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Design and Synthesis of Novel Discotic Liquid Crystals

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By

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Abstract

Columnar mesophases of discotic liquid crystals (DLCs) have attracted much attention as organic semiconductors and have been tested as active materials in light-emitting diodes, photovoltaic solar cells, and field-effect transistors. However, devices based on DLCs have shown lower performance than devices based on polymeric and small molecule glass semiconductors, despite their superior charge conducting and advantages self-organizing properties. Most DLCs also require relatively complex processing conditions for the preparation of electronic devices, which is another significant disadvantage. Consequently, new types of DLCs are sought-after to overcome these limitations and described in this thesis are new types of discotic materials and their synthesis.

Chapters 2 and 3 describe star-shaped discotic molecules for donor-acceptor columnar structures and as novel flexible core discotic molecules. Presented are the first examples of star-shaped heptamers of donor and acceptor discotic molecules which have six hexaalkoxy triphenylene ligands and a hexaazatriphenylene hexacarboxylate core or a hexaazatriphenylene hexaamide core. The hexaazatriphenylene cores were chosen because of their electron deficient character while the hexaalkoxy triphenylenes are known to be electron rich. Envisioned is the formation of super-columns in which the heptamers stack on top of each other and generate a material with electron acceptor and electron donor channels separated by aliphatic chains. This is an important difference to previously reported donor-acceptor star-shaped structures that were connected *via* conjugated linkers and do not form separate columnar stacks.

Star-shaped DLCs based on small aromatic groups linked together by short flexible spacers may represent a novel type of discotic core structure that does not require peripheral flexible chains. Softening of the core by the spacer group is expected to sufficiently lower melting points and not interfere with the columnar stacking as long as a disc-shaped structure can be adopted. Presented here

are synthetic approaches towards novel hexa(thiophen-2-yl)alkyl)benzene derivatives as star-shaped hetero-heptamer discotic cores.

New ionic and polymerizable discotic liquid crystals based on the commercial dye tetraazaporphyrin are presented in Chapters 4 and 5. Both areas have been given little attention despite their importance for the preparation of stable films for devices. Tetraazaporphyrins containing azide and acetylene groups at the end of aliphatic spacers have been prepared and cross-linked by cycloaddition (click chemistry). Some derivatives form columnar mesophases and could be thermally cross-linked in their columnar mesophase and their copper catalyzed cross-linking in Langmuir and Langmuir-Blodgett layers was also successful.

Dedication

To

My father

Subodh Gopal Kayal

Acknowledgements

I feel overjoyed to acknowledge all the people who have been explicitly and implicitly involved in my life during my PhD.

First and foremost, I would like to express my gratitude to Dr. Holger Eichhorn for being such a great Guide. Dr Holger is a wealth of knowledge. He always encouraged and inspired me with his intensive research capability. Dr Holger has contributed immensely in fostering my scientific point of view and enriching my research orientation. His constant direction has been significantly influential during my entire term of PhD. As an individual, he is a role model.

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It is with immense contentment I thank my family for being a pillar of support and leading me on the path of higher education in the field of Chemistry. It was my father's wish that I should go for the doctoral degree in Chemistry and I am extremely joyful to fulfill his dream. This is one of the initial stepping stone in achieving the ideals my father had in mind for me. I run out of words while expressing gratitude to my dear mother Mrs Dasabhuja Kayal who is in Kolkata, India who has been praying every moment for my wellbeing and success. I would not have been the same person that I am today without

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Last but not the least, I acknowledge the loving support of my wife Deepti, whom I met, courted and married during the strenuous PhD years. She was nice enough to keep up with my erratic time schedules and patiently waited for me till I reached home every day.

On a final note, I thank God for being such a positive influence throughout my life including my PhD years. In retrospect, I think of all the days of hard work that culminated this degree and end this note with a peaceful and content prayer.

Table of Contents

List of Figures

List of Schemes

List of Tables

List of Abbreviations

^{13}CNMR - carbon 13 nuclear magnetic resonance magnetic resonance

^{1}HNMR - proton nuclear magnetic resonance magnetic resonance

Ar - aromatic

br - broad

BOC - tert-Butyloxycarbonyl

BuLi - butyllithium

$CDCl_3$ - chloroform-d

$CHCl_3$ - chloroform

Col - columnar phase

Col_h - hexagonal columnar phase

Col_{hd} – hexagonal disordered columnar phase

Col_{ho} – hexagonal ordered columnar phase

Col_l – lamellar columnar phase

Col_{ob} – oblique columnar phase

Col_p - plastic columnar phase

Col_r - rectangular columnar phase

Col_{tet} - tetragonal columnar phase

CuAAC - copper catalyzed azide-alkyne 1, 3-dipolar cycloaddition

°C - degrees of Celsius

d - doublet

δ - chemical shift in ppm

dd - doublet of doublet

DCM - dichloromethane

DIAD - diisopropyl azo dicarboxylate

DLCs - discotic liquid crystal

DMF - dimethyl formamide

DMSO - dimethyl sulfoxide

DPPA - diphenyl phosphoryl azide

DSC - differential scanning calorimetry

eqiv. - equivalent

FET - field effect transistor

HAT - hexaazatriphenylene

HMPA - hexamethylphosphoramide

HPLC - high performance liquid chromatography

hrs - hours

iDLC - ionic discotic liquid crystal

IR - infrared spectroscopy

L - Langmuir

LB - Langmuir Blodgett

LCs - liquid crystals

LCD - liquid crystal display

LED - light emitting diode

m - multiplet

mol.sieve - molecular sieve

N* - chiral nematic

NMR - nuclear magnetic resonance

OLED - organic light emitting diode

p – pentate

Pcs - phthalocyanines

piDLC - polyionic discotic liquid crystal

POM - polarizing optical microscopy

PPh_3 - triphenylphosphine

ppm - parts per million

q - quartet

refl. - reflux

rt- room temperature

SAM - self assembled monolayer

t-BOC - tertbutoxycarbonyl

TAPs - tetraazaporphyrins

Temp - temperature

TFA - trifluoroacetic acid

TFAA - trifluoroacetic acetate

THF - tetrahydrofuran

TLC - thin layer chromatography

TMSA - trimethylsilylacetylene

TP - triphenylene

tt - triplet of triplets

XRD - x-ray diffraction

1 Chapter 1: Introduction

1.1 What is a liquid crystal?

Liquid crystals (LCs) are materials that have both order and mobility on a molecular, supramolecular level as well as macroscopic level. They are best known as active components in liquid crystal displays (LCDs) but many other commercial applications exist. LCs form phases that are intermediate between crystalline phases and the isotropic liquid phase, which is why they belong to a class of materials called mesophases (Fig. 1.1). In conventional crystals all molecules are arranged in a defined pattern that has long-range three dimensional orientational and positional orders. In contrast, isotropic liquids have no long-range positional and orientational order. Liquid crystals have at least long-range orientational order in one dimension and do not have 3-dimensional long-range positional order. Consequently, the least ordered LC phase has no long-range positional but long-range orientational order in one dimension (nematic phase), while the most ordered LC phases have 2-dimensional long-range positional and orientational order. Phases that have 3-dimensional positional order but remain less ordered than crystalline phases, such as plastic crystal phases and lamellar (or smectic) crystal phases, are also categorized as mesophases but not as liquid crystal phases.[1-12]

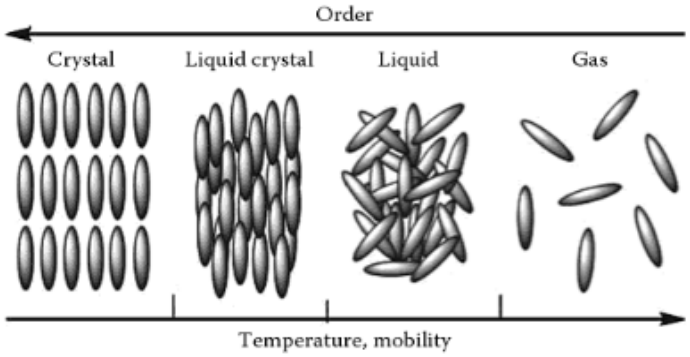

Figure 1-1: Different states of matter and molecular ordering.[6]

1.2 Classification of Liquid Crystals

Because of their orientational order many liquid crystal phases show anisotropic properties, similar to many crystal phases, but flow like liquids that usually have isotropic properties. Since their first discovery in 1888, many different LC phases have been described and can be separated into two main groups, thermotropic and lyotropic LCs (Figure 1.2).

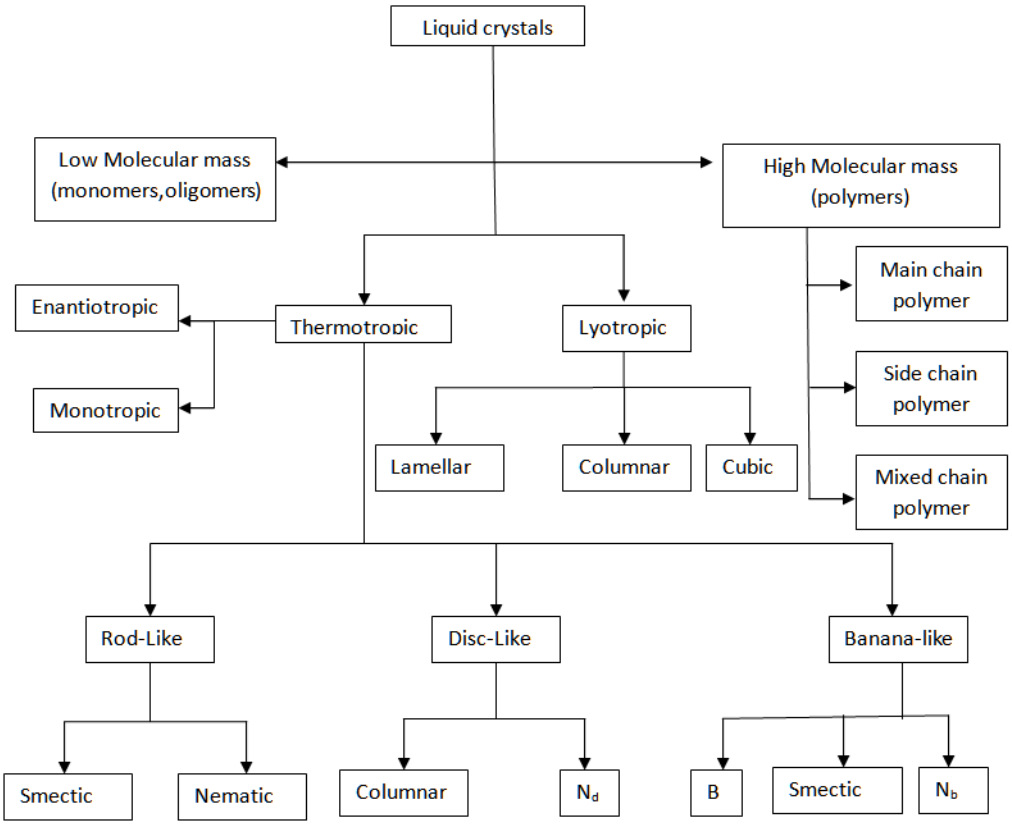

Figure 1-2: General classification of the different liquid crystalline phases.[6]

Thermotropic LCs may be pure or mixtures of compounds that form LC phases at specific temperatures and in the absence of any solvents. Lyotropic LCs are mixtures of at least one solute and one solvent that display LC phases depending on concentration and temperature. Thermotropic LCs are further subcategorized based on their molecular shape (calamitic or rod-like, discotic or disc-like, and bent-core or banana-like) and the supramolecular structure of their mesophases (nematic, smectic or

lamellar, columnar, and cubic). Hundreds of books and review articles have been published on LCs and the interested reader is referred to them for more details on synthesis, properties, and applications of mesophases not covered here.[1-10] The intention of the remaining parts of this introductory chapter is to provide the reader with a brief introduction into molecular design, mesomorphism, characterization, and electronic properties of discotic liquid crystals (DLCs). Synthesis and mesomorphism of the three classes of discotic compounds this thesis contributes to, discotic tetraazaporphyrins (TAPs), discotic star-shaped oligomers, and ionic DLCs, will be introduced at the beginning of their respective chapters.

1.3 Discotic Liquid crystals

Indian scientist Sivaramakrishna Chandrasekhar and co-workers at the Raman Research Institute, India were first to report disc-like compounds (discotic) as LCs in 1977.[13] They synthesized a number of benzene hexa-n-alkanoate derivatives and confirmed their LC properties employing optical, thermodynamic and X-ray studies. Chandrasekhar published... "….what is probably the first observation of thermotropic mesomorphism in pure, single component system of relatively simple plate like or more appropriately disk-like molecules" (Figure 1.3).[13]

The spontaneous self-organization behavior of disk-like (discotic) molecules opened up an entirely new class of LCs where molecules stack like plates to form 1-dimensional columns which are further self-organized into various two dimensional arrays. The third dimension remains void of any translational order. Generally, one can classify discotic mesophases into four major classes: Nematic, [14] smectic, [15] cubic [16] and columnar phases of which columnar mesophases are the by far most common discotic phases.[15, 17-20] A few examples of nematic discotic mesophases exist while very few smectic and cubic discotic phases have been reported. A DLC usually displays only one of the aforementioned four types of discotic mesophases and very few DLCs are known that show two of these mesophases (e.g. hexaalkanoates and benzoates of truxene form columnar and nematic phases). [18, 20, 21, 34, 36]

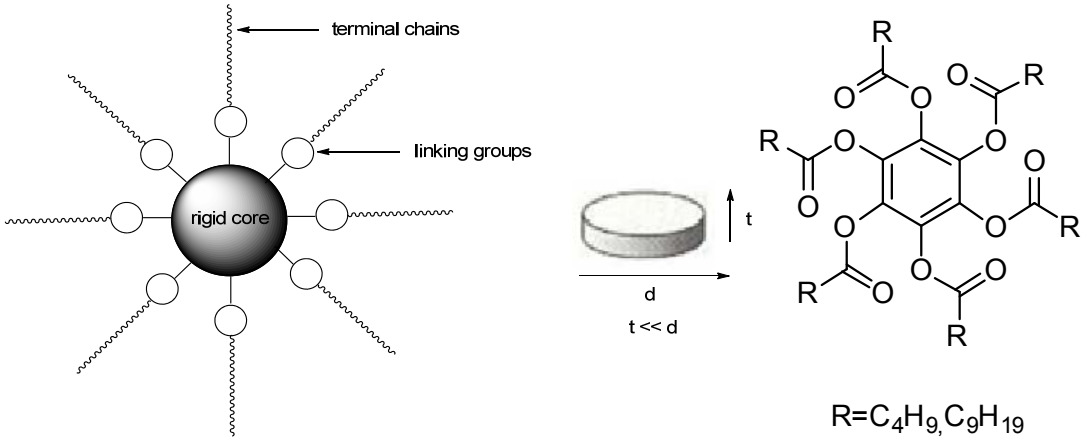

Figure 1-3: General design of DLCs and first discotic liquid crystalline molecules reported by Chandrashekar.

No single DLC has been reported to display more than two of these mesophases. However, DLCs that display more than one type of columnar mesophase are more common (columnar polymesomorphism).

1.4 Structure of Discotic Mesophases

A typical DLC has a central discotic core (usually aromatic) that is peripherally substituted by at least 3 flexible chains and the overall molecule often has two-, three-, four- and six-fold rotational symmetry. DLCs with lower symmetry and with non-aromatic cores have also been reported but are not common mainly because the synthetic approaches to these molecules are often more complex (Fig. 1.4).

The π-π stacking interactions between discotic cores often defines the weakly attractive stacking forces in columnar mesophases, although linking groups may play an important role if they engage in dipole-dipole interactions (e.g. carbonyl groups) or H-bonding (e.g. amide groups). The surrounding side-chains have two functions: they lower melting points and increase fluidity and they induce microphase segregation between cores and side-chains, which significantly promotes columnar stacking.

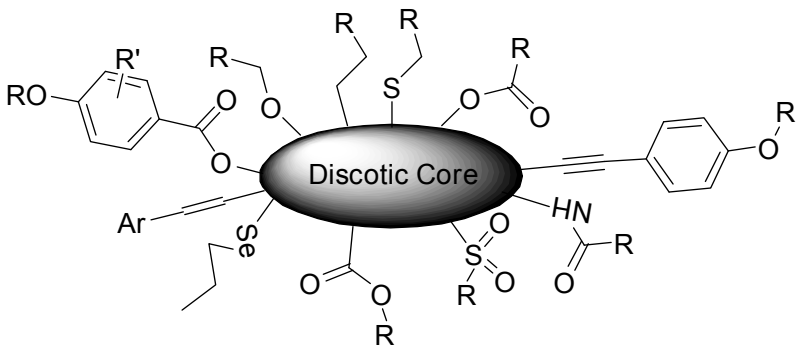

Figure 1-4: Typical linking groups between discotic core and flexible side-chains of discotic molecules.

Linking groups influence the properties of side-chains because they define the geometry and flexibility of their attachment but are usually considered to be a part of the core interactions.

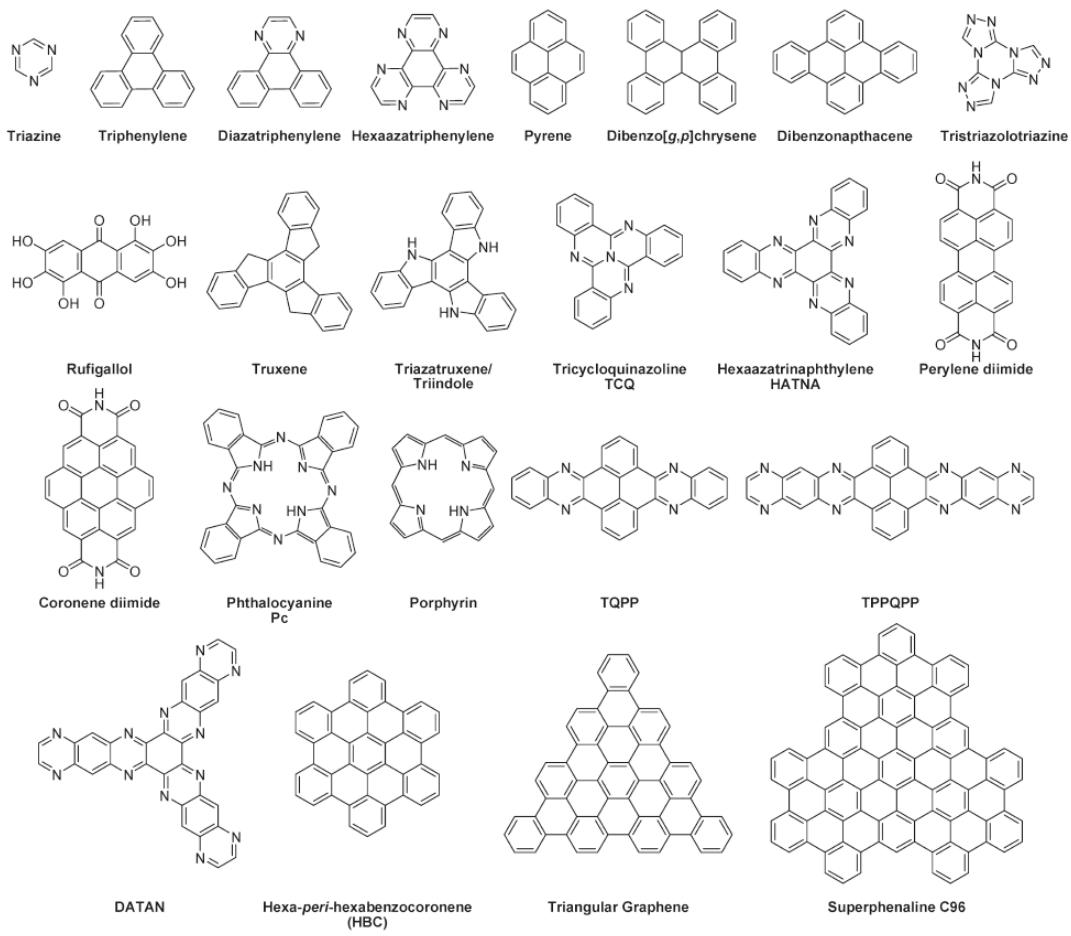

Figure 1-5: Examples of different central cores of known discotic liquid crystals.[19]

A large number of discotic cores (Figure. 1.5) and linking groups have been reported while side-chains are mainly limited to aliphatic chains (linear and branched) and polyethers. Some examples with fluorinated side-chains[22] have been reported and some side-chains have been functionalized, usually terminally, with groups such as OH, CN, and vinyl. [23-30]

1.5 Structures of Discotic Columnar Mesophases

In fluid columnar discotic mesophases the molecules self-organize into 1-dimensional stacks on average but their exchange between columns, flipping within columns and rotation about the stacking axis remain fast and their intra-columnar stacking distances oscillate. If no reflection for the intra-columnar stacking is observed by X-ray diffraction these columnar mesophases have historically been called "disordered".

