar), 4.2 (12H, t, OCH_2 , $J = 6.0$ Hz), 3.8 (3H, t, CH_2OH , $J = 6.0$ Hz), 1.9 (12H, m), 1.5 (32H, m), 0.9 (15H, t, CH_3 , $J = 6.0$ Hz).

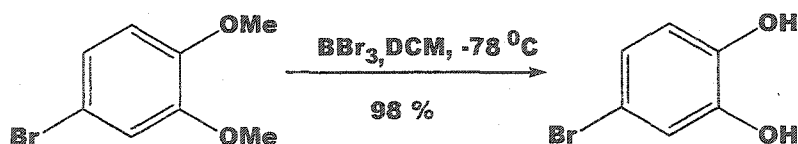
4.4 Approach 2: Synthesis of monofunctionalized triphenylenes via Suzuki cross coupling

4.4.1 Starting materials (dialkoxy benzene bromides and boronic esters)

Synthesis of lithium diphenylphosphine

Chlorodiphenylphosphine (14.4 mL, 17.70 g) was added drop wise to 2.4 g (0.346 atom) lithium wire in 80 mL dry THF and the mixture was stirred and cooled as necessary during the initial exothermic period. After 2 h of vigorous stirring at 25 °C the reaction was complete. The deep red solution obtained can be stored several days under argon without significant deterioration. The excess lithium metal is allowed to remain in the flask and the aliquots of the solution are removed by syringe as needed.

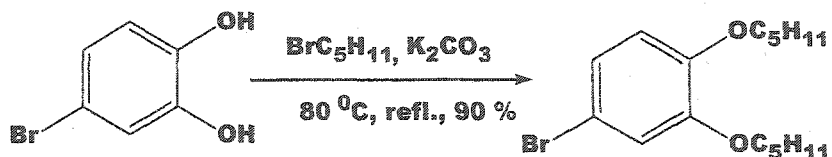
4-Bromo-benzene-1, 2-diol (27)



To a 500 mL round bottom flask was added 4-bromo-1, 2-dimethoxybenzene (20 g, 92.1 mmol) and dry DCM (60 mL) which was stirred at -78°C (dry ice + acetone). To this mixture was added boron tribromide (16 mL, 94 mmol) with the help of a syringe. After 2 days the solvent and rest of the boron tribromide were removed using a vacuum pump; 3 mL HCl + 250 mL H_2O were added at 0°C (ice bath) and the mixture was stirred for 30 min and later at RT until clear solution obtained. The reaction mixture was extracted with diethyl ether and the organic phase was filtered through MgSO_4 ; the reddish solution was evaporated in vacuum to remove the solvent. The resulting brown oily residue was purified by flash chromatography on silica gel using ethyl acetate/hexanes mixture 2:1 as solvent to yield **27** as colorless oil (20 g, 98 %).

^1H NMR (300 MHz, CDCl_3 , δ): 7.0 - 6.7 (3H, m, Ar), 5.0 (2H, b, OH). This data is spectroscopically identical to the literature report.⁵⁷

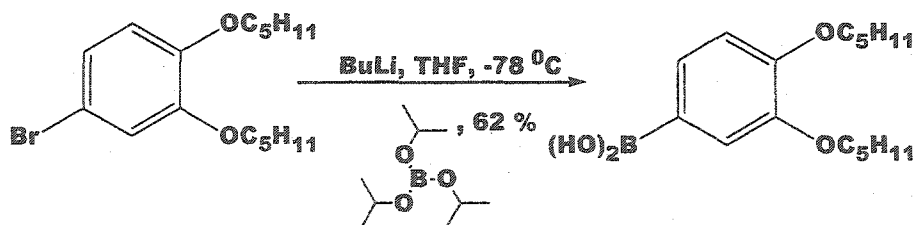
4-Bromo-1, 2-di-pentyloxy-benzene (28)



To a 500 mL round bottom flask added 4-bromo-benzene-1, 2-diol, (20 g, 105 mmol), 1-bromopentane (2.5 eq, 264 mmol, 39.9 g), potassium carbonate (2.5 eq, 264 mmol, 36.4 g) and DMF (150 mL). The mixture was refluxed at 70 °C. After 3 days the reaction mixture was filtered and the brown solution was evaporated under vacuum to remove the solvent. The resulting brown oily residue was purified by flash chromatography on aluminum oxide using hexanes as solvent to yield 28 as colorless oil (31 g, 90 %).