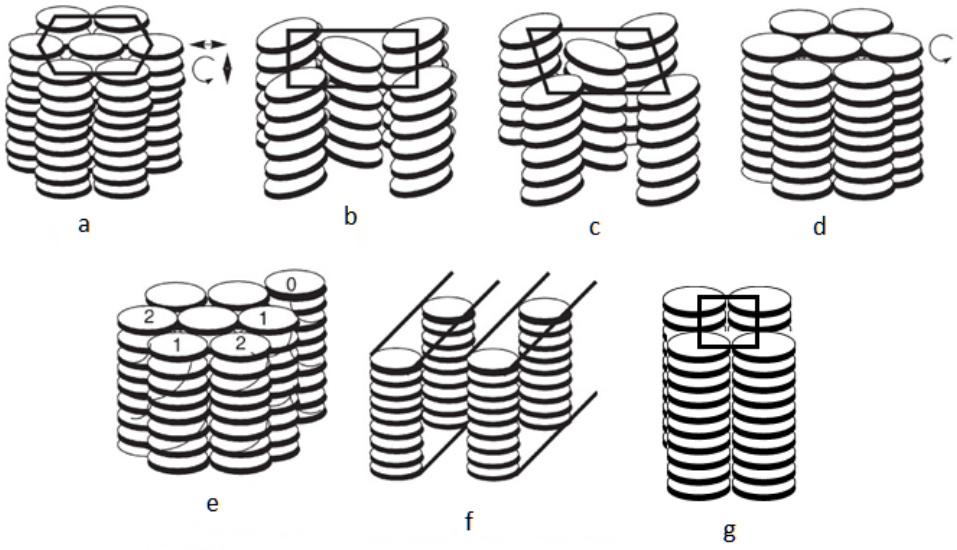

Figure 1-6: Schematic representations of (a) hexagonal, (b) rectangular, (c) oblique, (d) hexagonal plastic, (e) helical, (f) lamellar and (g) tetragonal columnar mesophases. [18]

Increase of the size of the DLC and/or incorporation of additional intracolumnar intermolecular interactions slows down or freezes in molecular motion at a given temperature and the mesophases show higher stacking order. These changes occur gradually but the appearance of a reflection peak in

the wide-angle X-ray diffraction pattern has often been considered to be sufficient for calling the columnar mesophase “ordered”.

The columnar stacks themselves self-organize into different 2D lattices shown in Figure 1.6. Most common is the least ordered uniaxial hexagonal columnar mesophase (Col_h) followed by biaxial rectangular (Col_r) and oblique columnar mesophases (Col_{ob}). Only few examples have been reported for plastic (Col_p), helical (H), square or tetragonal (Col_{tet}), and lamellar (Col_l) columnar mesophases.

Hexagonal packing of molecular columns is the typical feature of hexagonal columnar mesophases (Col_h). The planar space group of a Col_h mesophase is P6/mmm and sometimes the intracolumnar stacking order or disorder is denoted as Col_{ho} and Col_{hd}, respectively.[31,32]

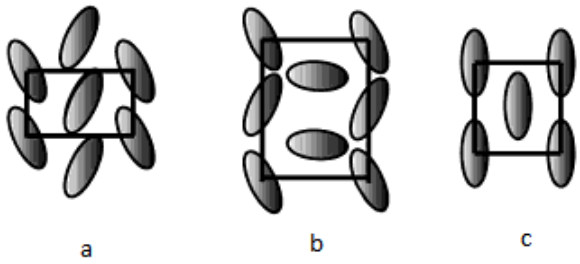

Figure 1-7: Different types of Col_r mesophases: a) Col_r ($P2_1/a$), b) Col_r (P2/a) and c) Col_r (C2/m).[6]

The columnar rectangular mesophases characterized by rectangular packing of molecular columns consist of aromatic cores that are titled with regard to the stacking axis. Three different planar space groups exist for rectangular columnar mesophases that are illustrated in Fig. 1.7. However, distinction between the three different phases based on X-ray diffraction data is often difficult because of insufficient numbers of observed reflections.[33,34]

Another columnar mesophase with elliptic cross sections is the oblique phase Col_{ob}. The planar space group of a Col_{ob} mesophase is *P*1 and the required strong core-core interactions make this mesophase relatively rare. [35, 36]

In columnar plastic mesophases (Col_p) columns are packed in two dimensional hexagonal lattices where the molecules have the ability to rotate about the columnar axis, although they are distinguished by three dimensional crystal-like orders of the centre of mass of the molecules. Unlike Col_h , lateral and axial displacements of the constituent molecules are not found in Col_p mesophase. [31, 37]

The columnar helical phase (H) is displayed by only few triphenylene derivatives such as triphenylene ester derivatives and hexahexylthiotriphenylene, where intracolumnar helicoidal stacking of the triphenylene core is observed, keeping the helical period being disproportionate with the intracolumnar spacing. Also, frustration because of molecular interdigitation in triangular symmetry results in the formation of three column super lattices in the H mesophase.[38, 39]

In the columnar lamellar phase (Col_L), columns of stacked discotic molecules are arranged in layers but the columns in different layers are devoid of any positional symmetry and the columns within layers can slide.[40, 41]

Finally, the arrangement of upright columns in a square lattice is characteristic of the columnar square (or tetragonal) phase (Col_{tet}). This mesophase is displayed by a very small number of phthalocyanine derivatives and sugar molecules.[42, 43]

1.6 Characterization of Discotic Liquid Crystalline Phases

Bulk behavior of discotic and all other mesogens is generally studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small and wide angle X-ray scattering (SAXS and WAXS). However, many other techniques such as solid state NMR, dilatometry, dielectric spectroscopy, and electron diffraction have significantly contributed to today's understanding of these materials. In POM the material is viewed in transmission or reflective mode under crossed polarized conditions while heated and cooled within a variable temperature stage.[2, 16, 44] This method is particularly sensitive to phase transitions that are indicated by discontinuous changes in birefringence,

texture, and fluidity. Crystalline phases are recognized by their geometric shapes and hardness. Crystal mesophases may have a similar appearance as crystal phases but usually deform under pressure while liquid crystal mesophases appear more fluid like, although their viscosity can be high. Most of the aforementioned phases are bifringent while the isotropic liquid phase is not easily identified. POM requires 0.5 mg or less of the material and also helps with the identification of inorganic impurities (e.g. silica and dust) as well as remaining solvent and lower melting organic impurities. POM is usually performed as the first characterization step.

DSC can easily cover a wide temperature range -150°C to 550°C and provides information on transition temperatures and enthalpies.[1-10,45-49] Glass transitions are also identified if sufficiently large. About 2 mg of sample is run in a small aluminum crucible and the quality of the obtained data depends on the sample preparation as well as the heating/cooling method. Several heating/cooling runs of different rates are usually conducted to probe reproducibility and find optimum settings. Molar enthalpies calculated from the integrated peaks reveal information about the two involved phases; a large transition enthalpy indicates major changes in the molecular arrangement and dynamic (e.g. crystalline to liquid crystalline) while small transition enthalpies are characteristic for transitions between different crystal phases or different liquid crystal phases.

Ultimate phase assignment often relies on X-ray diffraction data especially when different smectic and discotic mesophases are involved, because their differences in defect textures observed by POM are not sufficiently characteristic.[6,16,50,51] However, the information provided by 1-dimensional X-ray diffraction of liquid crystal mesophases is often limited because only a small number of reflections are observed. 2-Dimensional X-ray diffraction of aligned samples is a common remedy as it retains some of the spatial information. Especially the phase identification of higher ordered columnar mesophases often requires 2-dimensional diffraction data of aligned samples.

1.7 DLCs as Organic Semiconductors

Incorporation of organic molecules as an active material in electronic devices has drawn enormous scientific and industrial attention. Organic compounds with semiconducting properties originating from conjugated materials are essential to the manufacturing of these devices. Most prominent are organic semiconductors based on π conjugated polymers and small molecule glasses, and commercial devices based on these materials are already on the market, albeit as niche products. Semiconductors based on π-π stacked discotic materials have been tested in different devices such as LEDs, FETs or photovoltaic cells, but their performance is not yet competitive despite their often better charge conducting properties.

Charge conduction preferentially occurs along the self-organized columnar stacks of discotic molecules and is mediated by overlapping π-systems (intracolumnar stacking distance around 3.5 Å). Charge carrier mobility values of >1 $cm^2v^{-1}s^{-1}$ have been reported for both electrons and holes.[6,18-20] Expectedly, transport of charge carriers orthogonal to the columnar stacks is much slower (at least by a factor of 10^3) mainly because the columnar stacks are usually separated by "insulating" aliphatic side-chains (Fig. 1.8). The intercolumnar spacing is usually in the range of 20-40 Å, [6,18-20] which is too large for tunneling processes and requires high activation energy for charge hopping.

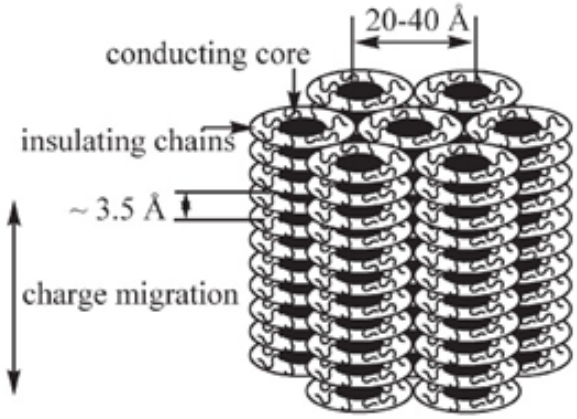

Figure 1-8: Schematic view of charge migration in a hexagonal columnar mesophase.[18]

This anisotropy of charge conduction requires an alignment of the columnar mesophase, which is one of the hurdles for commercial application of these materials. For devices such as FETs and TFTs the columns should be parallel to the substrate and orthogonal to the electrodes coated onto the substrate whereas in OLEDs and photovoltaic devices the columns must be orthogonal to the substrate to connect the two electrodes (Fig. 1.9). Both alignments are difficult to obtain over large areas and in high quality but alignment layers and coating methods (zone casting) exist for the homogeneous alignment while no generally applicable method has been developed for the homeotropic alignment.

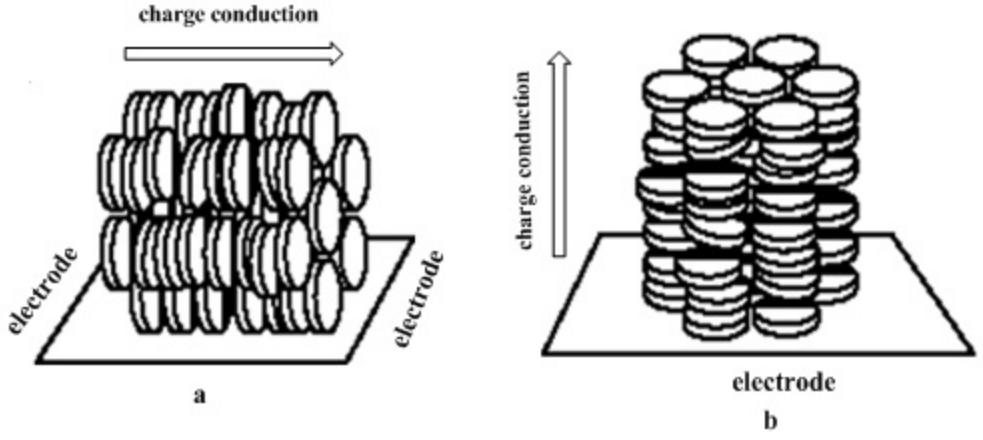

Figure 1-9: Anisotropic charge conduction and alignment of DLCs. A) homogeneous (edge-on) or parallel alignment for devices such as FETs and TFTs; B) homeotropic (face-on) or vertical alignment for (opto)electronic devices such as OLEDs and photovoltaic cells.[20]

However, large aligned monodomains of DLCs have been prepared by applying their self-organizing properties. Their fluid character also induces self-healing properties by repairing defect sites but the number of defect sites present at any given time is always larger than in single crystals. The ideal DLC displays a columnar mesophase at high temperatures that can be easily aligned and that crystallizes without significant changes to structure and alignment upon cooling. This type of material has not yet been realized.

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2 Chapter 2: Hole and Electron Conducting Star-Shaped Oligomers

2.1 Introduction

Discotic liquid crystals (DLCs) are an alternative class of organic semiconductors that provide high and anisotropic charge carrier mobilities along self-organized columnar π-π-stacks.[1-7] Their self-organization into columnar stacks and formation of domains is particularly interesting for the preparation of bulk-heterojunction materials in photovoltaic devices that contain domains of electron acceptor and electron donor organic semiconductors. Unfortunately, mixtures of miscible donor and acceptor DLCs form mixed columns of charge-transfer stacks[8-10] and mixtures of immiscible DLCs macrophase separate into two phases of small interfacial area.[11]

One possibility of overcoming this dilemma is to link immiscible donor and acceptor DLCs together so that they cannot macrophase separate but form domains of just donor and just acceptor DLCs, similar to block co-polymers. Other advantages of main-chain oligomeric and polymeric DLCs as organic semiconductors are increased intracolumnar stacking order and temperature range of their columnar mesophases as well as the formation of glasses rather than crystal phases. However, linear oligomers of DLCs have been shown to resist all alignment attempts. Larger monodomains are obtained with monomers and dimers but trimers and longer oligomers are rich in defects, possibly because individual DLCs of one main-chain oligomer can be in the same columnar stack and in neighbouring columns.[3,4,12-15]

Star-shaped oligomers of DLCs, in contrast, have been proposed to better align, especially if their structure matches the symmetry of a hexagonal columnar mesophase. The best match is obtained with star-shaped heptamers and the few previously reported systems are reviewed in the next part. Presented in this Chapter are star-shaped hetero-heptamers of DLCs that contain hexacarbonyl hexaazatriphenylene

as electron acceptor DLC in the centre and six hexapentyloxy triphenylenes as electron donor DLCs as ligands (Fig. 2.5). The syntheses of both hexaazatriphenylenes and mono-substituted hexapentyloxy triphenylenes will be briefly reviewed in sub-chapters 2.1.2. and 2.1.3.

2.1.1 Star-Shaped Discotic Heptamers

Ringsdorf and co-workers synthesized various star-shaped oligomers (heptamers) by linking six peripheral triphenylene fragments to central benzene,[17] triphenylene [16,18] and azacrown cores. [18] (Fig. 2.1) All of these compounds display hexagonal columnar mesophases but probably not super-columns of stacked heptamers. Instead, the heptamers are probably shifted with regard to each other but still ensuring that each discotic core is part of a columnar stack. Formation of super-columns can only be expected for hetero-heptamers **26**, **28** and **29** but the two different discotic cores are apparently miscible and do not bias the formation of super-columns versus the entropically preferred shifted stacks of heptamers. Astonishing is the mixed orientation of heptamers **27** in Langmuir and Langmuir-Blodgett films that have the central core aligned face-on and the six peripheral cores edge-on.[16,18]

Bisoyi and co-workers prepared star-shaped discotic heptamer **27d** with six triphenylene units linked to a central triphenylene core through alkylethers in lieu of the ester linkages used by Ringsdorf, but this did not significantly affect their hexagonal columnar mesomorphism.[16] Zelcer *et al.* prepared another triphenylene based heptamer that had disiloxane units in the linking chains[19] and Kumar and co-workers synthesized a hetero-heptamer **29** containing an electron deficient anthraquinone central core and six electron rich triphenylene peripheral units.[16] Finally, Müllen *et al.* reported an even larger discotic heptamer based on six hexabenzocoronene units linked to a central hexabenzocoronene unit *via* aliphatic spacers.[20]

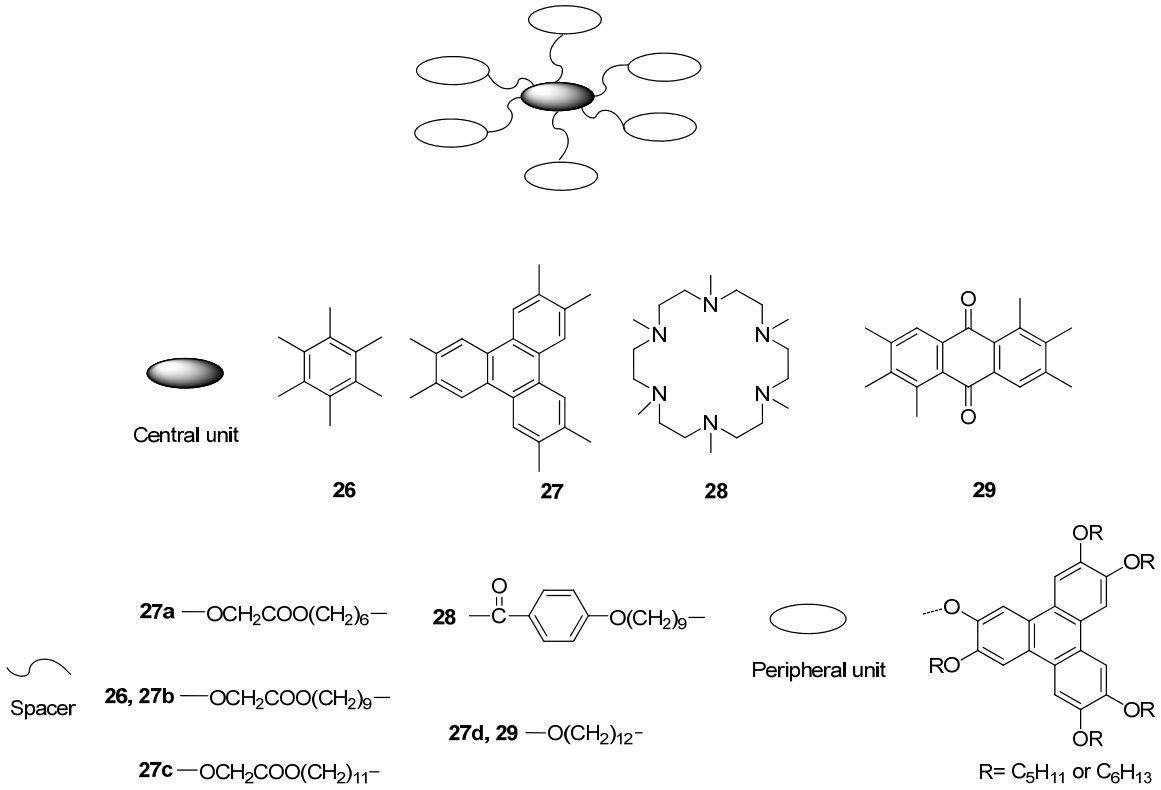


Figure 2-1: Examples of star-shaped discotic heptamers.[16-20]

The design of donor-acceptor discotic hetero-heptamers requires the use of electron acceptor and donor discotic building blocks. Examples of electron rich discotic molecules that could function as electron donors are shown in Fig. 2.2 (**30-32**) and examples of electron deficient discotic molecules that could function as electron acceptors are shown in Fig. 2.3 (**33-35**). Fig. 2.3 also depicts three acceptor molecules **36-38** that have been used for the formation of columnar donor-acceptor together with a donor DLC. The heteroheptamers presented herein are based on a hexaazatriphenylene central core and six triphenylene ligands and the synthesis and properties of these two cores is briefly reviewed in the following.