TLC (silica; toluene/hexanes 1:1) R_f : 0.34 small; ^1H NMR (300 MHz, CDCl_3 , δ): 7.0 - 6.7 (3H, m, Ar), 3.9 (4H, t, OCH_2 , $J=6.0$ Hz), 1.8 (4H, m), 1.4 (8H, m), 0.97 (6H, t, CH_3 , $J=6.0$ Hz).

4-Boronic acid-1, 2-bis-pentyloxy-benzene (29)



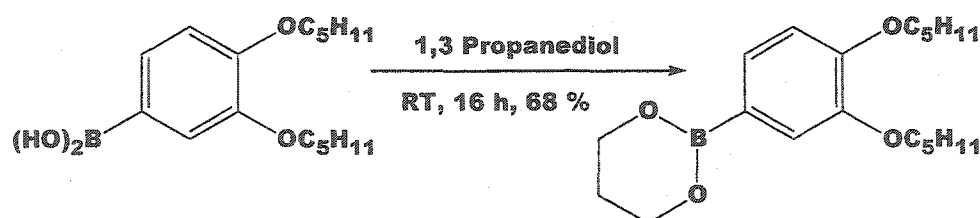
4-Bromo-1,2-dipentyloxybenzene (10 g, 30.3 mmol) was added to a three-neck flask and dried under vacuum overnight. Distilled THF (40 mL) was added to it and stirred. BuLi (19.3 mL, 31 mmol) was added drop wise to a stirred solution of the benzene derivative in THF under argon at -78 °C. Once the addition was completed, the reaction was stirred for further 2.5 h under these conditions. The distilled triisopropyl borate (1.5 eq, 45.4 mmol, 8.5 g, 10.4 mL) solution was added drop wise over approximately 15 min and the reaction was subsequently allowed to warm to room temp overnight. 80 mL of (3M HCl)

was added to the reaction mixture, with cooling in an ice bath and stirring for 2 h. The mixture was extracted with ether thrice, washed with water and filtered the ethereal layer through MgSO_4 . The solvent was removed under vacuum and the obtained pink solid was recrystallized from hexanes to yield **29** as white crystals (5.6 g, 62.8 %).

Note: triisopropyl borate was distilled at 180°C (temp in the thermometer was 145°C)

TLC (silica; EtAc) R_f : 0.6; ^1H NMR (300 MHz, CDCl_3 , δ): 7.8 – 7.0 (3H, m, Ar), 4.5 (2H, broad, OH), 4.0 (4H, t, OCH_2 , $J = 3.0$ Hz), 1.8 (4H, m), 1.4 (8H, m), 0.9 (6H, t, $J = 3.0$ Hz). All spectroscopic data agree with the values reported in literature.⁵⁸

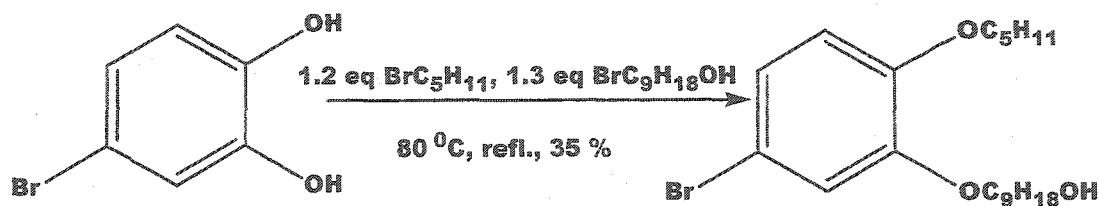
2-(3,4-Bis-pentyloxy-phenyl)-[1, 3, 2] dioxaborinane (**30**)



To a 250 mL round bottom flask was added **29** (8.033 g, 27.3 mmol), 1,3 propanediol (2 eq, 4.1g, 54.6 mmol), and hexanes (60 mL). The mixture was stirred at room temperature for 16 h. The alcohol phase was separated using separatory funnel and the remaining hexanes solution was dried over magnesium sulphate before evaporating under vacuum to remove the solvent. The resulting pale yellow oily residue was purified by fractional distillation at 210°C to yield **30** as colorless oil. (6.5 g, 68 %)

TLC (silica; toluene) R_f : 0.7; ^1H NMR (300 MHz, CDCl_3 , δ): 7.3 – 6.8 (3H, m, Ar), 4.1 (4H, t, OCH_2 , $J = 6.0$ Hz), 4.0 (4H, m, OCH_2), 2.0 (2H, m), 1.8 (4H, m), 1.4 (8H, m), 0.9 (6H, t, CH_3 , $J = 6.0$ Hz).