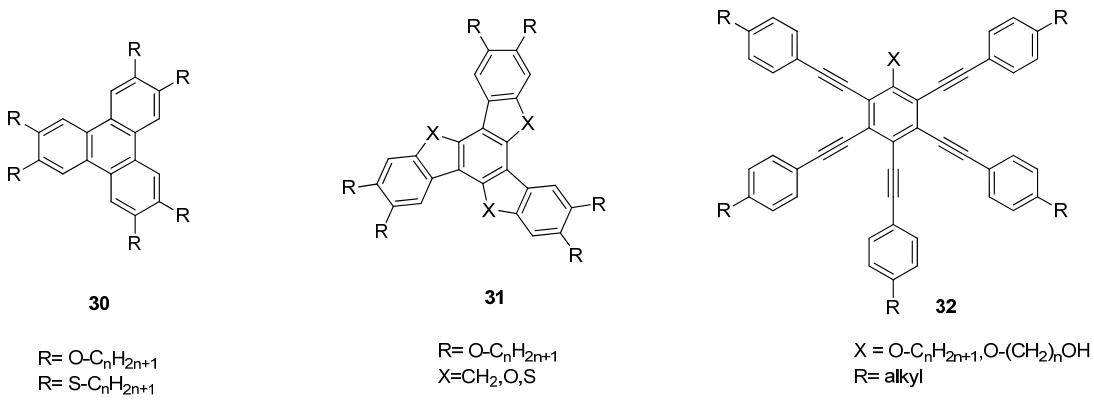


Figure 2-2: Examples of electron rich (p-type) DLC's based on (30) triphenylenes,[16] (31) truxenes,[21] oxatruxenes [22] and thiatruxenes[23]; and (32) five or six fold (phenylethynyl) substituted benzene.[24-27]

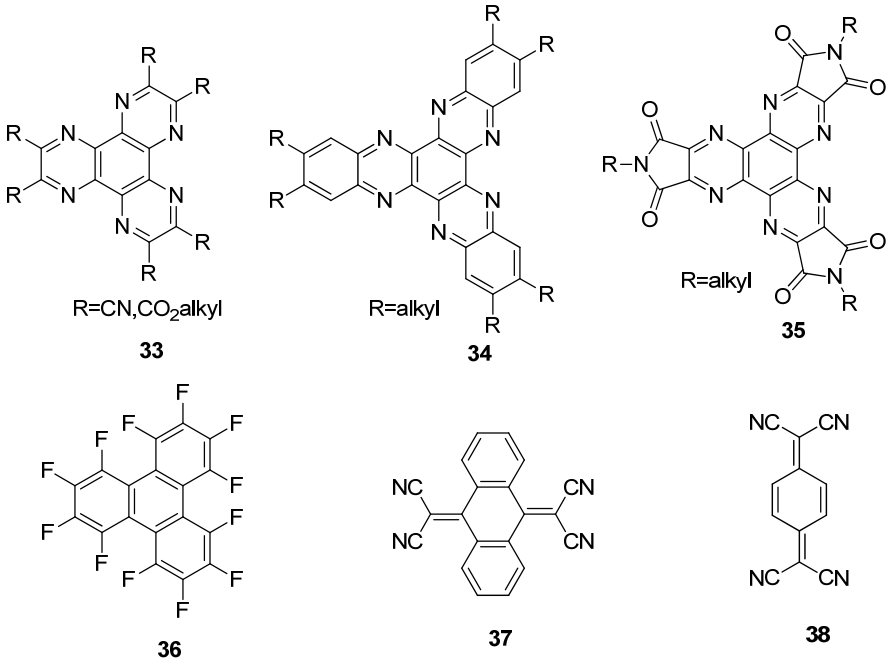
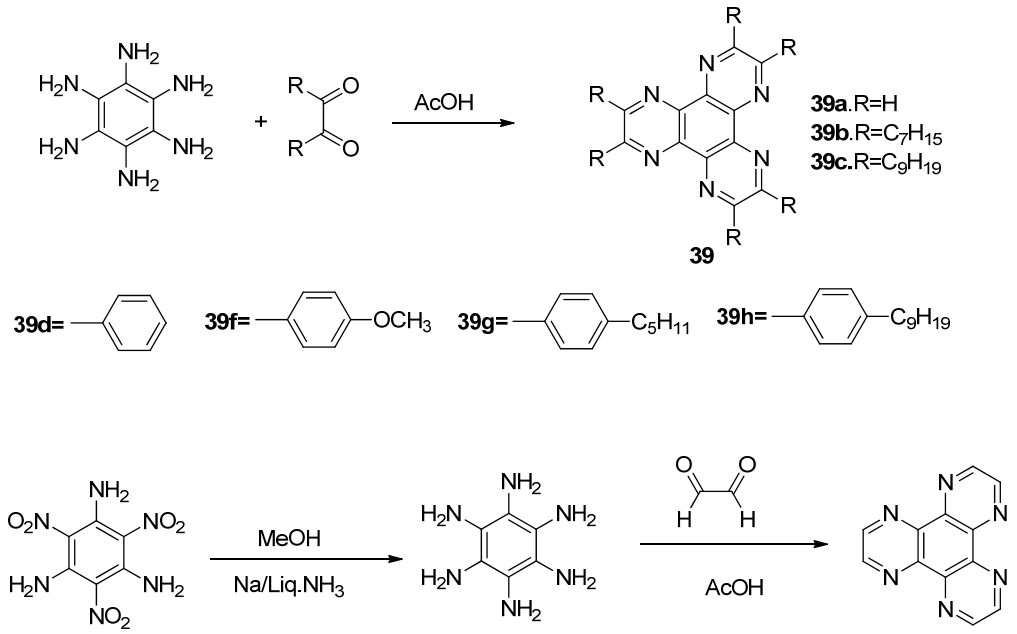


Figure 2-3: Examples of electron acceptors based on hexaazatriphenylene cores (33-35);[16,28-30] perfluorotriphenylene (36);[16] 11,11,12,12-tetracyananthraoquinodimethane (TCAQ) (37);[31] and 7,7,8,8-tetracyanoquinodimethane (TCNQ) (38).[32]

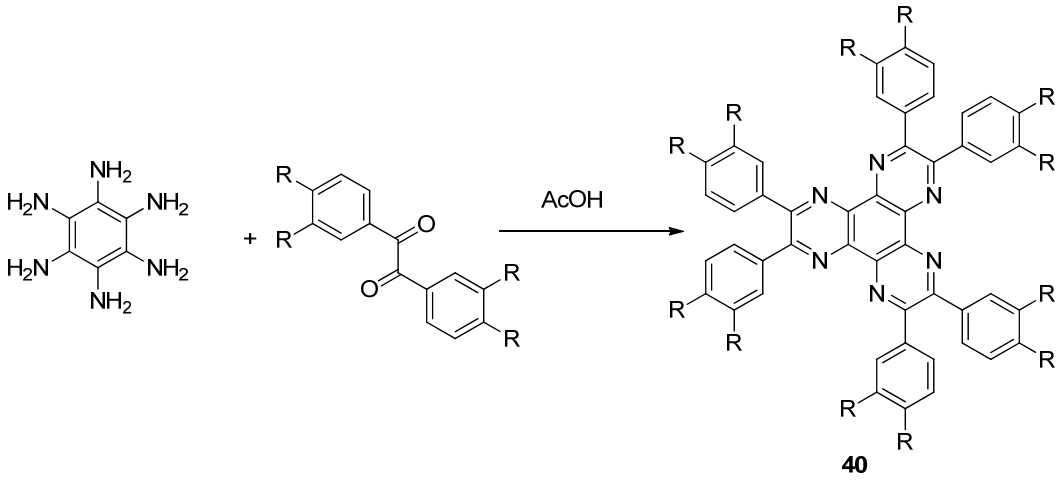
2.1.2 Hexaaztriphenylene core

1,4,5,8,9,12-hexaazatriphenylene (HAT) derivatives are electron deficient heteroaromatic polycyclic discotic cores because of the higher electronegativity of N. Praeffcke *et al.* developed a general synthetic approach to hexa-substituted HAT derivatives that they expected to display columnar mesophases similar to the structurally related triphenylene derivatives.[33] Unfortunately, none of these

derivatives turned out to be liquid crystalline. Praeffcke's synthesis required the preparation of hexa-aminobenzene from 1,3,5-trinitrobenzene, a listed military grade explosive, and its subsequent reaction with 3 eq. of 1,2-diketones to give the targeted HAT derivatives (Scheme. 2.1). This approach was not adopted by many other research groups because of its inherent risk. Roger and co-workers prepared the parent HAT core by condensation of glyoxal with freshly synthesized hexaaminobenzene,[34] and Bushby and co-workers reported the first liquid crystalline derivatives of HAT[35-39](Scheme 2.2). The same and other groups also studied mixtures of non-liquid crystalline HAT derivatives with DLCs that show columnar mesophases over large temperature ranges as a result of alternating stacking based on complementary polytopic interactions.[14,35-39]



Scheme 2.1 Synthesis of HAT derivatives.



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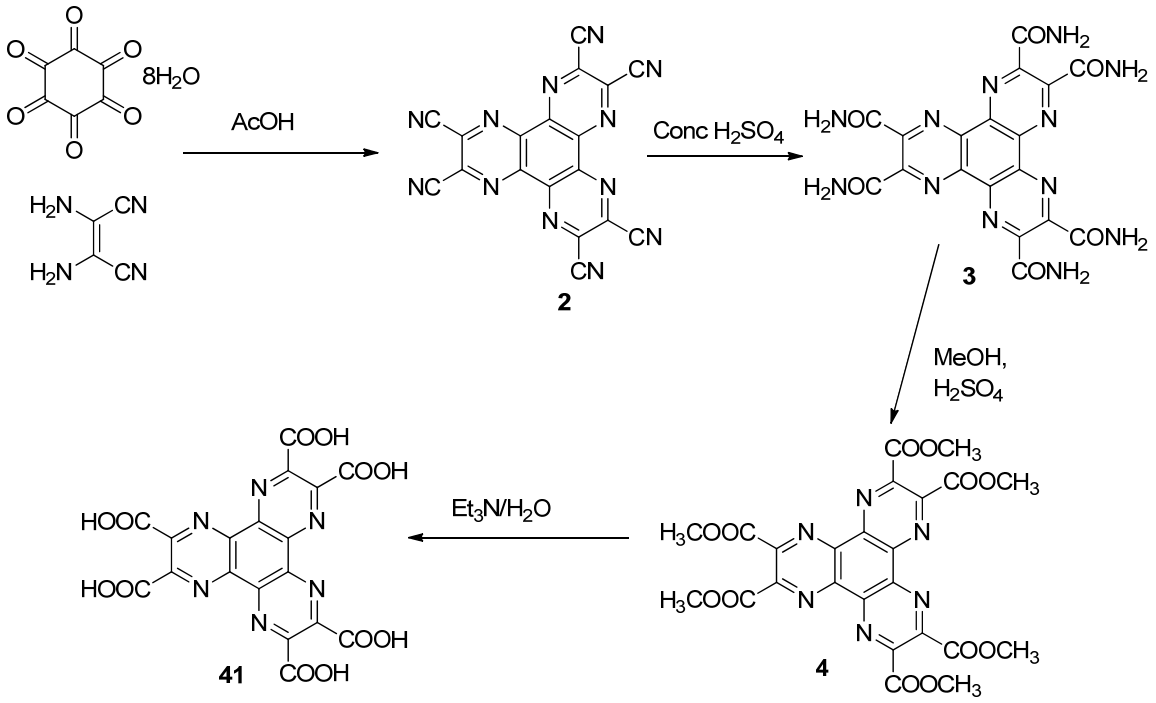
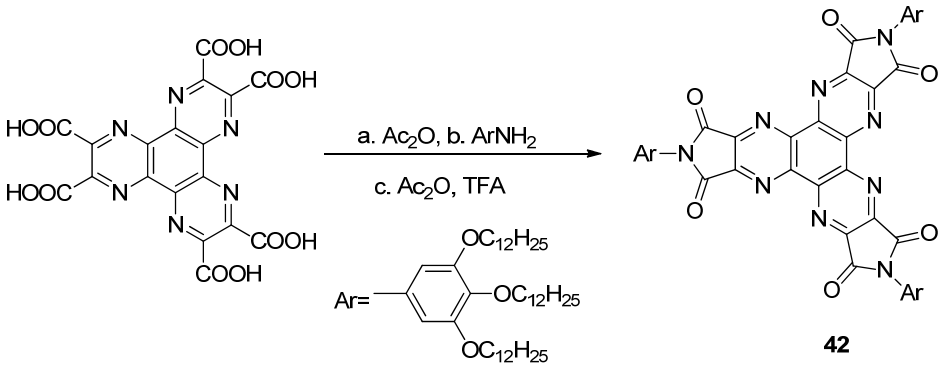
Scheme 2.2: Synthesis of liquid crystalline HAT derivatives, R=OC_6H_{13}

Czarnik *et al.* developed a new synthetic approach to more electron deficient HAT cores starting with the preparation of hexaazatriphenylene-hexacarbonitrile by condensation of commercially available hexaketocyclohexane with 3 eq. of diaminomaleodinitrile (Scheme 2.3).[40,102] Precursor **2** was successfully converted into numerous functionalized HAT derivatives such as hexaamide **3**, hexamethoxy carbonyl **4**, and hexaacid **41** and other groups used them as precursors to several novel DLCs. [41,42]



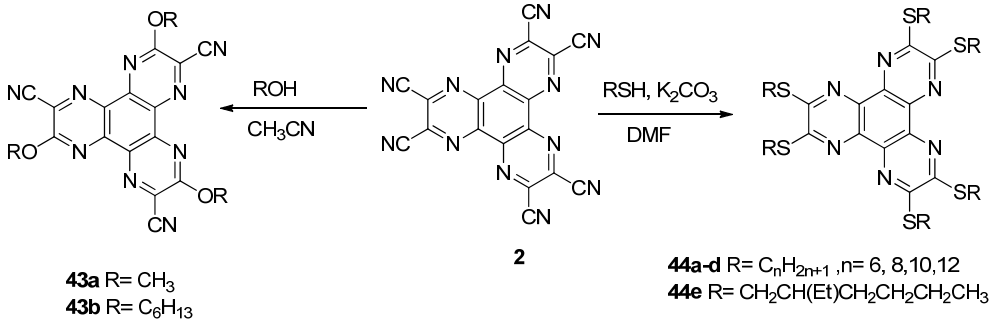
Scheme 2.3:Synthesis of hexaazatriphenylenehexacarbonitrile and its derivatives.

Czarnik's HAT derivatives drew substantial attention not only from the liquid crystal but many other communities for their convenient synthesis, diverse peripheral functionality coupled with π-complexation ability, co-ordination properties and electron deficient nature. Several of these HAT derivatives have been used as n-type organic semiconductors, fluorescent dyes, magnetic materials, self-assembled organogels, octapolar non-linear chromophores, etc.[43-50] Several metal complexes of HAT derivatives have also been prepared to study their co-ordination chemistry.[51-56] Recently, some new liquid crystalline HAT derivatives have been reported. Meijer and co-workers prepared triimide HAT derivatives shown in Scheme 2.4 that display columnar mesophases.[57]



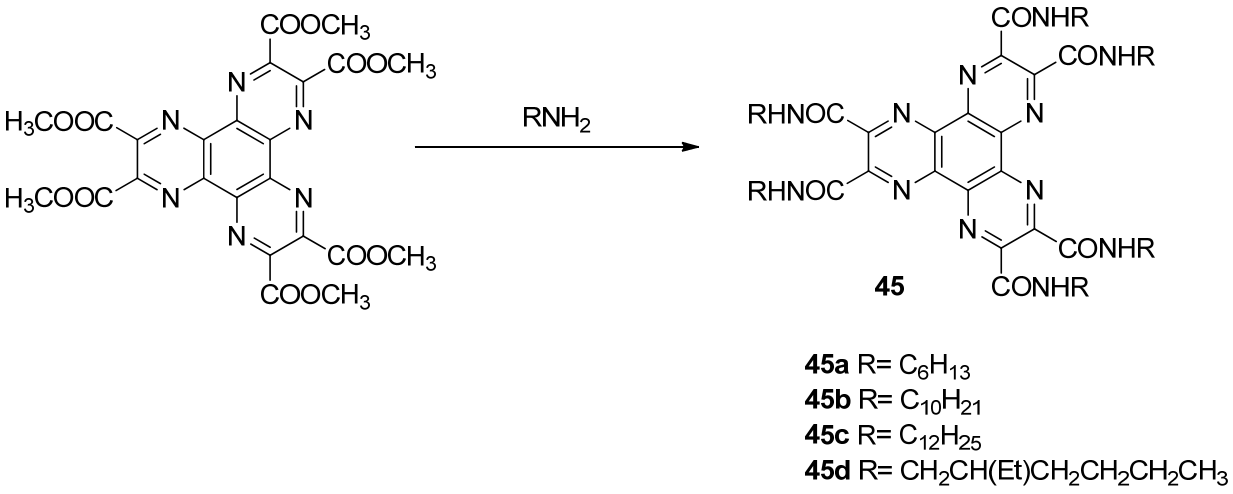
Scheme 2.4: Synthesis of dendritic HAT derivatives.

Chang *et al*. demonstrated that the cyano groups can also be partially replaced with alcohols and fully substituted with thiols to generate HAT derivatives (Scheme 2.5) of different acceptor strength.[58] Compound **43b** forms a hexagonal columnar mesophase whereas compounds 43**a** and **44a-e** do not form mesophases similar to their oxygen ethers analogues.[59]



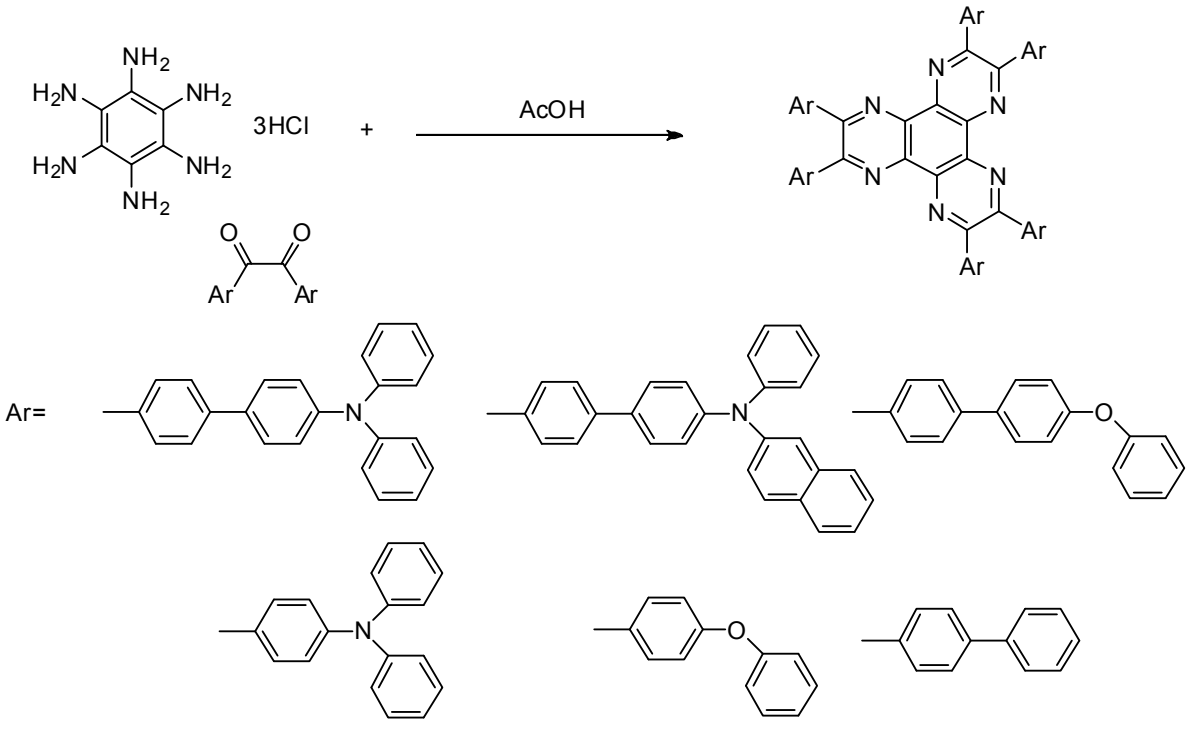
Scheme 2.5: Synthesis of HAT derivatives with alternating electron donating and withdrawing substituents (8) and hexathioether substituents (9)[59]

Hydrogen bond assisted hexagonal columnar mesomorphism was observed for novel hexacarboxamido HAT derivatives of which compound **45c** displays the smallest reported stacking distance of only 3.18 Å (Scheme 2.6).[60,61] Furthermore, its intercolumnar correlation length was found to be high with 120- 180 Å, extending over 40 to 55 disks, which both contribute to the observed high charge carrier mobility of 0.04 to 0.08 $cm^2\ V^{-1}s^{-1}$ in comparison to similarly sized DLCs. Hexaamide derivative **45d** containing branched aliphatic chains exhibits multiple oblique columnar mesophases that are rare and its surface coating was also studied in detail.[62,63]