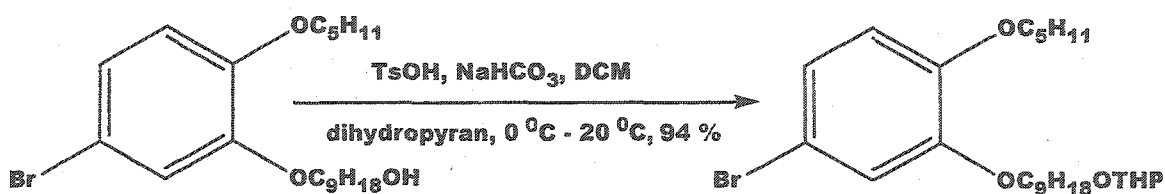
9-(5-bromo-2-pentyloxy-phenoxy)-nonan-1-ol (32)



To a 250 mL round bottom flask was added 4-bromobenzene 1,2-diol (4 g, 21.16 mmol), 1-bromopentane (1.2 eq, 25.3 mmol, 3.8 g), 9-bromononan-1-ol (1.3 eq, 27.5 mmol, 6.1 g), potassium carbonate (2.5 eq, 52.9 mmol, 7.3 g) and ethanol (150 mL) and refluxed at 80 °C. After 3 days filtered the reaction mixture and the resulting brown solution was evaporated in vacuum to remove the solvent. The resulting brown oily residue was purified by flash chromatography on silica gel using toluene as solvent to yield **32** as light yellow oil (2.8 g, 35 %). The side products were separated during the purification on flash chromatography using silica gel and toluene/hexanes 3:2 solvent mixture for 4-bromo-1, 2-di-pentyloxy-benzene, DCM/hexanes 1:1 solvent mixture for 4-bromo-2-pentyloxy-phenol and DCM for 4-bromo-benzene-1, 2-diol.

TLC (silica; toluene/hexanes 1:1) R_f : 0.3; ^1H NMR (300 MHz, CDCl_3 , δ): 6.9 – 6.7 (3H, m, Ar), 3.9 (4H, t, OCH_2 , $J = 6.0$ Hz), 3.6 (3H, t, CH_2OH , $J = 6.0$ Hz), 1.8 (4H, m), 1.3 (16H, m), 0.9 (3H, t, CH_3 , $J = 6.0$ Hz).

2-[9-(5-Bromo-2-pentyloxy-phenoxy)-nonyloxy]-tetrahydro-pyran (34)

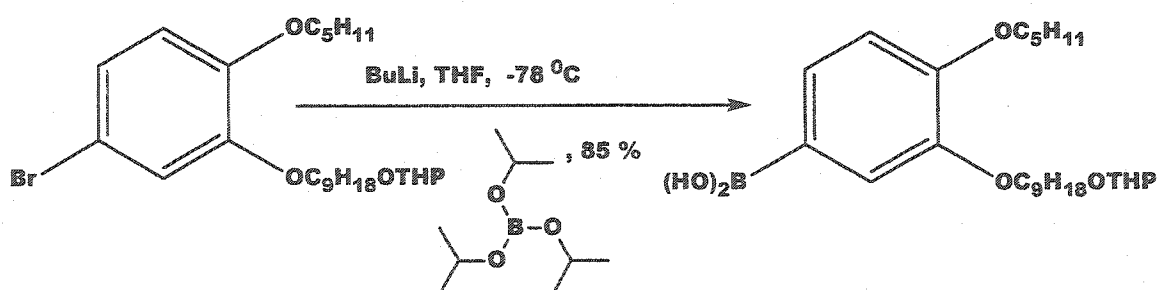


To a stirred solution of 9-(5-bromo-2-pentyloxy-phenoxy)-nonan-1-ol, **32** (2.8 g, 6.97 mmol) in DCM, dihydropyran (1.2 eq, 8.37 mmol, 704 mg) was added drop wise at 0-

5°C. After the solution became clear, TsOH was added. The solution was stirred at 20 °C for 2 h, and then it was quenched with NaHCO₃ and few drops of water. After stirring for 5 min at 20 °C the solvent was removed under vacuum. The resulting yellow oily residue was purified by flash chromatography on silica gel using DCM/DEE 1:1 solvent mixture to yield **34** (3.6 g, 94 %).

TLC (silica; DCM/DEE 1:1) R_f: 0.6; ¹H NMR (300 MHz, CDCl₃, δ): 7.0 – 6.7 (3H, m, Ar), 4.5 (1H, t, CH, *J*= 6.0 Hz), 3.9 (6H, m, OCH₂), 3.7 (2H, m), 3.4 (2H, m, CH₂), 1.8 (6H, m), 1.3 (18H, m), 0.9 (3H, t, *J*= 6.0 Hz).

2-{4-Pentyloxy-3-[9-(tetrahydro-pyran-2-yloxy)-nonyloxy]-phenyl-1,phenylboronic acid (35)

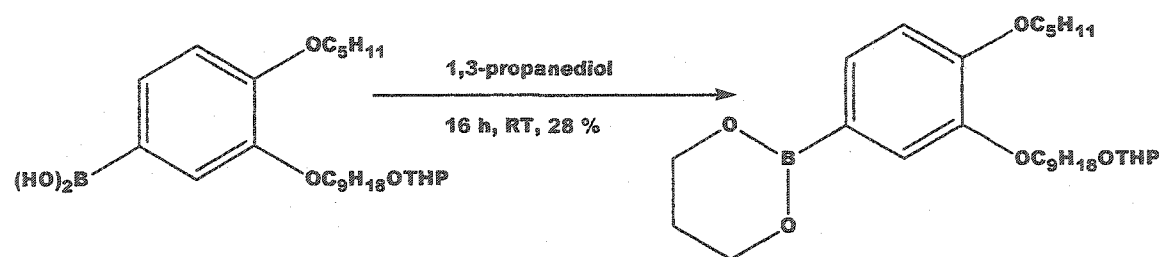


The compound, **34** (3.6 g, 7.42 mmol) was added to a three-neck flask and dried under vacuum overnight. Distilled THF (20 mL) was added to it and stirred. BuLi (1.2 eq, 5.56 mL, 8.89 mmol) was added drop wise to a stirred solution of the benzene derivative in THF under argon at -78 °C. Once the addition was completed, the reaction was stirred for further 2.5 h under these conditions. The distilled triisopropyl borate (1.5 eq, 11.2 mmol, 2.09 g, 2.45 mL) solution was added drop wise over approximately 15 min and the reaction was subsequently allowed to warm to room temp overnight. 50 mL of (3M HCl) was added to the reaction mixture, with cooling in an ice bath and stirring for 2 h. The mixture was extracted with ether thrice, washed with water and filtered the ethereal layer through MgSO₄. The solvent was removed under vacuum to yield **35** as pink solid (2.9 g,

85 %). The obtained solid was recrystallized from hexanes. Crystals were not observed even after 3-4 days.

^1H NMR (300 MHz, CDCl_3 , δ): 6.9 (1H, d, $J = 3.0$ Hz), 6.8 (1H, s), 6.7 (1H, d, $J = 6.0$ Hz), 5.3 (2H, b, OH), 4.5 (1H, t, CH, $J = 6.0$ Hz), 3.9 (6H, m, OCH_2), 3.7 (2H, m), 3.4 (2H, m, CH_2), 1.8 (6H, m), 1.3 (18H, m), 0.9 (3H, t, CH_3 , $J = 6.0$ Hz).

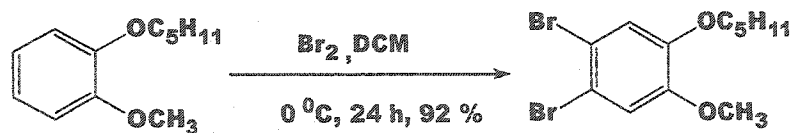
2-{4-Pentyloxy-3-[9-(tetrahydro-pyran-2-yloxy)-nonyloxy]-phenyl}-[1,3,2]dioxaborinane (36)



To a 250 mL round bottom flask was added **35** (2.97 g, 6.59 mmol), 1,3 propanediol (2 eq, 1 g, 13.1 mmol), and hexanes (50 mL). The mixture was stirred at room temp for 16 h. The alcohol phase was separated using separatory funnel and the remaining hexanes solution was dried over magnesium sulphate before evaporating under vacuum to remove the solvent. The resulting orange oily residue was purified by flash chromatography on a pre-packed silica gel column using DEE/hexanes 1:2 as solvent to yield **36** as light yellow oil. (0.94 g, 28 %)