Scheme 2.6:Synthesis of hexacarboxamido derivatives of HAT

Ishi and co-workers published an unusual set of HAT derivatives that show columnar mesomorphism because they lack any aliphatic side-chains but are substituted with aromatic peripheral substituents (Scheme 2.7).[64]



Scheme 2.7:Synthesis of all aromatic HAT derivatives that form columnar mesophases

2.1.3 Triphenylene Moiety

One of the most studied symmetrically fused aromatic polycyclic systems in the field of DLCs are triphenylene (TP) derivatives (Fig. 2.4). Triphenylene was first separated from pyrolytic products of benzene by Schultz.[65] It was also synthesized from cyclohexanone and Zann *et al.* were first to introduce triphenylene as a novel discotic core.[66] Triphenylene derivatives have drawn immense attention among all liquid crystal researchers for their 1-dimensional charge and energy migration and have inspired many different synthetic approaches towards triphenylene based DLCs.[67-69]

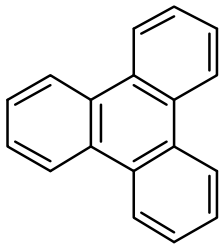
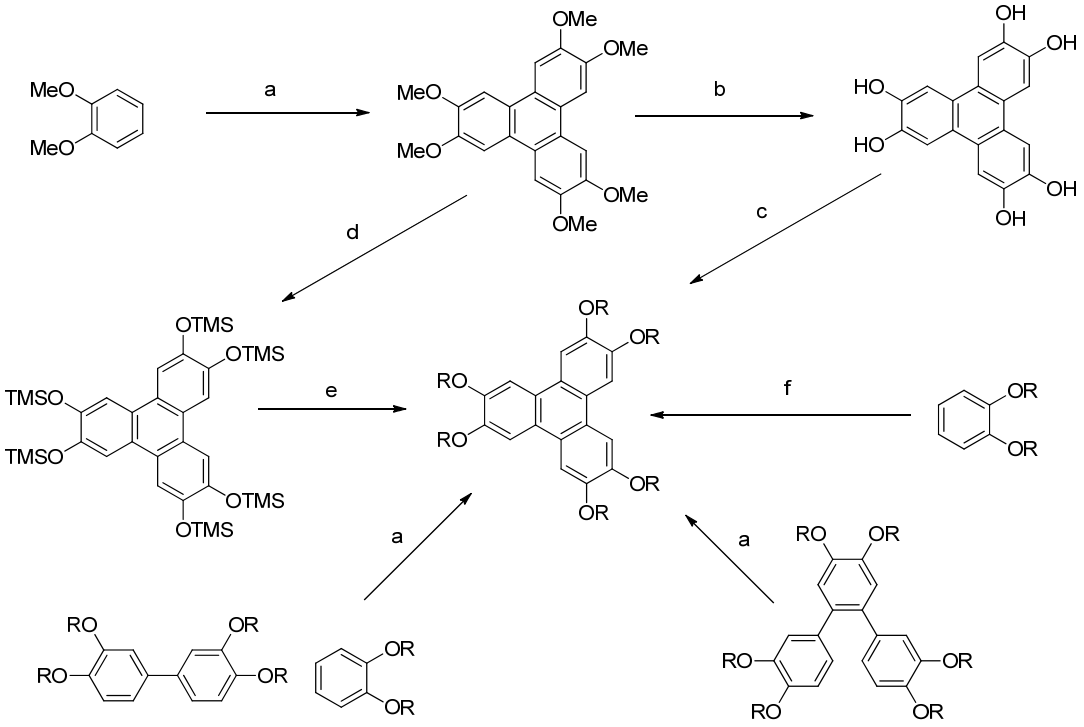


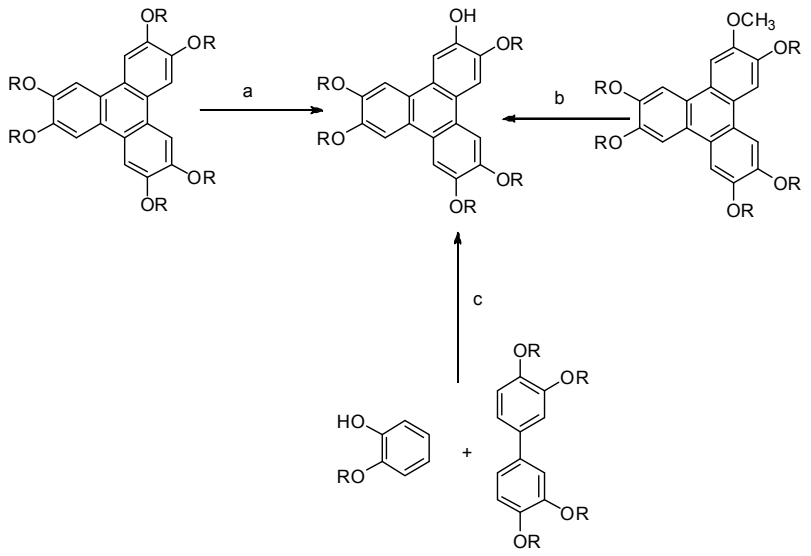
Figure 2-4: Triphenylene core.

Hexaalkoxy substituted TPs are among the best studied discotic mesogens. They are successfully used as the p-type (electron rich) semiconductors. Originally, hexaalkyoxy TP derivatives were prepared by alkylation of hexahydroxy TP which was synthesized by demethylation of hexamethoxy TP. Hexamethoxy TP is prepared by oxidative coupling of dimethoxy benzene in the presence of strong acid that forms three aryl-aryl bonds in a single operation. However, hexahydroxy TP is difficult to handle because of its low solubility and easy oxidation and a better approach to hexaalkyloxy TPs is based on an oxidative coupling of the corresponding dialkyoxy benzene in the absence of strong acid.[70-72] The cyclized products are enthalpically favored over linear products because of their aromatic character and the most commonly used oxidizing reagents are $MoCl_3$, $VoCl_3$, and $FeCl_3$ in mixtures of dichloromethane and nitromethane (Scheme 2.8).[12,73-79]



Scheme 2.8: Synthetic routes to prepare hexaalkoxytriphenylenes: a. Chloranil, H_2SO_4; b. BBr_3 or HBr; c. RBr, base; d. TMSI, e. TBAF, RBr; f. $MoCl_3$ or $VoCl_3$ or $FeCl_3$, CH_2Cl_2.

TP derivatives with unsymmetrical substitution patterns are comparatively more difficult to prepare than their symmetrical analogues. Kumar is the pioneer in the preparation of several mono di- and tri-functionalized triphenylenes from readily obtainable hexakis (pentyloxy) triphenylene by selective de-alkylation using bromocatecholborane or 9-Br-BBN.[80] The monohydoxy alkoxy-TPs are valuable precursors for discotic dimers, oligomers, and polymers[39,80-86] as well as numerous discotic TPs containing five alkoxy substitutents and one different substituent. However, separation of monohydoxy pentapentyoxlytriphenylene from remaining hexakis(pentyloxy)triphenylene is tedious and requires highly efficient column chromatography. A better methodology selectively cleaves aryl methyl ether in the presence of five alkyl ethers with lithium diphenylphosphide to give the monohydoxy alkoxy-TPs in almost 70% yield.



Scheme 2.9: Synthetic routes toward the formation of monohydroxy-pentaalkoxytriphenylenes: a. bromocatecholborane, b. lithium diphenylphosphide; c. $FeCl_3$, CH_2Cl_2

The direct oxidative coupling of alkoxyphenol and tetraalkoxybiphenyl to afford monohydoxy pentaalkoxy-TPs has also been reported. This method works best for guaiacol, while alkoxyphenols with longer alkyl chains do not give satisfactory yields (Scheme. 2.9).[14,39,87,89]

2.2 Objective

Presented here is the synthesis of star-shaped discotic heteroheptamers **18a,b** containing hexaazatriphenylene hexacarboxylate or hexaamide groups as the electron acceptor central core and six hexaalkoxy triphenylene ligands as electron donor cores. Envisioned is the formation of super-columns in which the heptamers stack on top of each other to generate a material with electron acceptor columnar stacks in the centre that are surrounded by electron donor columnar stacks. A cartoon of this supramolecular design and the incorporation of such a material into a bulk heterojunction photovoltaic device is shown in Figure 2.5.

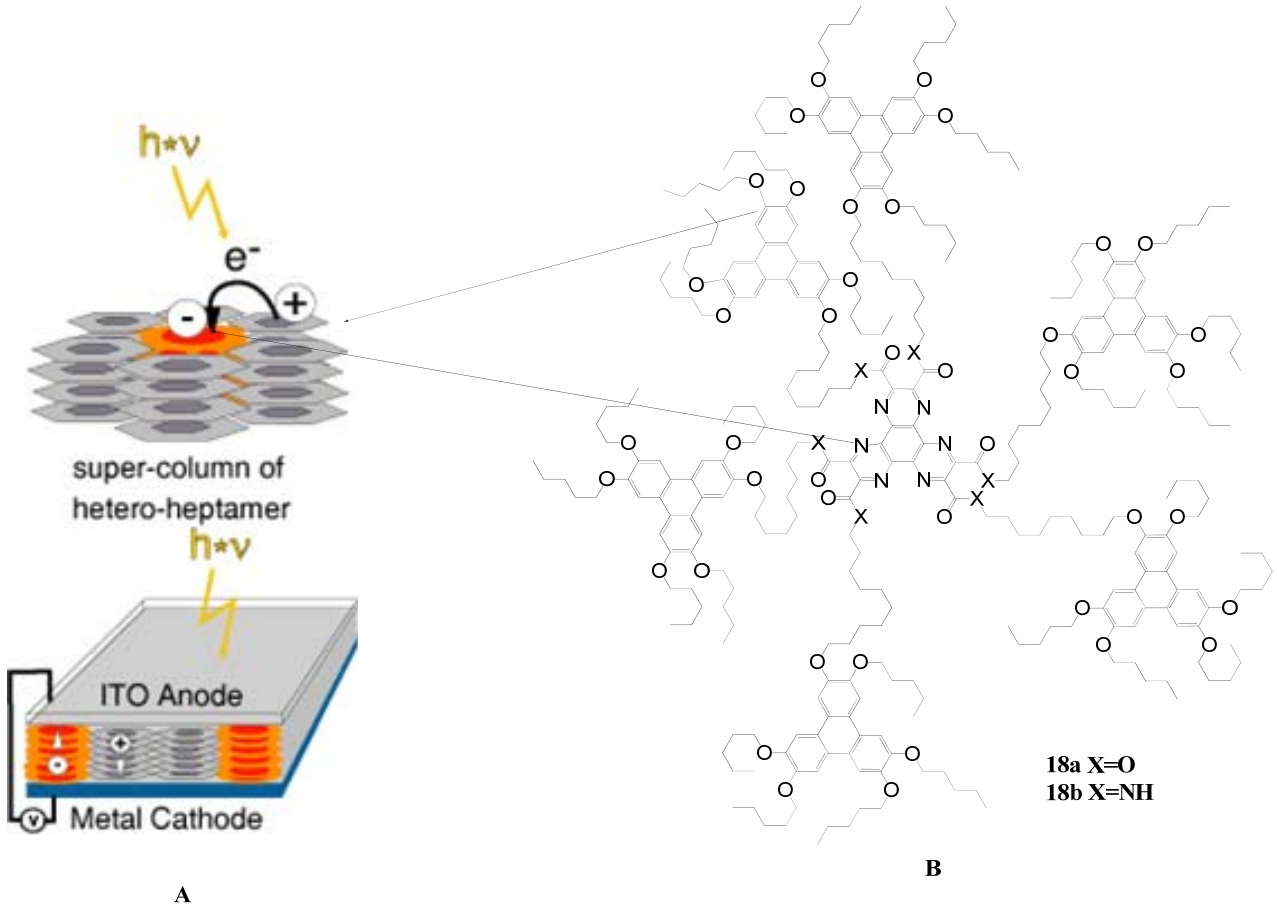
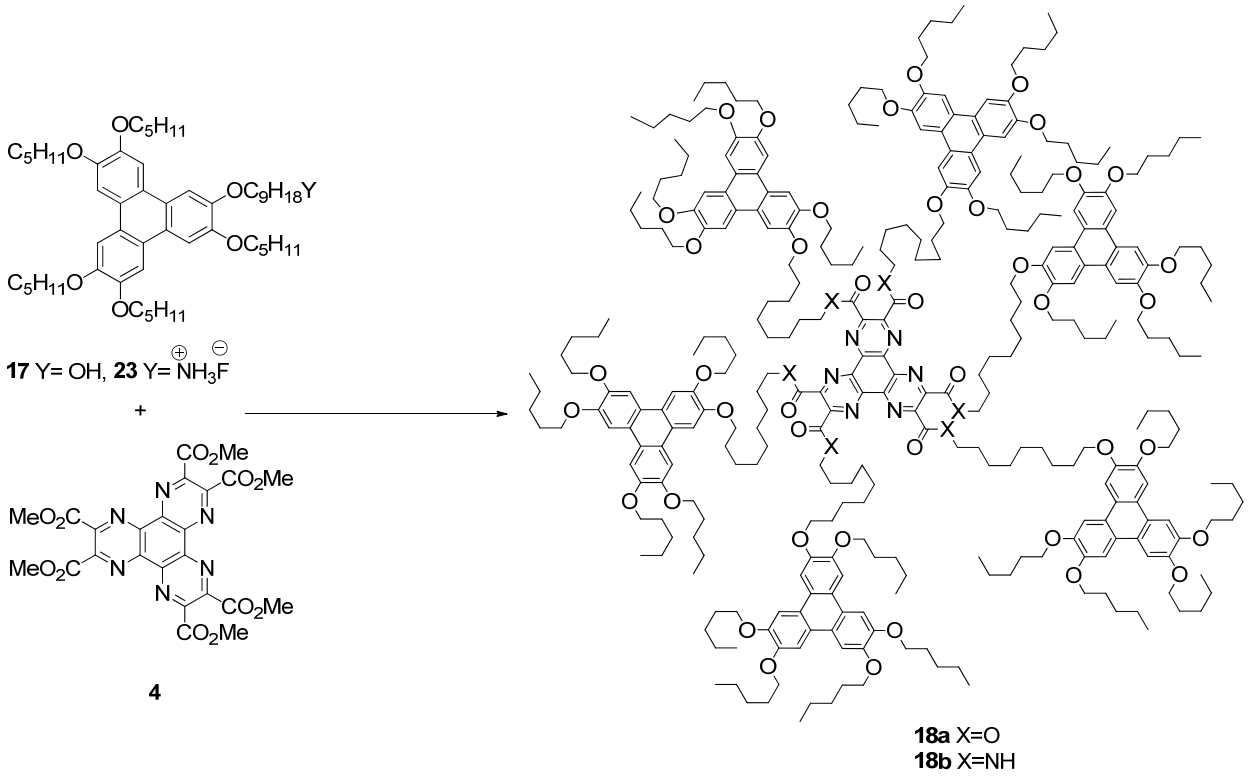


Figure 2-5: Simplified cartoon of a photovoltaic device containing star-shaped heteroheptamers self-organized and self-aligned into nano-separated columns of acceptor hexaazatriphenylenes (red) and donor triphenylene ligands (grey).

Charge carriers (exciton) generated by photoexcitation are always close to the heterojunction between acceptor and donor columns where they are expected to easily disperse into two free charge carriers on two separated columns. The two charge carriers can now quickly move along the columns to the electrodes of opposite charge because of the applied voltage and the high charge carrier mobility of the columnar mesophases. However, recombination of hole and electron may compete with charge separation because of their close proximity on neighbouring coulmns.

2.3 Synthesis of heteroheptamers 18a and 18b

The final step of the heteroheptamer formations involves either hexa-transesterification or hexa-amidation of **4** with **17** or **23**, respectively (Scheme 2.10).

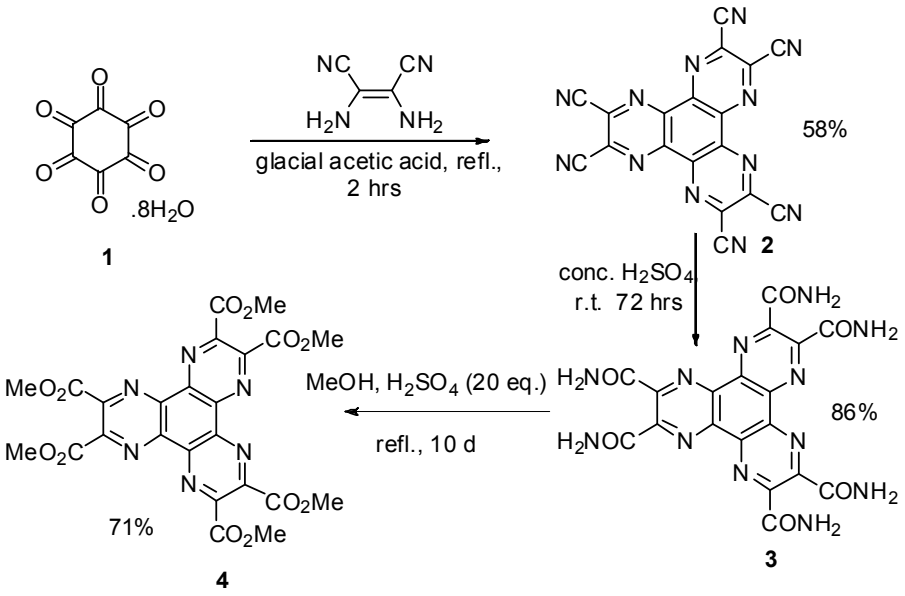


Scheme 2.10: General scheme for both transesterification and amidation of 4

2.3.1 Synthesis of hexamethyl dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarboxylate (4)

The preparation of HAT derivative **4** follows Czarnik's procedure[40] that begins with a cyclocondensation of hexaketocyclohexane octahydrate **1** with diaminomaleonitrile to form triphenylenehexacarbonitrile **2**. Compound **2** was converted into the corresponding hexaamide **3** in the

presence of sulfuric acid and **3** was transformed into hexamethoxy carbonyl derivative **4** using Methanol and sulfuric acid (Scheme 2.11).



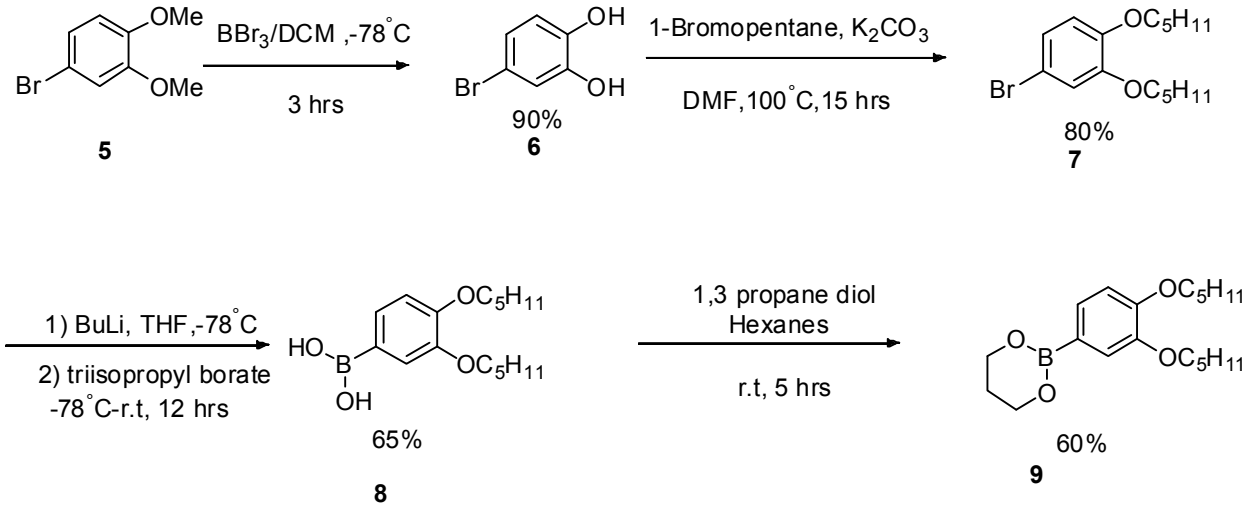
Scheme 2.11: Synthesis of hexamethyl dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarboxylate 4

2.3.2 Preparation of mono functionalized triphenylene ligands 17 and 23

Both mono-functionalized triphenylene ligands were synthesized *via* an ortho-terphenyl intermediate that is obtained by a double Suzuki cross-coupling of 1,2-dibromo-4-methoxy-5-(pentyloxy) benzene **13** with boronic ester **9** (Schemes 12-14).