TLC (silica; toluene) R_f 0.5; ^1H NMR (300 MHz, CDCl_3 , δ): 6.9 – 6.7 (3H, m, Ar), 4.5 (1H, t, CH, $J = 6.0$ Hz), 4.0 (4H, m, OCH_2), 3.9 (6H, m), 3.7 (2H, m), 3.4 (2H, m, CH_2), 2.0 (2H, t, $J = 6.0$ Hz), 1.8 (6H, m), 1.3 (18H, m), 0.9 (3H, t, CH_3 , $J = 6.0$ Hz).

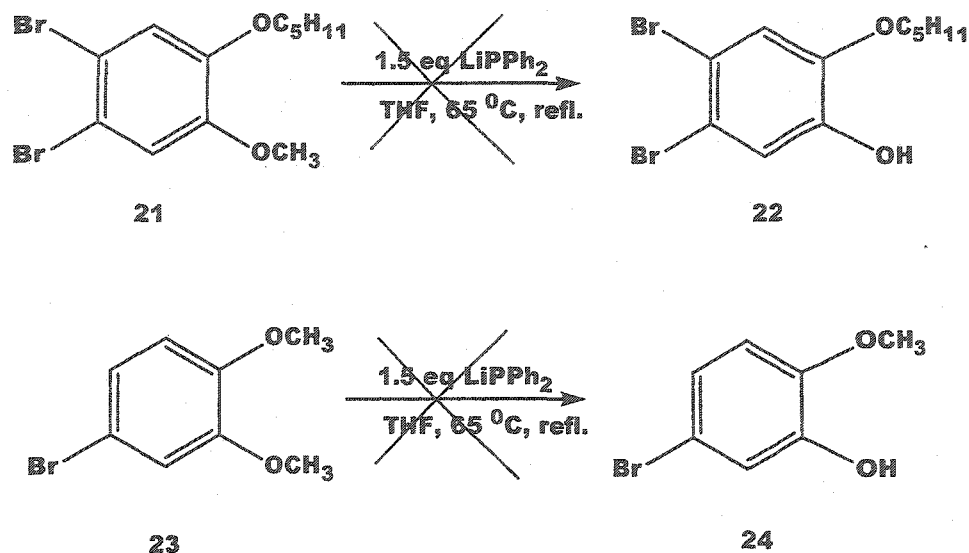
1, 2-Dibromo-4-methoxy-5-pentyloxy-benzene (21)



1-Methoxy-2-pentyloxy-benzene (41 g, 213 mmol) was dissolved in DCM and stirred at 0°C (ice bath + NaCl salt). To this was added Br₂ (2.1 eq, 447 mmol, 71.4 g, 23 mL) through a dropping funnel, purging with nitrogen and trapping HBr using wash bottles. The reaction system was left to warm up to room temp, gradually, to complete the reaction. The reaction was conducted for about 24 h. The reaction mixture was washed subsequently with 10 % aqueous Na₂CO₃ many times and then with water. The solution then was evaporated under vacuum to remove the solvent and the obtained dark yellow solid was recrystallized from methanol to yield **21** as pale yellow crystals (73 g, 92 %).

¹H NMR (300 MHz, CDCl₃, δ): 6.9 (2H, s, Ar), 3.9 (2H, t, OCH₂, *J*= 6.0 Hz), 3.8 (3H, s, OCH₃), 1.8 (2H, m), 1.4 (4H, m), 0.9 (3H, t, *J*= 6.0 Hz).

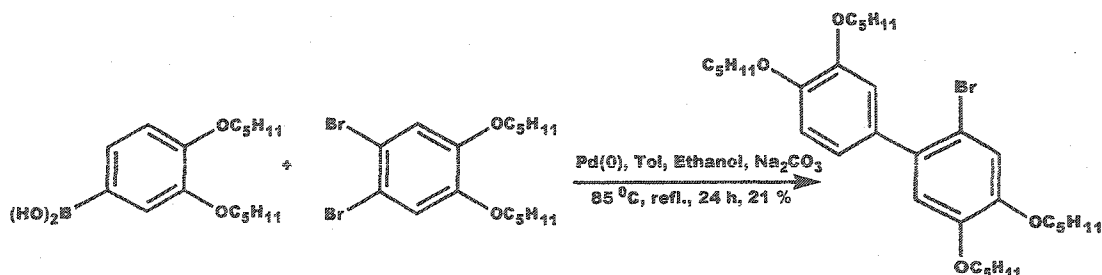
Attempted methoxy cleavage of (21) and (23) to 4,5-dibromo-2-pentyloxy-phenol (22) and 5-bromo-2-methoxy-phenol (24)



Lithium diphenylphosphine (0.1 M in THF) (1.5 eq, 14.4 mmol, 28 mL) was added to 21/23 (5 g, 14.2 mmol) in dry THF and refluxed at 65 °C for 2-3 days. After 3 days DCM and water were added to the reaction mixture at 0 °C, which was extracted with water and then with 0.1M HCl. After evaporation of the solvent in vacuum, the resulting brown oil was purified by flash chromatography on silica gel using toluene to yield 22/24. ¹H-NMR spectra confirmed the presence of starting material.

4.4.2 Synthesis of biphenyls and terphenyls

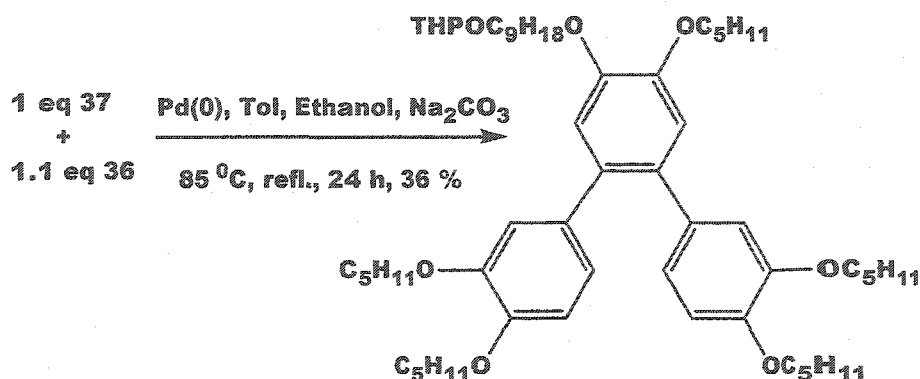
1-Bromo- 3,4,3',4'-tetrakis-pentyloxy-biphenyl (37)



Into a 250 mL two neck round bottom flask was added **31** (7.7 g, 19 mmol), toluene (10 mL), 2M Na₂CO₃ (5 mL) and 95 % ethanol (5 mL). The flask was attached to a reflux condenser and an argon balloon on the top of reflux condenser and the contents degassed under argon (pump and freeze method). The catalyst tetrakis (triphenylphosphine) palladium (0), (0.51 mmol, and 0.5 g) was then added under argon. The solution of the boronic acid, **29** (1 eq, 5.6 g) was added to the bromo derivative and the mixture refluxed for 24 h. 0.5mL of 30 % H₂O₂ was added to the stirred solution at room temp. After 30 min, 20 mL of toluene was added. The separated brown toluene phase was filtered, washed with saturated aqueous NaCl and water before drying over MgSO₄ and evaporation. The resulting light yellow oil was purified by flash chromatography on silica gel using toluene/hexanes mixtures 1:4 as solvent to yield **37** as light yellow oil (2.3 g, 21 %).

¹H NMR (300 MHz, CDCl₃, δ): 6.95 – 6.85 (5H, m, Ar), 4.0 (8H, m, OCH₂), 1.8 (8H, m), 1.4 (16H, m), 0.9 (12H, m, CH₃).

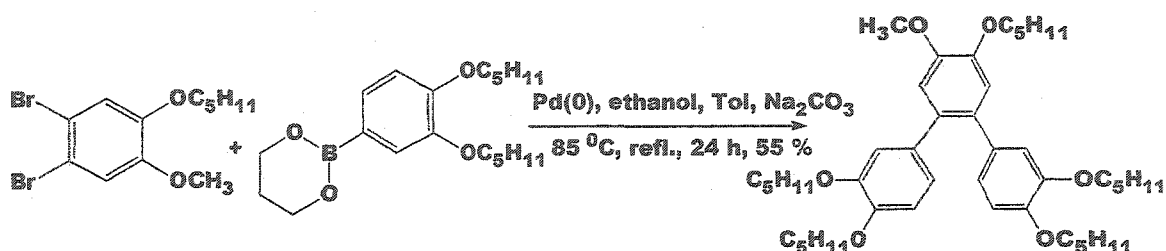
Attempted 2-[9-(3,4,5',3'',4''-Pentakis-pentyloxy-[1,1',2',1'']terphenyl-4'-yloxy)-nonyloxy]-tetrahydro-pyran (38)