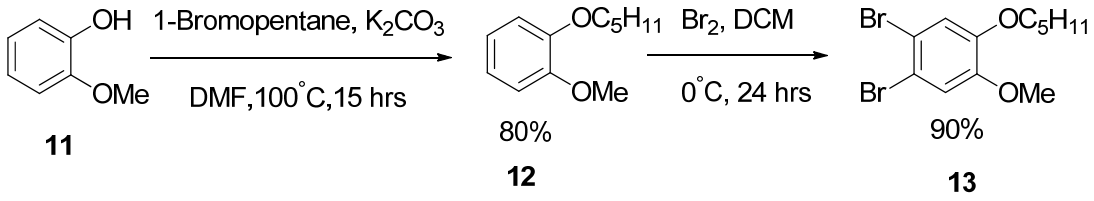
Boronic ester **9** was obtained by starting with the demethylation of 4-bromo-1,2-dimethoxy benzene **5** with boron tribromide to quantitatively generate 4-bromo-benzene-1,2-diol **6**, which was successfully dialkylated with pentyl bromide in 80% yield (Scheme 2.12). 4-Bromo-1,2-dipentyloxybenzene **7** was subsequently converted into the corresponding boronic acid derivative **8** in 65% yield by reacting the in-situ generated Li salt with freshly distilled triisopropylborate. Distillation removes *iso*-propanol that is usually present in stored triisopropylborate and results in the formation of 1,2-dipentyloxybenzene **10** as side-product that can be separated from the boronic acid **8** by column

chromatography on silica gel with hexanes. Boronic acid **8** was then converted into boronic ester **9** by reaction with 1,3-propanediol in 60% yield because the boronic ester was found to give better yields in the subsequent Suzuki coupling than the boronic acid.



Scheme 2.12: Synthesis of boronic ester derivative 9

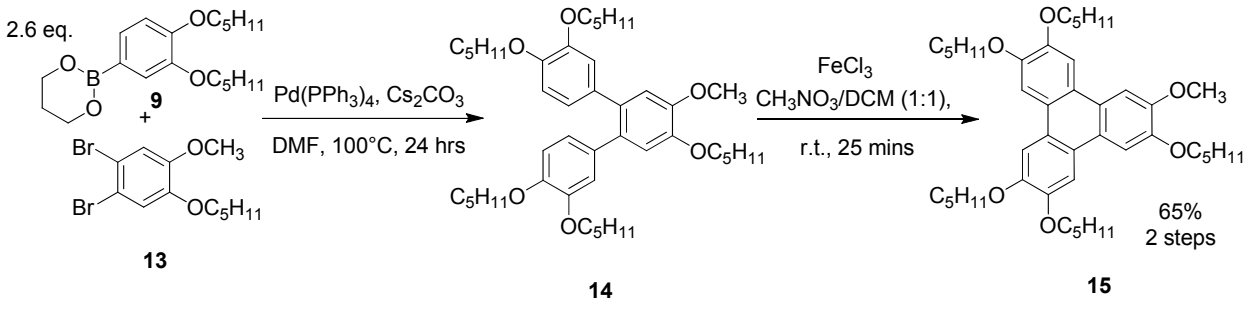
1,2-dibromo-4-methoxy-5-(pentyloxy)benzene **13** was obtained by dibromination of 1-pentyloxy-2-methoxybenzene **12** with Br_2 in more than 90% yield and **12** was obtained from commercially available guaicol **11** by alkylation with in 80% yield (Scheme 2.13).



Scheme 2.13:Synthesis of 1,2-dibromo-4-methoxy-5-pentyloxybenzene 13

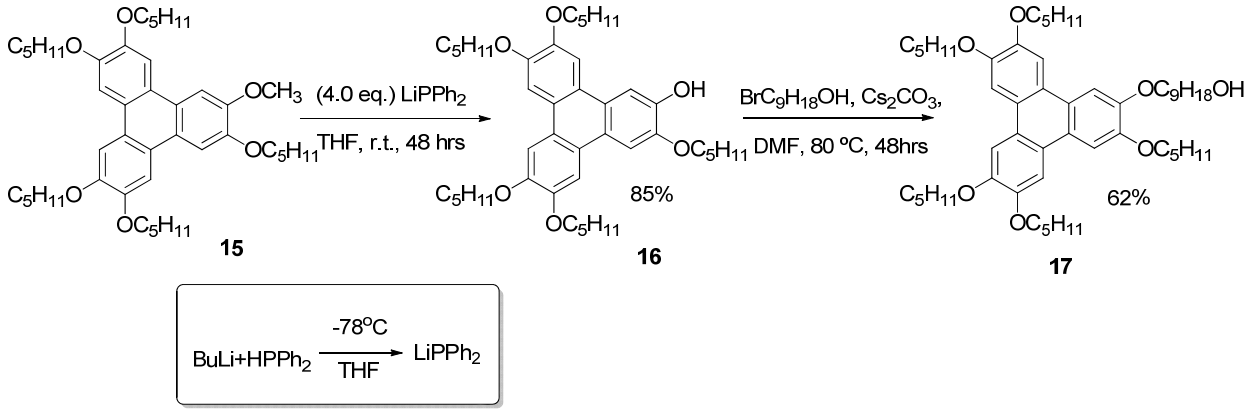
Suzuki coupling of dibromo compound **13** with boronic ester **9** gave ortho-terphenyl **14** as a gel-like material that could not be crystallized Consequently, purification of terphenyl **14** was difficult and avoided by performing the oxidative coupling to triphenylene **15** on the crude compound **14** (Scheme

2.14). $FeCl_3$ in 1:1 nitromethane and dichloromethane was used for the oxidative coupling and generated triphenylene **15** in 65% yield for both steps.



Scheme 2.14: Synthesis of 2-methoxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene 15

The methyl group of **15** was selectively cleaved with freshly prepared $LiPPh_2$ to form the corresponding hydroxyl derivative **16** in 85% yield (Scheme 2.15).

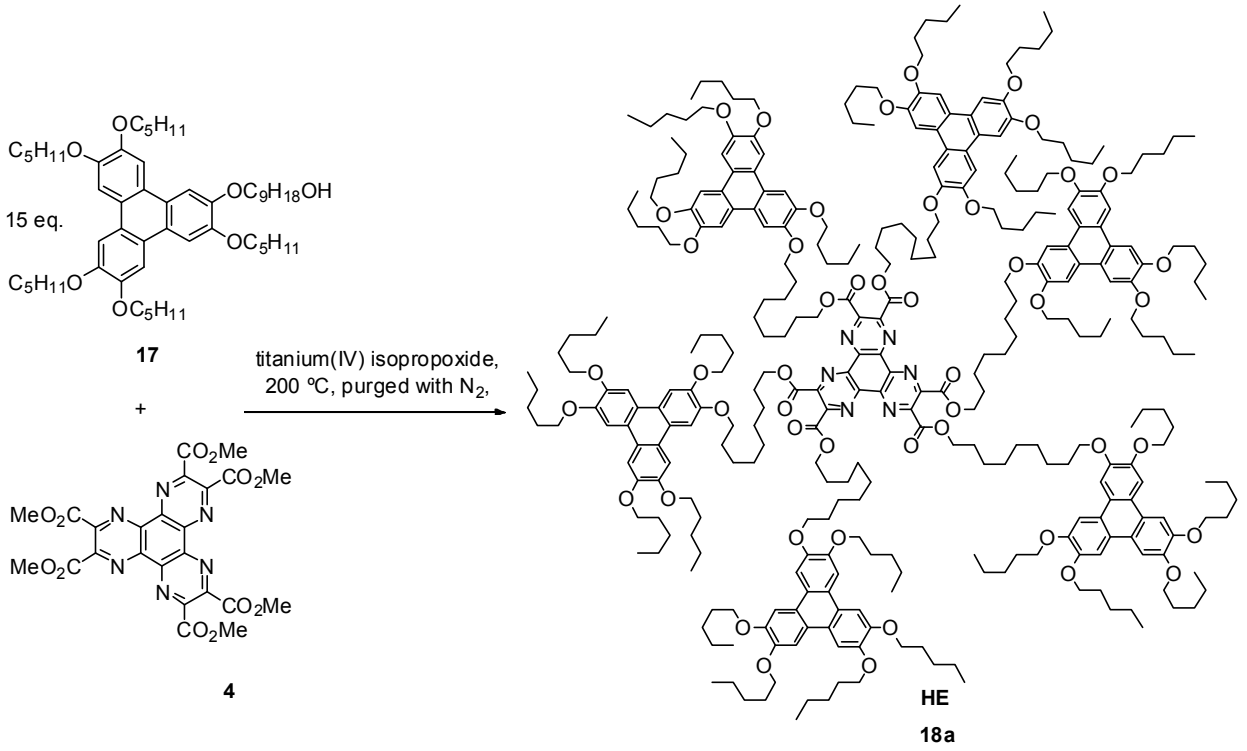


Scheme 2.15: Synthesis of 9-((3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yl)oxy)nonan-1-ol 17

Finally, alkylation of the hydroxy group of triphenylene **16** with 9-bromononanol generated the ligand **17** in 62% yield. Chromatographic separation followed by recrystallization from MeOH was necessary to obtain analytically pure compound **17** that should be kept in a freezer under inert atmosphere to avoid slow decomposition over time.

2.3.3 Synthesis of heptamer ester HE (18a).

Heptamer ester **18a** was successfully synthesized by reacting 15 eqiv. of **17** with hexamethoxy carbonyl HAT **4** in the presence of titanium(IV) isopropoxide at 200 °C for 4 days. Size-exclusion gel chromatography was performed to remove excess of **17** from **18a** and the crude product heptamer was subsequently purified by preparative TLC on silica gel followed by recrystalization from CH_2Cl_2/MeOH (1:1) (Scheme 16). The yield after purification based on **4** was 50%.

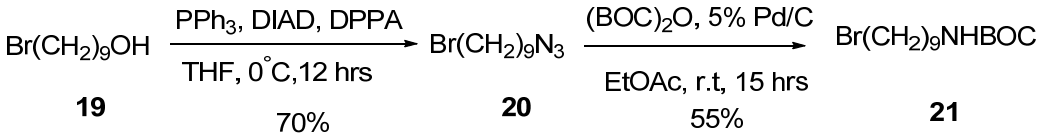


Scheme 2.16: Synthesis of heptamer ester 18a.

2.3.4 Synthesis of 2-((9-aminononyl)oxy)-3,6,7,10,11-pentakis(pentyloxy)triphenylene (25) and its ammonia salt (23)

Synthesis of triphenylene ligands **23** and **25** for the preparation of the hexaamide heptamer requires the preparation of a bromoalkyl chain with amine or ammonium end group as a conversion of the hydroxyl group of triphenylene **17** appears to be a less valid approach.

We found that Mitsunobu-type exchange of an alcohol group with an azide group followed by a single step conversion of the azide to a BOC-protected amine is the most suitable and straightforward method for the synthesis of **21** from commercially available terminal bromo alcohols.[89,90] 9-bromo-1-nonanol **19** was reacted with diphenylphosphoryl azide (DPPA) in the presence of diisopropyl azodicarboxylate (DIAD) and triphenylphosphine in THF at 0 °C to afford compound **20**. The bromide group, essential functionality for the alkylation remained unaffected (Scheme 2.17). Compound **21** was obtained by a one pot conversion of the azido group of **20** to a BOC-protected amine group. A solution of compound **20** and BOC anhydride in ethyl acetate was added to a dihydrogen saturated suspension of Pd/C in ethyl acetate. Presaturation of Pd/C with dihydrogen was found to be essential to avoid the formation of side products due to dehydrogenation of the amine, since Pd/C also serves as a dehydrogenation catalyst for conversion of amines to nitriles, and the combined addition of compound **20** and BOC anhydride is important to prevent the formation of unprotected amine.

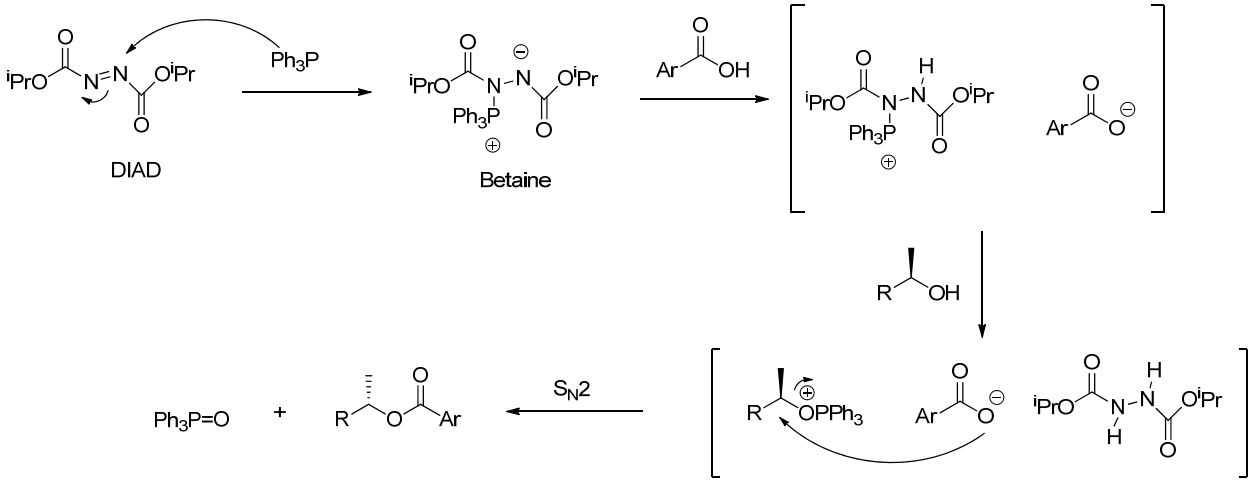


19 **20** **21**

Scheme 2.17: Synthesis of tert-butyl (9-bromononyl)carbamate 21

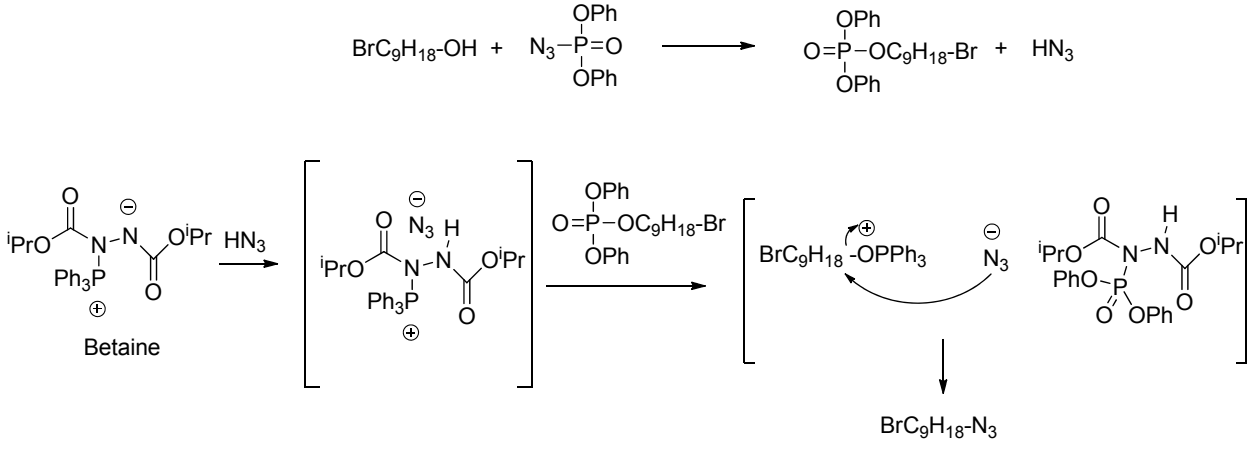
The Mitsunobu reaction occurs under comparatively milder condition (0 °C to room temperature) in neutral environment. Various functional groups can be utilized in these kinds of mild reaction conditions and the only essential requirement is a sufficient acidity of the nucleophile to be

deprotonated by the betaine intermediate (pKa 13). A general mechanism of the Mitsunobu reaction is shown in Scheme 2.18 based on a carboxylic acid as nucleophile. Several other nucleophiles, such as acidic alcohols, azides, thiols, amides, sulfomamides and imides, have also been used for this reaction.



Scheme 2.18: General mechanism for Mitsunobu reaction between carboxylic acid and alcohol

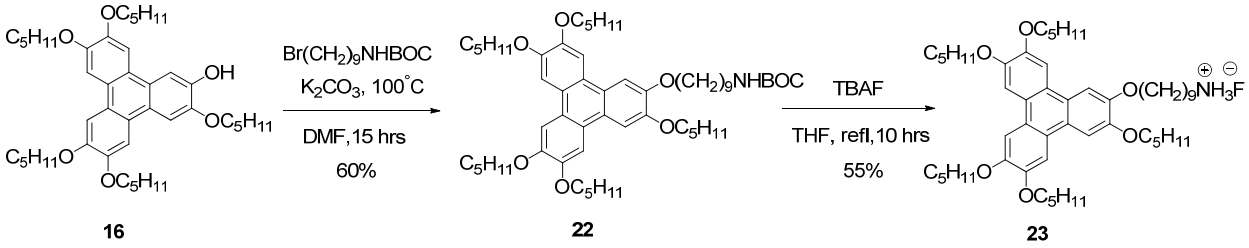
Here, the acidic nucleophile is HN_3 but the usage of this highly sensitive compound was avoided by using DPPA as an azide source for the substitution of the hydroxyl group. However, the reaction of DPPA with bromoalcohol **19** generates HN_3 in situ, which then protonates the betaine (Scheme 2.19).



Scheme 2.19: Mechanism of azidation reaction of alcohol using DPPA

2.3.5 Synthesis of 2-((9-fluorononyl)oxy)-3,6,7,10,11-pentakis (pentyloxy) triphenylene, ammonium salt (23)

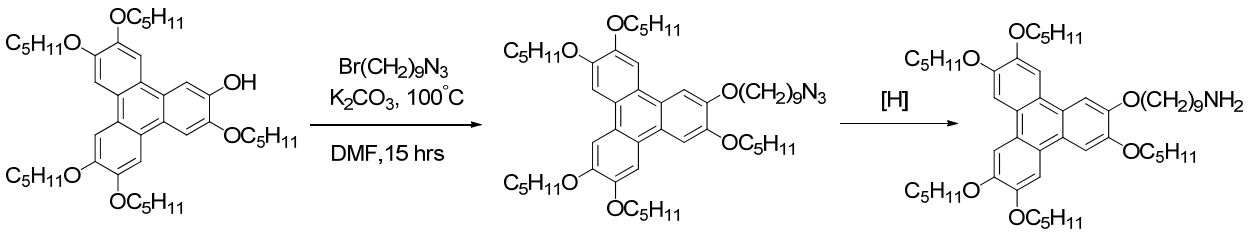
Alkylation of compound **16** with **21** in the presence of potassium carbonate gave compound **22** in 60% yield. Deprotection of the Boc group with 1 M tetrabutyl ammonium fluoride (TBAF) solution in THF generated ammonium salt **23** as a stable compound. It is necessary to maintain absolutely dry conditions for the deprotection of the BOC group; otherwise this method is ineffective and low yielding. Most other deprotection methods for BOC protected amines require the use of strong acids, such as HCl and trifluoroacetic acid, that also cleave the pentyl ether bonds (Scheme 2.20).



16 **22** **23**

Scheme 2.20: Synthesis of 2-((9-fluorononyl)oxy)-3,6,7,10,11-pentakis(pentyloxy)triphenylene, ammonium salt 23

we also tested another synthetic pathway to the unprotected amine **25** that has previously been reported by Paraschiv *et al*.[91] Alkylation of **16** was carried out with azide **20** to obtain compound **24** which was finally reduced using triphenyl phosphine or hydrogen in presence of Pd/C to give the unprotected amine **25** (Scheme 2.21). This approach gave reasonably good yields (50%) but was abandoned because amine **25** is rather sensitive to air and moisture in contrast to its hydrofluoride salt **23**.