Into a 250 mL two neck round bottom flask was added 37 (1.1g, 1.97 mmol), toluene (5 mL), 2M Na₂CO₃ (2 mL) and 95 % ethanol (2 mL). The flask was attached to a reflux condenser and an argon balloon on the top of reflux condenser and the contents degassed under argon (pump and freeze method). The catalyst tetrakis (triphenylphosphine) palladium (0), (0.027 eq, 0.045 g) was then added under argon. The solution of the boronic ester, 36 (1.1eq, 1.2 g, 216 mmol) was added to the bromo derivative and the mixture refluxed for 24 h. 0.5mL of 30 % H₂O₂ was added to the stirred solution at room temp. After 30 min, 20 mL of toluene was added. The separated brown toluene phase was filtered, washed with saturated aqueous NaCl and water before drying over MgSO₄ and evaporation. The resulting yellowish oil was purified by flash chromatography on silica gel using toluene as solvent to yield 38 as light yellow oil (0.635, 36 %). The side product biphenyl was separated during flash chromatography on silica gel using toluene/hexanes 1:4 as solvent mixtures. According to ¹H-NMR spectral analysis, the THP group was cleaved off.

¹H NMR (300 MHz, CDCl₃, δ): 7.1- 6.7 (8H, m, Ar), 4.2 (12H, t, OCH₂, J= 6.0 Hz), 3.8 (3H, t, CH₂OH, J= 6.0 Hz), 1.9 (12H, m), 1.5 (32H, m), 0.9 (15H, t, CH₃, J= 6.0 Hz).

5'-Methoxy-3,4,4',3'',4''-pentakis-pentyloxy-[1,1',2',1''] terphenyl (39)



Into a 250 mL two neck round bottom flask was added 1, 2-dibromo-4-methoxy-5-pentyloxy-benzene, **21** (200 mg, 0.568 mmol), toluene (10 mL), 2M Na₂CO₃ (5 mL) and 95 % ethanol (5 mL). The flask was attached to a reflux condenser and an argon balloon on the top of reflux condenser and the contents degassed under argon (pump and freeze method). The catalyst tetrakis (triphenylphosphine) palladium (0), (3 mol %, and 50 mg) was then added under argon. The solution of the boronic ester, **30** (2.2 eq, 1.24 mmol, 437 mg) was added to the bromo derivative and the mixture refluxed for 24 h. 0.5mL of 30 % H₂O₂ was added to the stirred solution at room temp. After 30 min, 20 mL of toluene was added. The separated brown toluene phase was filtered, washed with saturated aqueous NaCl and water before drying over MgSO₄ and evaporation. The resulting light yellow oil was purified by flash chromatography on silica gel using toluene/hexanes mixtures 1:4 as solvent to yield **39** and side product biphenyl as light yellow oil (133 mg, 35 %, before purification).

TLC (silica; toluene) R_f: 0.55;

1,2-dibromo-4-methoxy-5-pentyloxy-benzene, **21** (500 mg, 1.4202 mmol) was added to a mixture of ethylene glycol-1, 2-dimethyl ether and water. Argon was bubbled through the suspension for 15 min before catalyst Pd(PPh₃)₄ (3 mol %) was added. The boronic ester, **30** (2.2 eq, 2.982 mmol, 1.044 g) was added carefully under a stream of argon and stirring was continued for 10 min. Finally barium hydroxide. H₂O (2.1 eq, 2.9 mmol, 549 mg) was added. The mixture was heated to 80 °C, reflux and stirred under argon until TLC (toluene) indicated the completion of the reaction. After two days cool water was added to the reaction mixture and extracted with DCM; the organic phase was separated,