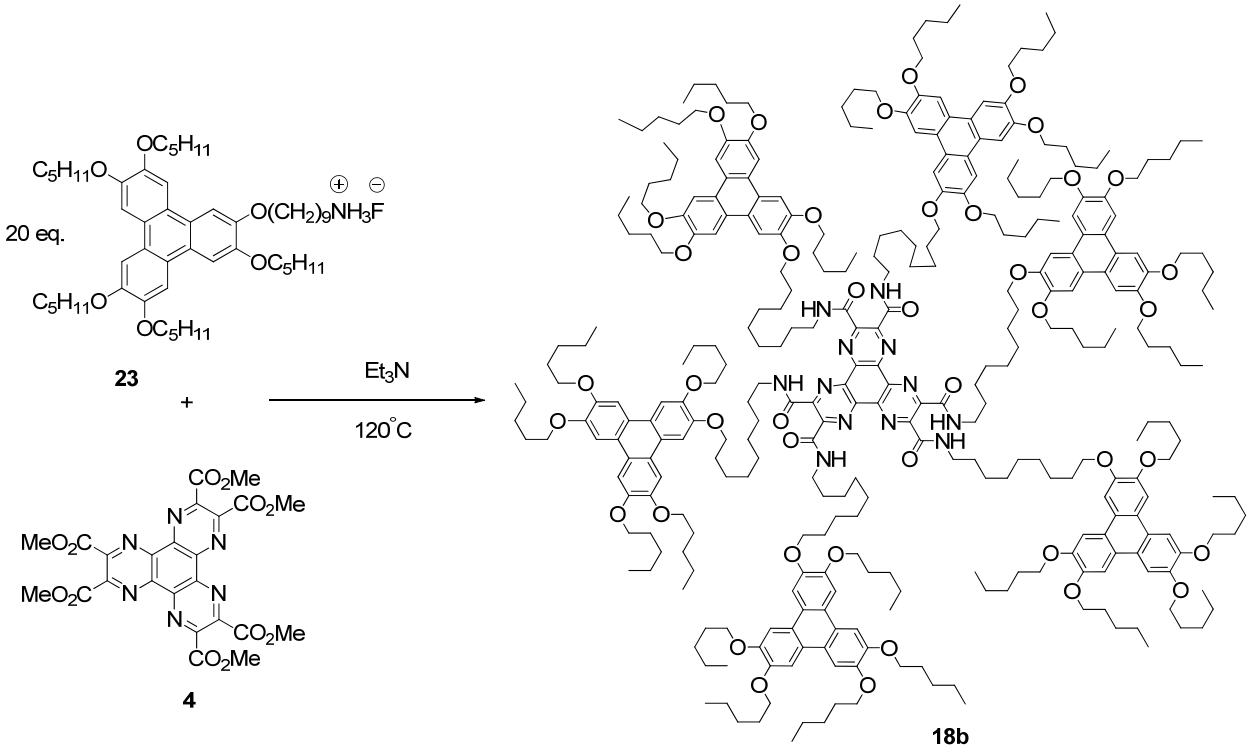


16 **24** **25**

Scheme 2.21:Synthesis of 9-((3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yl)oxy)nonan-1-amine 25

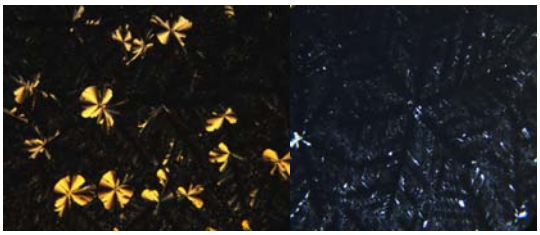
2.3.6 Synthesis of heptamer amide (18b)

Heptamer amide **18b** was synthesized by reacting 20 eq. of **23** with hexamethoxy carbonyl HAT **4** in the presence of triethylamine at 120° C for 4 days (Scheme 2.22). Size exclusion chromatography removed excess **23** and **25** but remaining impurities, that probably included decomposition products of **25**, had to be removed by preparative TLC on silica gel and several recrystalizations from CH_2Cl_2/MeOH (1:1). ^{13}C- and ^{1}H-NMR spectra of **18b** confirmed the formation of **18b** but still contain absorption peaks of impurities.



Scheme 2.22: Synthesis of heptamer amide 18b

2.4 Mesomorphism of Heptamer ester (18a)



$$Col_h \underset{195.24\ (52.40)}{\overset{197.10\ (-68.86)}{\rightleftharpoons}} iso$$

Figure 2-6 :Phase behavior of 18a as determined by POM, DSC and XRD (Temperature in ºC and enthalpy in kJ/mol). Pictures obtained from POM at 28°C.

Variable temperature POM measurements of **18a** revealed a birefringent phase at 25 °C that cleared into an isotropic liquid at 198°C (Fig. 1). The texture was focal conical and large homeotropic domains were observed on glass substrates upon slow cooling (at 0.1 °C/min) from isotropic state. No textural changes occurred in the monitored temperature range.

Differential Scanning Calorimetry (DSC) of **18a** confirmed the reversible Col_h phase to isotropic transition at 197.1 °C. Its unusually high molar transition enthalpy of 69 kJ/mol can be reasoned with the contribution of seven discotic units per molecule. DSC also confirms the absence of any crystallization down to -50 °C. It is likely that the material undergoes a glass transition at about 55 °C because a softening is observed by POM but no glass transition was resolved by DSC even at scan rates of 30 °C/min.

X-ray diffraction patterns of **18a** reveal a hexagonal columnar packing at two length scales (Fig. 2). The reflection at 1.7 nm consistent with (10) reflections usually observed for Col_h phases of hexapentyloxy-

triphenylene while the reflections at 4.4 nm and 2.6 nm are interpreted as the (10) and (11) reflections of the hexagonal packing of the heptamers.

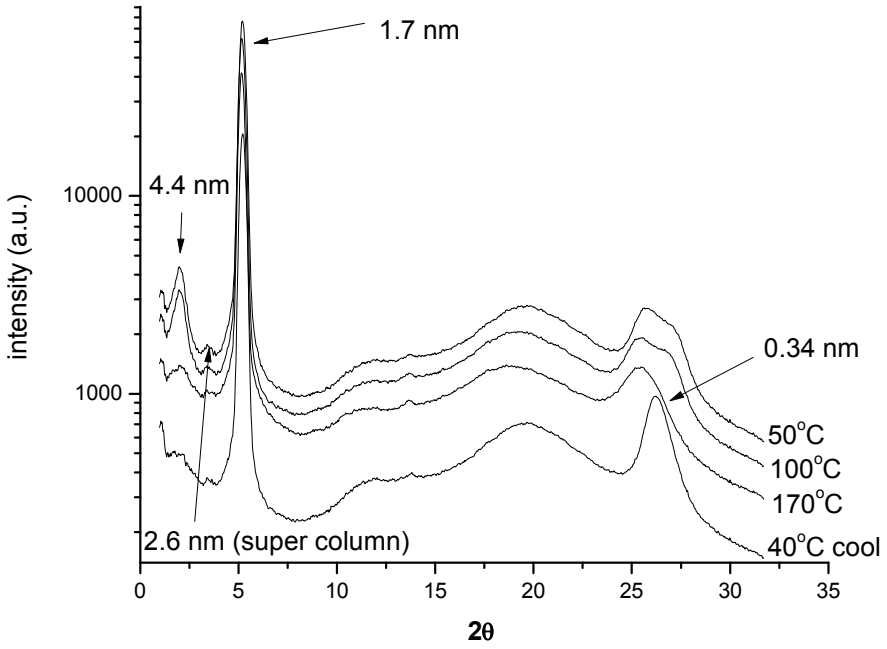


Figure 2-7 :Powder VT-XRD pattern of 18a. The y-axis has been shifted for clarity.

The reflection of the intracolumnar stacking order at about 0.34 nm remains of high intensity even at 170 °C and is split into two reflections for the material as precipitated from solution. This splitting could be explained with different packing distances between the hexaazatriphenylene cores and the triphenylene ligands in the super-column but only one reflection of intermediate peak position is observed after heating the material to 170 °C.

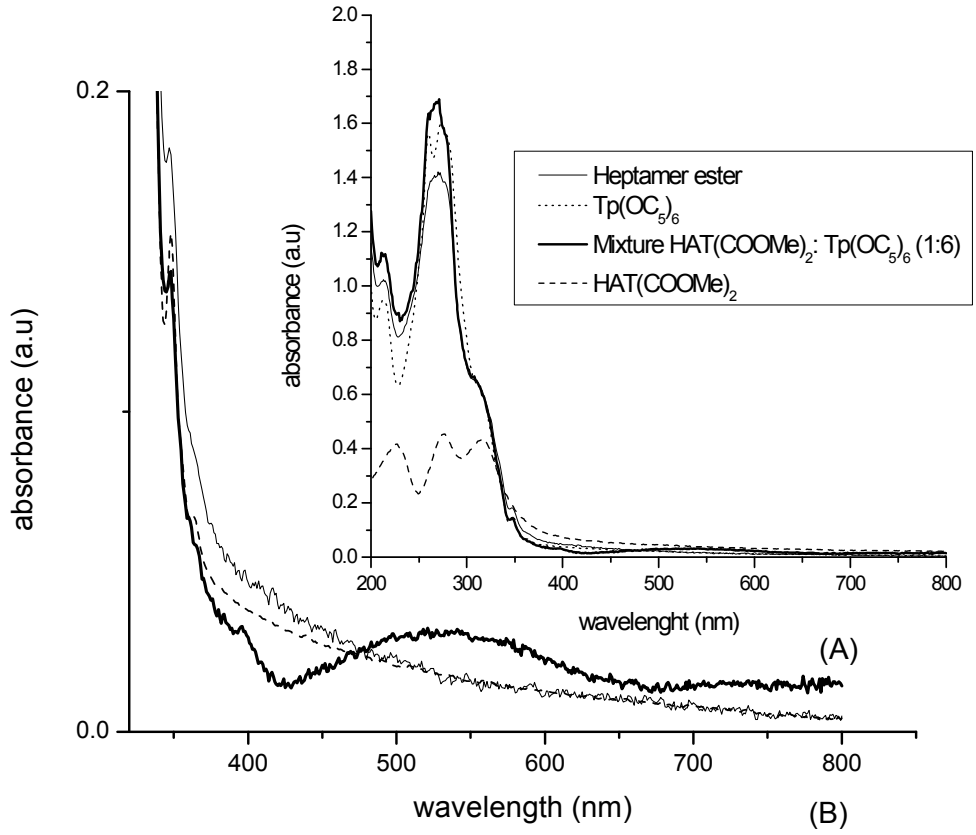


Figure 2-8 :UV/VIS Spectra of thin films of 18a on quartz .

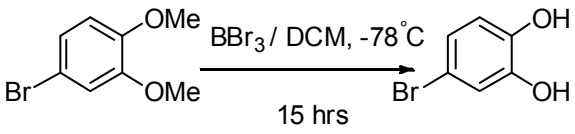
The formation of the super-column is independently verified by UV-Vis spectroscopy on thin films of **18a** and mixtures of a hexaazatriphenylene and a triphenylene on quartz (Fig. 3). A 1:6 mixture of the hexaazatriphenylene hexamethyl carboxylate and the hexapentyloxy triphenylene shows a weak absorption at around 550 nm that is absent in the individual compounds and interpreted as a charge transfer band. This absorption is absent in the film of **18a**, which confirms the absence of columnar stacks that contain both types of cores.

2.5 Conclusions

A feasible synthetic pathway to heptamer ester **18a** and heptamer amide **18b** has been developed but purification was successful only for the heptamer ester.The heptamer amide was more difficult to purify because of its H-bonding amide groups and decomposition products of triphenylene **25**. Most promising for further purification is the use of GPC stationary phases with smaller exclusion volumes while chromatographic separations on silica are limited by the strong aggregation of **18b**. Phase behavior of **18a** as determined by POM, DSC and XRD confirms the formation of super-column. Furthermore, the structure of **18b** must be confirmed by MS and EA measurements before their mesomorphism is studied by polarized optical microscopy, thermal analysis, X-ray diffraction, and variable temperature UV-Vis and IR spectroscopy.

2.6 Experimental

2.6.1 Synthesis of 4-bromo benzene 1,2 diol (6)[92]

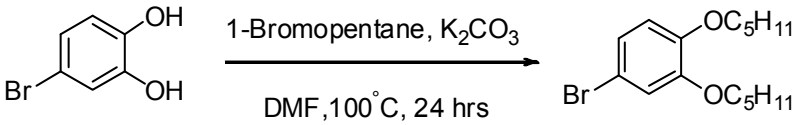


To a stirred solution of 4 bromo 1,2 dimethoxy benzene (20 g, 92.1 mmol) in 100ml dry dichloromethane, BBr_3 (16 ml, 94 mmol) was added drop wise under argon gas at -78°C over a 5 minute. Then the stirred solution was allowed to warm up to room temperature overnight. The mixture was cooled to 0 °C again and 0.1M HCl (300 mL) was added drop wise until it became clear. The mixture was extracted with (50 mL X 3) diethyl ether and dried using anhydrous $MgSO_4$, concentrated in vacuo. Flash

chromatography on silica using 2:1(ethyl acetate:hexanes) to give 4-bromo benzene 1,2 diol (20 g, 98%) as a white powder.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.0 (s, 2H), 6.7- 7.0 (m, 3H) (consistent with reported values[92])

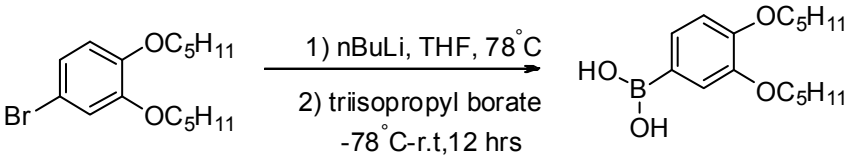
2.6.2 Synthesis of 4 bromo 1, 2 dipentyloxybenzene(7). [93-96]



To a 500 mL round bottom flask equipped with magnetic stirrer, 4-bromo benzene 1,2 diol (20 g, 105 mmol) , 1-bromo pentane (264 mmol, 39.9 g), potassium carbonate (264 mmol, 36.4 g) and DMF (250 mL) were added. The mixture was stirred under argon at 100 °C for 24 hrs. The reaction mixture was filtered and brown colored solution was concentrated *in vacuo* to get a brown oily residue. The residue was purified by column chromatography on neutral aluminum oxide eluting with hexanes to yield 4-bromo-1, 2-dipentyloxybenzene as a colorless oil (31 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.97 (t, J = 7.0 Hz, 6H), 1.4 (m, 8H), 1.8 (m, 4H), 3.9 (t, J = 6.0 Hz, 4H), 6.7 - 7.0 (m, 3H); (consistent with reported values[93-96])

2.6.3 Synthesis of 3,4-dipentyloxybenzeneboronic acid(8). [97-98]

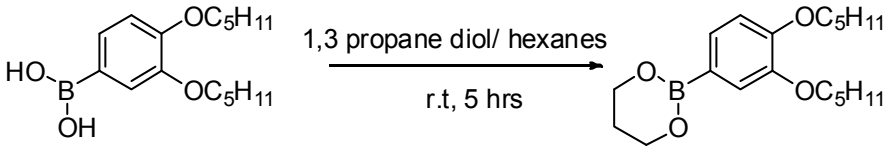


To a 250 mL round bottom flask equipped with magnetic stir bar, was added 4-bromo-1,2-dipentyloxybenzene (10 g, 30.3 mmol). Distilled THF (50 mL) was added to it and the mixture was stirred at -78°C .To it 1.6(M) nBuLi (20 mL, 32 mmol) was added drop wise under argon atmosphere. Once the addition was complete the mixture was kept stirring for 3 hrs at -78°C .Distilled isopropylborate (10.4

mL, 8.47 g, 45.4 mmol) was added drop wise to it over 15 minutes .The mixture was allowed to reach room temp and stirred for 12 hrs.The mixture was cooled to 0°C and 0.1M HCl (100 mL) was added to it and stirred for 2 hrs. Mixture was extracted with diethyl ether (3 X 50 mL) and dried using anhydrous $MgSO_4$, concentrated *in vacuo*, recrystallized from hexanes to give 3,4-dipentyloxybenzeneboronic acid (5.6 g, 63%) of a white solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ):, 0.9 (t, J = 7.1 Hz, 6H), 1.4 (m, 8H), 1.8 (m, 4H), 4.0 (t, J = 6.2 Hz, 4H), 4.5 (broad, 2H), 7.0– 7.8 (m, 3H); (consistent with reported values[97-98])

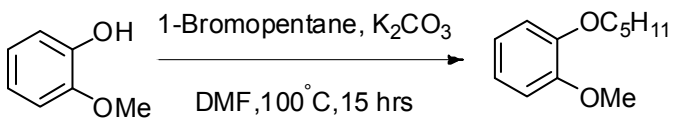
2.6.4 Synthesis of 2-(3, 4-bis-pentyloxy-phenyl)-[1, 3, 2]-dioxaborinane(9). [13,99]



To a 250mL round bottom flask 3,4-dipentyloxybenzeneboronic acid (5 g, 17 mmol), 1,3-propanediol (2.6 g, 34 mmol) and 100 mL hexanes were added. The mixture was stirred at room temperature for 5 hrs. The mixture was then extracted with diethyl ether (3 X 50 mL), dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting pale yellow oily residue was purified by fractional distillation at 210°C to yield 2-(3,4-bis-pentyloxy-phenyl)-[1,3,2]-dioxaborinane as a colorless oil (3.58 g, 63%)

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, J= 7.0 Hz, 6H), 1.4 (m ,8H), 1.8 (m,4H), 2.0 (m ,2H), 4.0 (m, 4H), 4.1 (t, J= 6.3 Hz, 4H), 6.8– 7.3 (m, 3H); (consistent with reported values[13,99])

2.6.5 Synthesis of 1-pentyloxy-2-methoxybenzene(12). [24,78,100]



Guaiacol (20 g, 0.161 mol), 1-bromopentane (36.479 g, 0.242 mol), potassium carbonate (fine powder, 33.446 g, 0.242 mol) were added to 200 mL of DMF (filtered through Al_2O_3 of activity 1) and heated to 100°C for 15 hrs. The mixture was filtered, combined with toluene (200 mL) and extracted with water (4 x 200 mL) dried using anhydrous $MgSO_4$ and concentrated in vacuo The brownish organic layer was concentrated in vacuum and filtered through a short column of Al_2O_3 (activity 1) to give a pale yellow solution. Toluene was removed and the remaining pale yellow oil was distilled under vacuum to give 1-pentyloxy-2-methoxybenzene as a colourless liquid. (24.815 g, 79%)

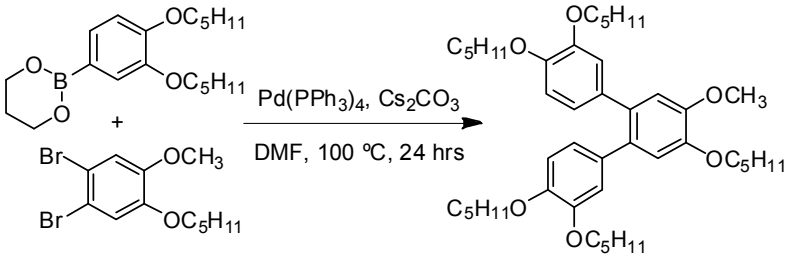
^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, J = 7.1 Hz, 3H), 1.4 (m , 4H), 1.8 (m, 2H), 3.8 (s, 3H), 4.0 (t, J = 6.3 Hz, 2H), 6.9 (m, 4H); (consistent with reported values[24,78,100])

2.6.6 Synthesis of 1, 2-dibromo-4-pentyloxy-5-methoxybenzene(13). [93-96]

1-methoxy-2-pentyloxy benzene (20 g, 106 mmol) was dissolved in 250 mL dichloromethane and cooled to 0°C .To it Br_2 (2.1 equiv, 223 mmol, 35.7 g, 11.5 mL) was added using a dropping funnel, purging with argon, trapping HBr in 5(M) KOH solution in Erlenmeyer flask .The reaction system was left to warm upto room temperature gradually to complete the reaction for 24 hrs. The reaction mixture was washed with 10% aqueous Na_2CO_3 (3 X 100 mL) and finally with water (3 X 100 mL) to get rid of excess HBr. The organic layer was dried using anhydrous $MgSO_4$, concentrated *in vacuo* to obtain dark yellow solid which was recrystallized from methanol to yield 1,2-dibromo-4-pentyloxy-5-methoxybenzene as a pale yellow crystals (34.32 g, 92%)

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, J = 7.0 Hz, 3H), 1.4 (m, 4H), 1.8 (m, 2H), 3.8 (s , 3H), 3.9 (t, J = 6.1 Hz, 2H), 6.9 (s , 2H); (consistent with reported values[93-96])

2.6.7 Synthesis of 4'-methoxy-3,3'',4,4'',5'-pentakis (pentyloxy)-1,1':2',1''-terphenyl (14). [39,78,100.]

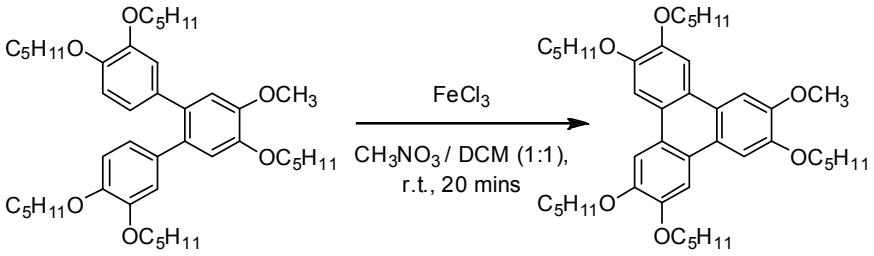


To a 250 mL round bottom flask with a magnetic stir bar, 1,2-dibromo-4-methoxy-5-pentyloxy benzene (4 g, 9 mmol), 2-(3,4-bis-pentyloxy-phenyl)-[1,3,2]-dioxaborinane (8 g, 24 mmol), Cs_2CO_3 (7.82 g, 24 mmol) were added. Then the flask was purged with argon and palladium(0)tetrakis triphenyl phosphine (500 mg, 22 mmol) was added to it. To this mixture 200 mL DMF was added, heated to 100°C and stirred for 24 hrs. The reaction mixture was then cooled to room temperature and 200 mL distilled water was added, extracted with (3 X 100 mL) diethyl ether and dried using anhydrous magnesium sulfate then concentrated *in vacuo* to obtain yellowish oil. The yellowish oil was further purified by column chromatography on silica using 2:1 hexanes: diethyl ether as an eluent to yield crude 4'-methoxy-3,3'',4,4'',5'-pentakis(pentyloxy)-1,1':2',1''-terphenyl as about (4.975 g, 7.2 mmol, 80%) pale yellow oil which was used for the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, J= 6.0 Hz, 15H), 1.5 (m, 20H), 1.9 (m, 10H), 3.7 (t, J= 6.0 Hz, 4H), 3.9 (s , 3H), 4.0 (d, J= 6.0 Hz, 4H), 4.1 (t, J= 6.0 Hz, 2H), 6.6 (m, 2H), 6.7 (m, 4H), 6.9 (s, 2H).

(consistent with reported values[39,78,100]).

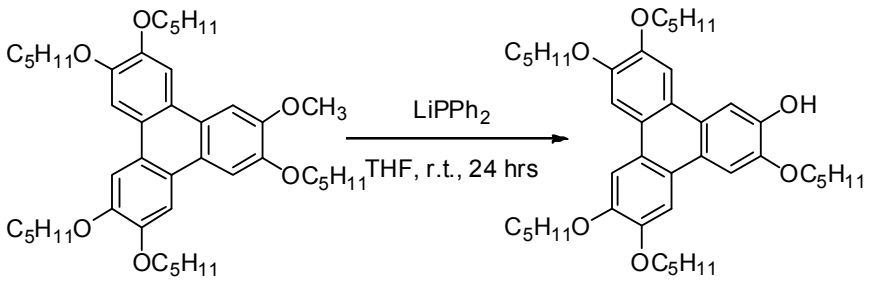
2.6.8 Synthesis of 2-methoxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene (15).[39,78,100.]



To a stirred solution of 4'-methoxy-3,3'',4,4'',5'-pentakis(pentyloxy)-1,1':2',1''-terphenyl (4.975 g, 7.2 mmol) in 200ml 1:1 mixture of $MeNO_2$: dichloromethane, $FeCl_3$ (3.440 g, 21.6 mmol) was added portion wise using a solid additional funnel over 10 minutes under an argon atmosphere at 0°C. The mixture was stirred for 20 minutes at 0°C. Then 150 mL anhydrous MeOH was added drop wise to precipitate out the product.The mixture was kept at 5°C for 4 hrs and filtered to get white solids which were recrystallized from methanol to give 2-methoxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene as white solid (3.472 g, 70%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, J = 6.9 Hz, 15H), 1.5 (m, 20H), 1.9 (m, 10H), 4.1 (s, 3H) , 4.2 (t, J = 6.1 Hz, 10H), 7.7 (s, 6H); (consistent with reported values[39,78,100]).

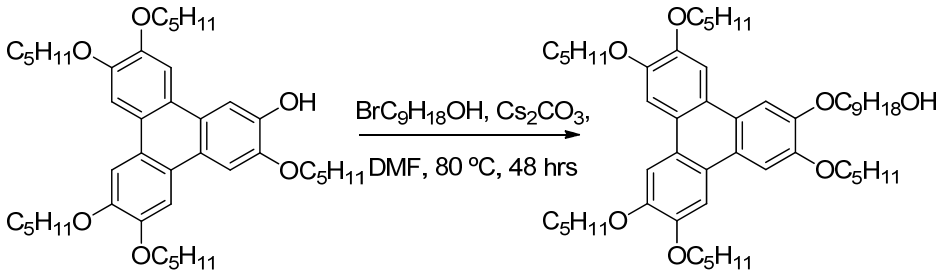
2.6.9 Synthesis of 2-hydroxy,3,6,7,10,11-pentakis(pentyloxy)triphenylene(16).[39]



To 20 mL of dry THF were added under argon 0.6 mL (2.9 mmol) of diphenylphosphine and 1.7 mL (2.7 mmol) of *n*BuLi (1.6 M solution in THF) and the mixture was stirred for 30 min at room temperature. 2-methoxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene (500 mg, 0.7 mmol), dissolved in 5 mL of dry THF, was added to the deep red solution *via* a syringe. The mixture was stirred for 24 h at room temperature, quenched with 10 mL of 0.1 M HCl and poured into 25 mL of diethyl ether. The ether phase was washed with water (3 x 25 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Column chromatography (silica gel, 4:1 hexane/diethyl ether) and recrystallization from EtOH gave 2-hydroxy,3,6,7,10,11-pentakis(pentyloxy)triphenylene (0.393 g, 83%) as an off-white solid.

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.9 (t, J = 7.0 Hz, 15H), 1.3 - 1.5 (m, 20H), 1.8 - 1.9 (m, 10H), 4.2- 4.3 (m, 10H), 5.9 (broad, 1H), 7.7 - 7.9 (m, 6H); (consistent with reported values[39])

2.6.10 Synthesis of 2-(9-hydroxynonyloxy)-3,6,7,10,11-pentakis (pentyloxy) triphenylene(17).[101]

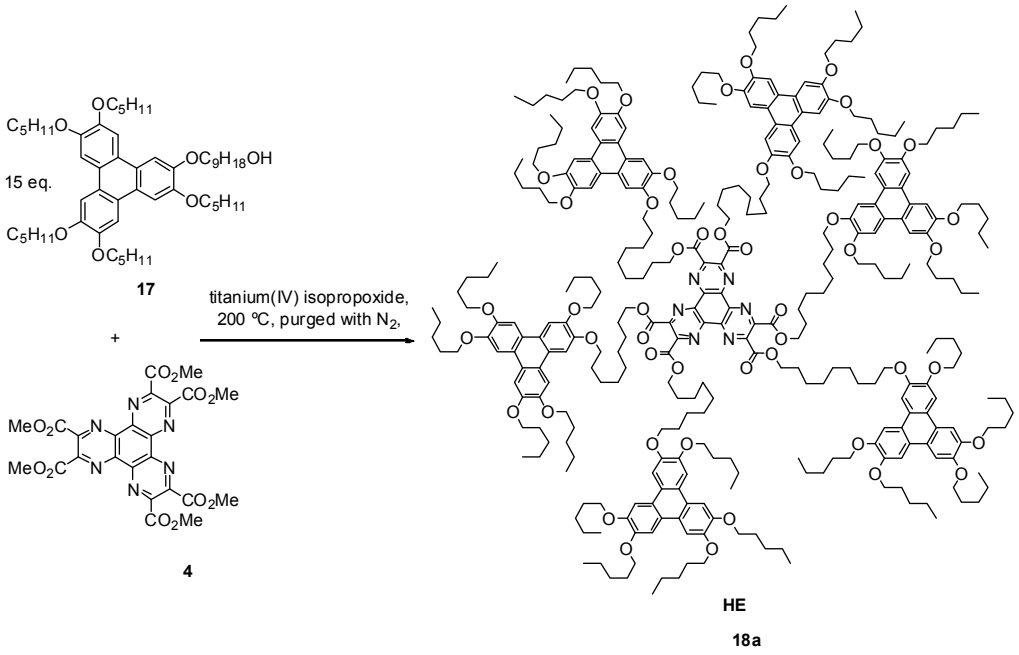


To a 200 mL round bottom flask equipped with a magnetic stir bar was added 2-hydroxy,3,6,7,10,11-pentakis(pentyloxy)triphenylene (300 mg, 0.44 mmol) , bromononanol (150 mg, 0.67 mmol), potassium carbonate (93 mg, 0.67 mmol) and 80 mL of dried DMF. The reaction was heated to 80°C and stirred for 48 hours. Then 25 mL of 0.1 M HCl (aq.) was added to the DMF and the solution was washed with DCM (3 x 25 mL). The organic layers were collected and rotovaped to near dryness. The product was recrystallized from 95% EtOH to give 240 mg of an off-white product (67%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.97 (t, J= 7.19 Hz, 15H), 1.3 - 1.59 (m , 32H), 1.95 (p, J = 6.9 Hz, 12H), 3.63 (t, J=6.9 Hz, 2H) , 4.0 (t, J= 6.5 Hz, 1H) 4.23 (t, J= 6.5 Hz, 12H), 7.83 (s, 6H).

^{13}C NMR (300 MHz, $CDCl_3$, δ): 14.24, 22.69, 25.87, 26.28, 28.48, 29.25, 29.56, 29.72, 32.93, 69.80, 107.42, 123.72, 149.078. (consistent with reported values[101])

2.6.11 Synthesis of Star-shaped Heteroheptamer Ester (18a):



To 10 mL r.b flask equipped with a magnetic stir bar was added hexaazatriphenylene 2,3,6,7,10,11-hexakis(methyl ester) (18 mg, 0.031 mmol) and 2-(9-hydroxynonyloxy)-3,6,7,10,11-pentakis(pentyloxy)triphenylene (200 mg, 0.24 mmol). The flask was then transferred to the glovebox where titanium (IV) isopropoxide (18 mg, 0.062 mmol) was added. The flask was then sealed, removed from the glovebox and placed under a constant stream of nitrogen. The slurry was then heated to 160°C and left to stir for 48 hours. The slurry was then allowed to cool to room temperature and water (5 mL) was added to quench the remaining titanium (IV) isopropoxide. The crude product was dissolved in EtOAc and run through a column of size-exclusion gel to remove small impurities. The crude product was

then dried under vacuum and then dissolved in a small amount of DCM (5 mL) and run through a column of silica gel with DCM to remove the excess triphenylene side chain. The heptamer was then eluted with diethyl ether. The solvent was removed under vacuum and finally crude product was recrystallized from CH_2Cl_2/MeOH (1:1) solution to yield 82 mg (50%) of dark purple product.

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.97 (t, J= 6 Hz, 90H), 1.44 - 1.55 (m , 192H), 1.94 (broad, 72H), 4.21 (broad, 72H) , 4.53 (broad, 12H), 7.78 (s, 36H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 14.15, 22.62, 25.86, 26.24, 28.42, 29.20, 29.59, 67.46, 69.69, 107.31, 123.56, 141.28, 146.84, 148.99, 163.90.

2.6.12 Synthesis of 1-azido-9-bromononane (20).

$$Br(CH_2)_9OH \xrightarrow[THF,\ 0^{\circ}C,12\ hrs]{PPh_3,\ DIAD,\ DPPA} Br(CH_2)_9N_3$$

In an oven dried round bottom flask, 9-bromononan-1-ol (5.580 g, 25 mmol) was dissolved in 150 mL of THF. To this mixture PPh_3 (7.200 g, 27.5 mmol) was added and the solution was stirred for 15 minutes at 0°C in an ice bath. Then, diisopropylazodicarboxylate (DIAD) (6 mL, 27.5 mmol) was added via pipette over 1 minute, followed by diphenylphosphorylazide (DPPA) (6.53 mL, 27.5 mmol) via pipette, over 1 minute. The resultant yellow cream colored mixture was allowed to warm up to room temperature and stirred over night. The crude mixture was concentrated to half of its volume and 25 mL of dry diethyl ether along with 10 mL of hexanes were added to the solution, producing a white cloudy precipitate. The flask was then chilled in the freezer for 1 h to allow excess PPh_3 and generated $OPPh_3$ to precipitate out. The mixture was filtered and the collected precipitate was washed with dry diethyl ether. The collected filtrate was concentrated to a quarter of the original volume. A clear yellow/orange

viscous oil formed as a separate phase and was purified by column chromatography (silica gel, ethyl acetate: hexane 1:4) to yield the pure 1-azido-9-bromononane as a yellow oil (4.033g, 65%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.30-1.41 (m, 10H), 1.55-1.58 (m, 2H), 1.84(p, J=5.1Hz, 2H), 3.25(t, J=3.6Hz, 2H), 3.40 (t, J=3.9Hz, 2H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 26.78, 28.21, 28.75, 28.92, 29.14, 29.37, 32.88, 34.12, 51.57.

MS [HR-CI]: Theoretical: 205.0592 [M - N_2]; Found: 205.0587 [M - N_2]$^{+}$.

2.6.13 .Synthesis of tert-butyl (9-bromononyl)carbamate(21).

$$Br(CH_2)_9N_3 \xrightarrow[EtOAC,\ r.t,15\ hrs]{(BOC)_2O,\ 5\%\ Pd/C} Br(CH_2)_9NHBOC$$

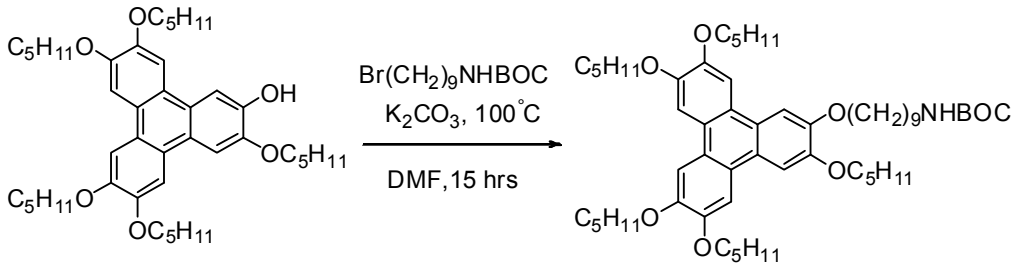
A suspension of 5% Pd/C (10 mg) in 100mL EtOAc was bubbled with hydrogen for 25 mins. To this, mixture of 1-azido-9-bromononane (2.482 g, 10 mmol) and di-*t*-butyldicarbonate (2.615 g, 12mmol) in EtOAc were added; the resulting solution was stirred under hydrogen at room temperature until disappearance of azide as monitored by TLC .The reaction mixture was then filtered, Subjected to the addition of NaOH (10 mL, 1 M), and 20 mL MeOH, and stirred for 15 hrs at room temperature to remove unreacted $(BOC)_2O$. The mixture was extracted with EtOAc and washed with water several times until neutral, dried using $MgSO_4$, and concentrated in vacuo. The resulting solid was purified using column chromatograph on silica gel eluting with 2:1 Hexanes: EtOAc to give tert-butyl (9-bromononyl)carbamate as a white solids (1.827 g, 55%)

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.29 (s, 9H), 1.43 (s, 12H) 1.84 (p, J=6.9Hz, 2H), 3.06-3.12 (m, 2H), 3.4(t, J=6.82Hz, 2H), 4.48 (broad, 1H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 26.78, 28.17, 28.48, 28.71, 29.2, 29.37, 30.11, 32.84, 34.01, 40.65, 78.08, 156.03

MS [HR-CI]: Theoretical: 321.1303; Found: 321.1309.

2.6.14 Synthesis of tert-butyl (9-((3,6,7,10,11-pentakis(pentyloxy) triphenylen-2-yl)oxy)nonyl) carbamate (22).



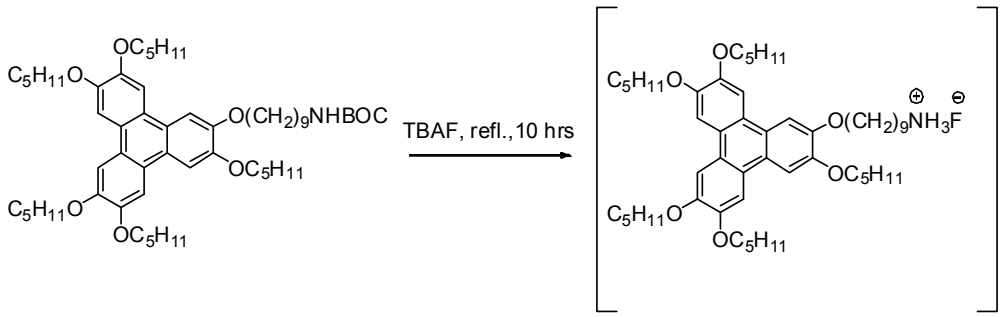
To a 200 mL round bottom flask equipped with a magnetic stir bar was added **16** (300 mg, 0.44 mmol), tert-butyl (9-bromononyl) carbamate (216 mg, 0.67 mmol), potassium carbonate (93 mg, 0.67 mmol) and 80 mL of dried DMF. The reaction was heated to 100°C and stirred for 15 hours. Then 25 mL of 0.1 M HCl (aq.) was added to the DMF and the solution was washed with DCM (3 x 25 mL). The organic layers were collected dried using $MgSO_4$, concentrated in vacuo. Crude product was recrystallized from MeOH to give pure tert-butyl(9-((3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yl)oxy)nonyl)carbamate as a white solid (270 mg, 67%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.99 (t, *J*= 6.0 Hz, 15H), 1.33 (s ,3H), 1.43-1.58 (m, 38H), 1.95 (p, J=6.6Hz, 12H), 3.09-3.11 (m, 2H),4.23 (t, J=6.6 Hz, 12H), 4.49 (br, 1H), 7.83 (s, 6H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 14.24, 22.68, 26.29, 26.96, 28.48, 29.24, 29.41, 29.58, 29.69, 30.21, 40.74, 69.78, 107.40, 123.71, 149.06, 156.09.

MS [HR-CI]: Theoretical: 915.6588; Found: 915.6561.

2.6.15 Synthesis of heptamer amide(18b)

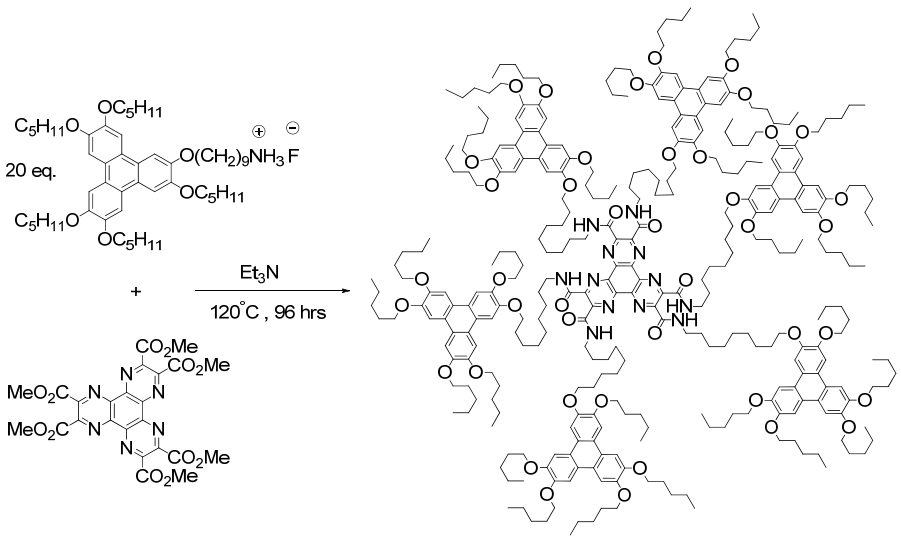


To a stirred solution of tert-butyl (9-((3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yl)oxy)nonyl)carbamate (917 mg, 1 mmol) in 100 mL THF, 3 mL 1(M) tetrabutyl ammonium fluoride solution in THF was added at room temperature.Then the mixture was heated to reflux for 10 hrs. Reaction progress was monitored by proton NMR. THF was removed under reduced pressure and mixture was extracted using (3 X 50 mL) DCM .The organic layer was dried using anhydrous $MgSO_4$ and concentrated *in vacuo* .The crude product was precipitated out from mixture using MeOH (669 mg, 80%) which was used for the next reaction without further purification.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1 (t, J= 5.3 Hz, 15H), 1.36- 1.95 (m, 42H), 1.95-2.26 (m, 2H), 2.94- 3.00 (m, 2H), 4.03 (m, 3H), 4.23 (t, J= 6.68 Hz, 12H), 7.84 (s, 6H)

^{13}C NMR (300 MHz, $CDCl_3$, δ): 14.20, 19.76, 20. 53, 22.73, 26.39, 27.13, 28.41, 29.18, 29.73, 37.19, 52.41, 69.75, 107.43, 123.58, 123.68, 149.06.