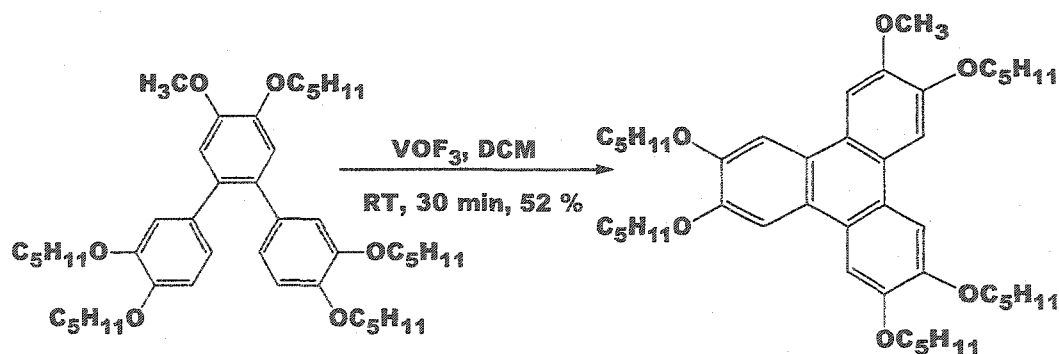
dried over magnesium sulphate and evaporated. The resulting yellow oil was purified by silica plate using toluene. The eluant was collected in 24 sample tubes.

According to TLC the fractions 1 to 26 showed three spots at R_f values 0.25, 0.4 and 0.5 (mixture of product + side product biphenyl) and fractions 27 and 28 showed only one spot at R_f value of 0.25. Fractions 27 and 28 were added and the solvent was evaporated, resulting in yellow oil. Fractions 1 to 26 were added; the solvent was removed observing dark yellow oil. Recrystallization from methanol yielded **39** as white crystals. (530 mg, 55%)

TLC (silica; toluene) R_f : 0.55; ^1H NMR (300 MHz, CDCl_3 , δ): 6.9 (2H, s, Ar), 6.7 (4H, m, Ar), 6.6 (2H, m, Ar), 4.1 (2H, t, OCH_2 , $J = 6.0$ Hz), 4.0 (4H, d, OCH_2 , $J = 6.0$ Hz), 3.9 (3H, s, OCH_3), 3.7 (4H, t, $J = 6.0$ Hz) 1.9 (10H, m), 1.5 (20H, m), 0.9 (15H, t, CH_3 , $J = 6.0$ Hz).

4.4.3 Oxidative ring closure

2-Methoxy-3,6,7,10,11-pentakis-pentyloxy-triphenylene (14)



To a stirred solution of terphenyl, **39** (0.133 mg, 0.1926 mmol) and 0.27 mL BF_3 etherate in 60 mL anhydrous DCM was added (VOF_3) (2.2 eq, 0.423 mmol, 52 mg) under N_2 . This mixture was stirred at RT for 30 min, and then poured into 200 mL 10 % citric acid solution. The organic layer was separated and the aqueous layer was extracted with

DCM. The combined organic fractions were washed with water, dried over magnesium sulphate and the solvent was removed. The obtained yellow oil was recrystallized using EtAc/MeOH to yield 14 as white crystals (69 mg, 52 %).

TLC (silica; toluene) R_f 0.3; ^1H NMR (300 MHz, CDCl_3 , δ): 7.7 (6H, s, Ar), 4.2 (10H, t, OCH_2 , $J = 6.0$ Hz), 4.1 (3H, s, OCH_3) 1.9 (10H, m), 1.5 (20H, m), 0.9 (15H, t, CH_3 , $J = 6.0$ Hz).

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Vita Auctoris

Name: Anupama Adavelli

Place of birth: Andhra Pradesh, India.

Date of birth: May 25, 1978

Education: Stanley Jr. College
Hyderabad, India.
April 1995, High school diploma.

Kakatiya University
Warangal, India
April 1998, B.S.c

University Of Windsor
Windsor, ON, Canada
December 2003, M.Sc Chemistry

Publications and conference presentations:

S.H. Eichhorn, A. Adavelli, H. Li and N. Fox "Alignment of discotic liquid crystals, molecular crystals and liquid crystals", published in proceedings of the 19th International Liquid Crystal Conference, Edinburgh, UK, July 2002.

S.H. Eichhorn and A. Adavelli, "Synthesis of star-shaped hetero heptamers: New building blocks for organic electronic devices" presented at the 85th CSC conference, Vancouver, 2002.

S.H. Eichhorn and A. Adavelli, "Star-Shaped Heptamers of Discotic Liquid Crystals", presented at the 39th IUPAC Congress and 86th Conference of The Canadian Society of Chemistry, Ottawa, Aug 2003.