MS [HR-CI]: Theoretical: 815.6064; Found: 815.6043.



18b

To 50 mL r.b flask equipped with a magnetic stir bar was added hexaazatriphenylene 2,3,6,7,10,11-hexakis(methyl ester) (18 mg, 0.031 mmol),9-((3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yl)oxy)nonan-1-aminium fluoride (518 mg, 0.62 mmol)and 2 mL Et_3N . The flask was then sealed and placed under a constant stream of nitrogen. The mixture was then heated to 120°C and left to stir for 96 hours. To the mixture 20 mL DCM was added and washed with water (3 X 20 mL). The organic layer was dried using anhydrous $MgSO_4$ and run through a column of silica gel to remove the excess triphenylene side chain. The heptamer was then eluded with pyridine. Pyridine was removed under reduced pressure and the resultant solid was dissolved in 50 mL of DCM washed with 2(M) acetic acid (3 X 20 mL) finally with distilled water (3 X 20 mL).The organic layer was dried using anhydrous $MgSO_4$ and concentrated *in vacuo* to give Heptamer Amide as a purple solid (82 mg, 50%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 0.9 (broad, 90H), 1.44-1.61 (m, 204H), 1.94 (broad, 72H), 3.49-3.74 (m, 6H), 4.21 (broad, 72H), 7.79 - 7.82 (m, 36H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 14.17, 22.64, 28.44, 29.20, 29.75, 40.49, 62.79, 69.72, 107.37, 123.62, 129.78, 138.55, 149.01.

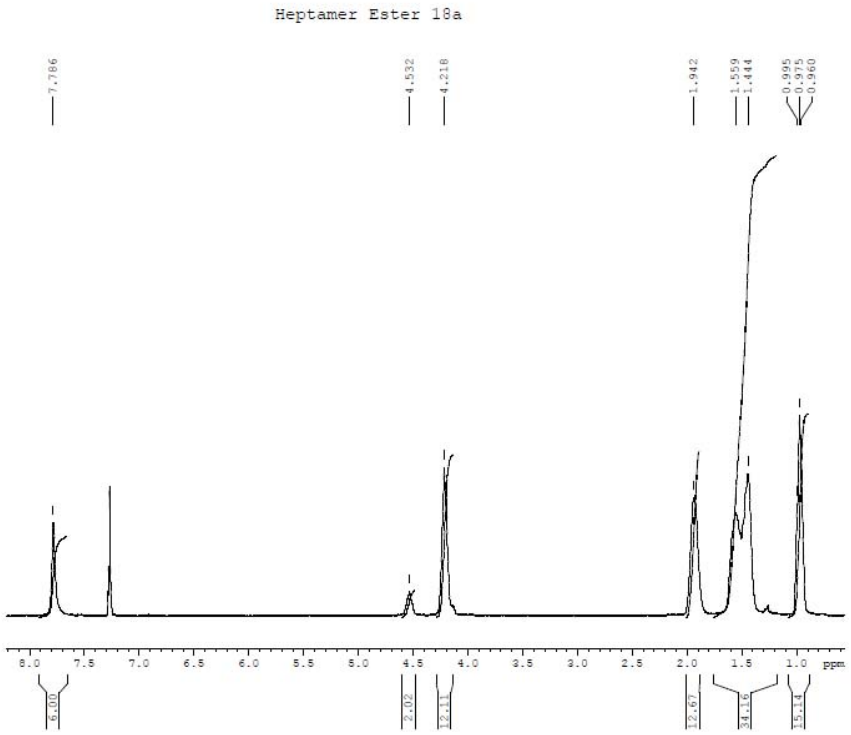


Figure 2-9: ^{1}H-NMR of Heptamer Ester 18a (in $CDCl_3$).

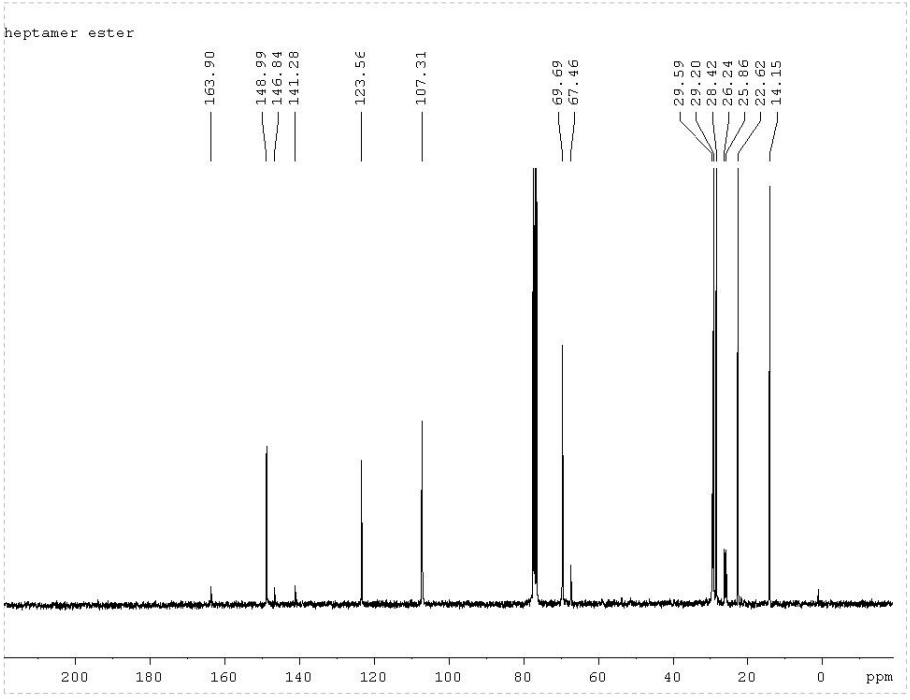


Figure 2-10: ^{13}C NMR of Heptamer Ester 18a (in $CDCl_3$).

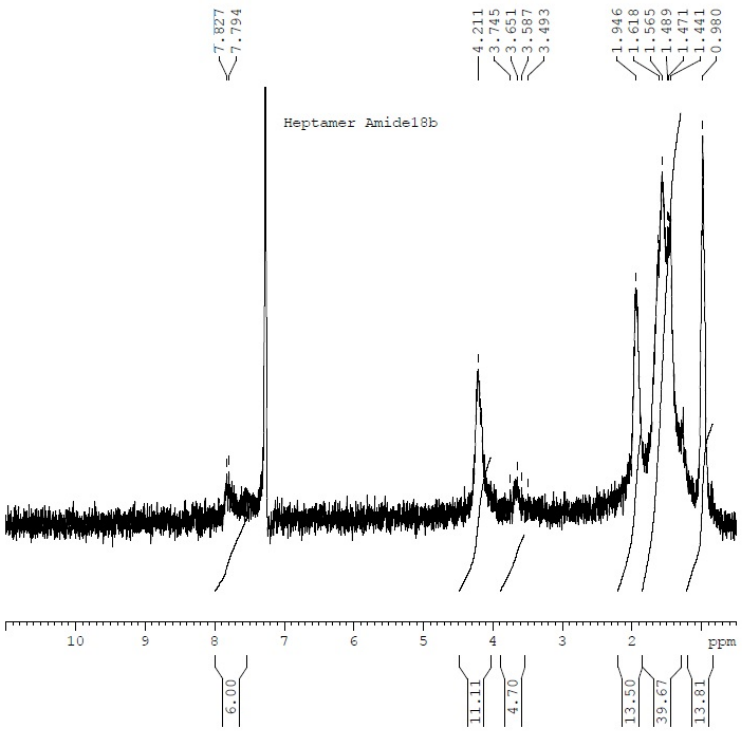


Figure 2-11: ^{1}H-NMR of Heptamer Amide 18b (in $CDCl_3$)

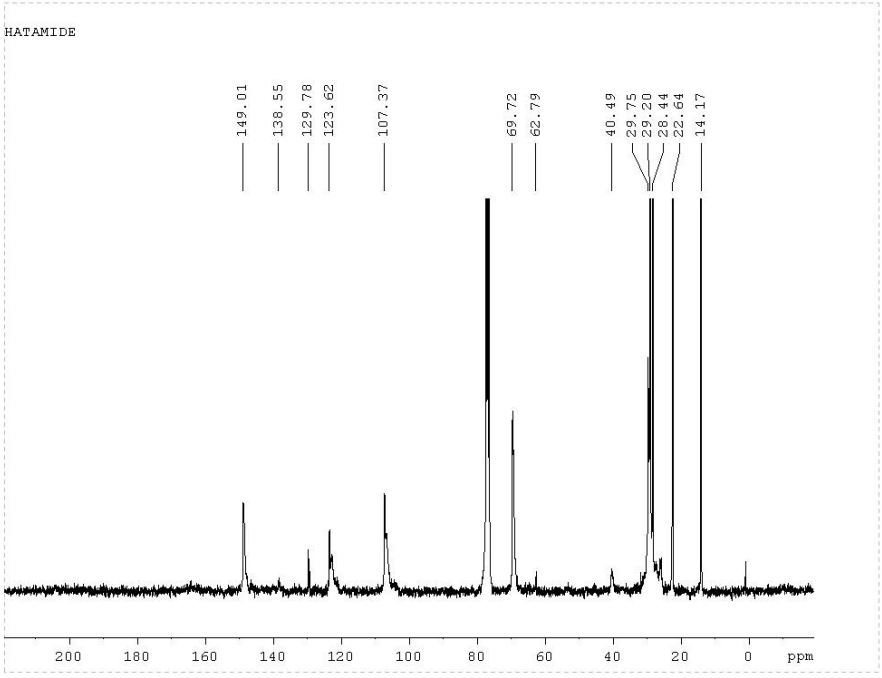


Figure 2-12: ^{13}C NMR of Heptamer Amide 18b (in $CDCl_3$).

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3 Chapter 3: Inverted Discotic Liquid Crystals

3.1 Introduction

The classical design of a discotic liquid crystal is based on a more or less spherical polyaromatic core that is surrounded by flexible, usually aliphatic, side-chains.[1-6] Side-chains are mainly attached to lower the melting points of these compounds and to support columnar stacking due to microphase segregation between the aromatic cores and the side-chains.

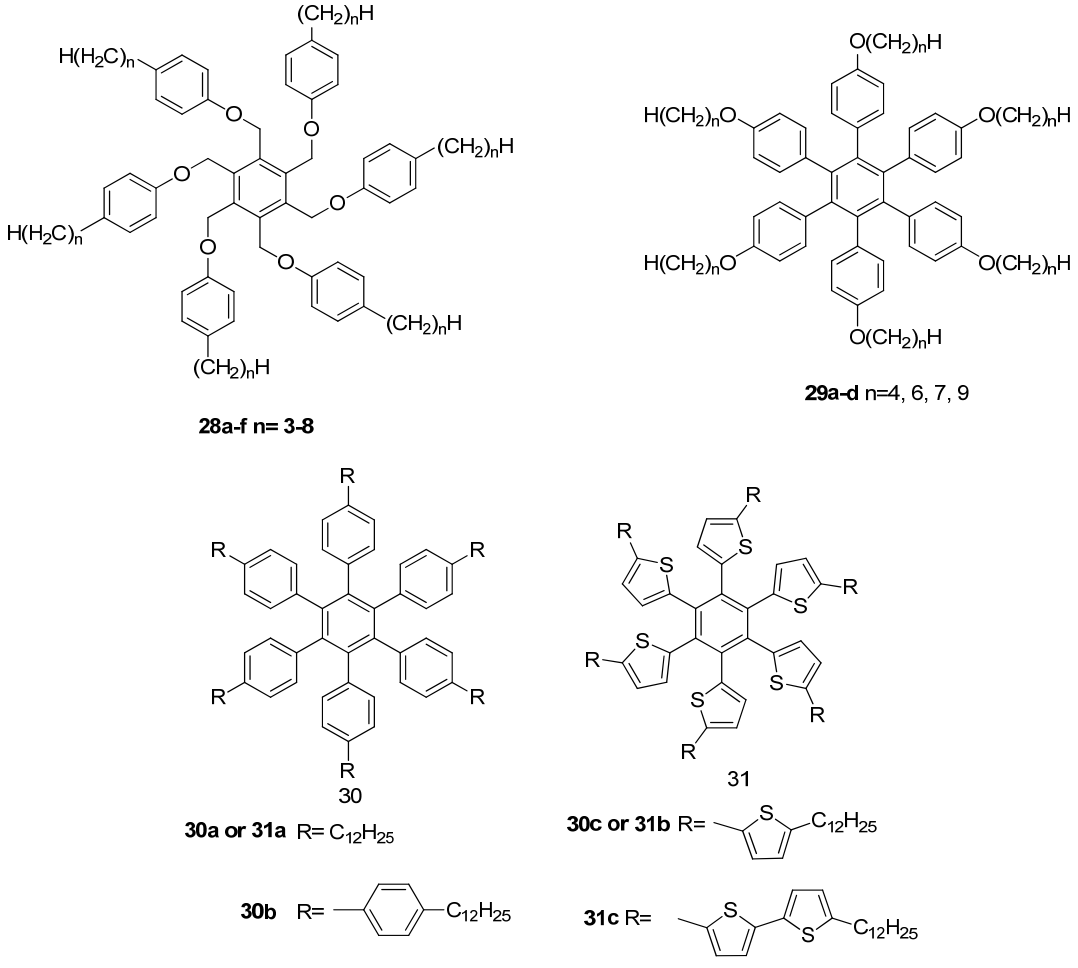


Figure 3-1: Known star-like substituted hexaarylbenzene-based DLCs 28a-f,[11] 29a-d,[11] 30a-c[12] and 31a-c.[12]

This design, however, has some disadvantages for applications of these materials as organic semiconductors because they function as an insulating sheath that lowers charge carrier mobility orthogonal to the columnar stacks by several orders of magnitude [7-9] and they often occupy 50% or more of the volume. Previous work has shown that star-shaped structures, such as **28** and **29** in Fig. 3.1,[11] with conformationally more flexible cores require fewer and shorter side-chains for the formation of columnar mesophases than rigid cores of comparative size. Another unusual feature of compounds **29** is their non-planar structure which also applies to the extended core examples **30** and **31** reported by Müllen and co-workers.[12] Note here that while all compounds **30** and **31** display mesophases of various order only compound **30c** displays a hexagonal columnar mesophase over a wide temperature range. However, all four examples illustrate that both internal flexible spacer chains and non-planar conformationally flexible cores are tolerated for the formation of columnar mesophases.

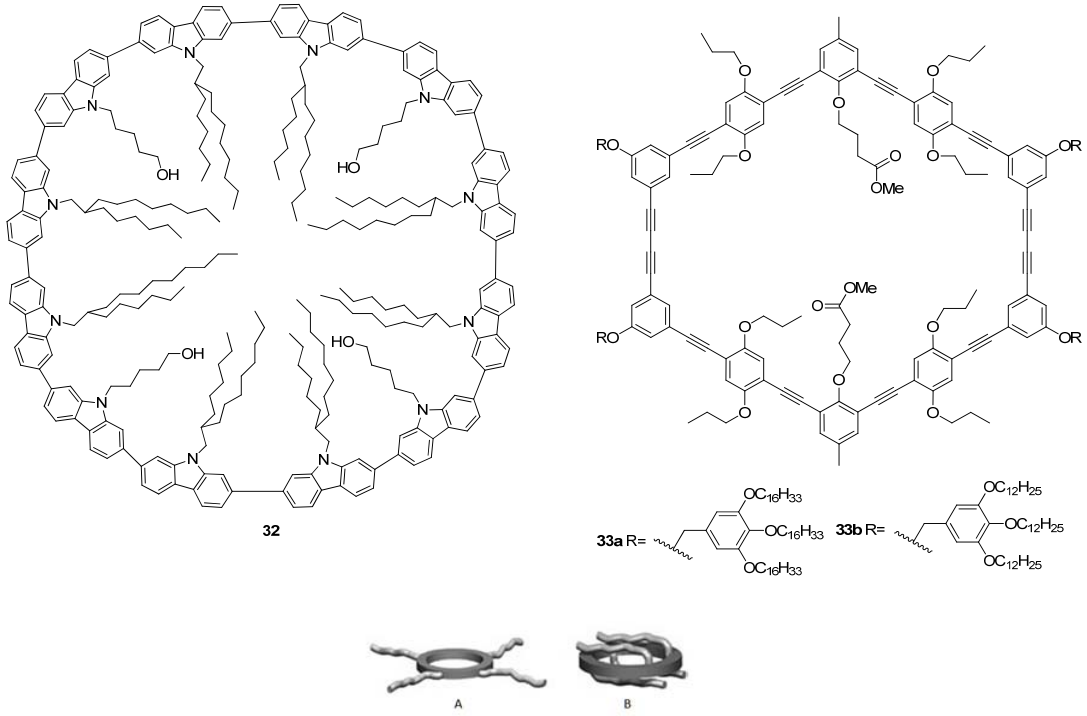


Figure 3-2: Reported inverted discotic liquid crystals 32 and 33. Cartoon of a conventional macrocycle A that is unfavoured because of the large cavity within the macrocycle and the inverted macrocyclic structure B.[6, 13-16]

All the aforementioned compounds **28** to **31** contain aliphatic side-chains pointing outwards. Macrocyclic structures **32**[15, 16] and **33**[6, 13, 14] demonstrate that side-chains can also point inwards and still promote columnar mesomorphism (Fig. 3.2). These compounds have been termed inverted discotic liquid crystal because of their inverted orientation of the side-chains. The authors of compound **32** noted that the electronic communication between aromatic parts in neighboring columns should increase because the insulating side-chains point inwards but I do not expect them to be good organic semiconductors because the actual area occupied by the aromatic units is rather small in comparison to the area occupied by the insulating aliphatic side-chains. In fact, compounds **32** and **33** are both unlikely to show high charge carrier mobility along their stacks and have probably been intended to generate tubular columnar stacks rather than organic semiconductors.[13-16]

3.2 Objective

Objective of this project is to develop a new design for discotic molecules as organic semiconductors that avoids the attachment of peripheral side-chains. Instead, we envisage new discotic molecules that have aromatic groups linked together by short flexible spacers. Softening of the core by the spacer group is expected to sufficiently lower melting points and not interfere with the columnar stacking as long as a disc-shaped structure can be adopted. These structures may also be called inverted discotic liquid crystals because the spacer chains can be described as internal flexible side-chains. This chapter will focus on hexa(thiophen-2-yl)alkyl)benzene derivatives as our first target structures (Figure. 3.3).

Control of the self-organization and transition temperatures is possible by varying the length of the attached internal alkyl spacers and potentially the substitution position at the thiophene. Compounds **24** are unprecedented, to the best of our knowledge, but hexathiophenylbenzene has been prepared and is expectedly not liquid crystalline.[10]

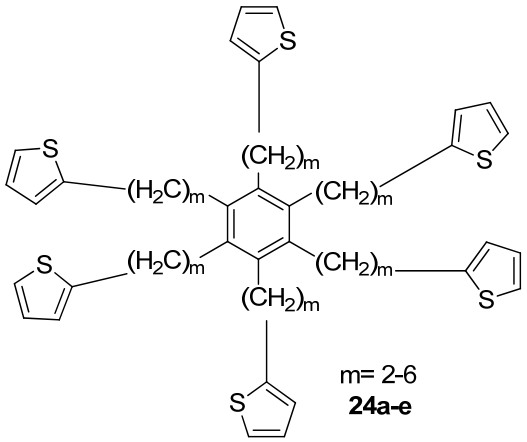
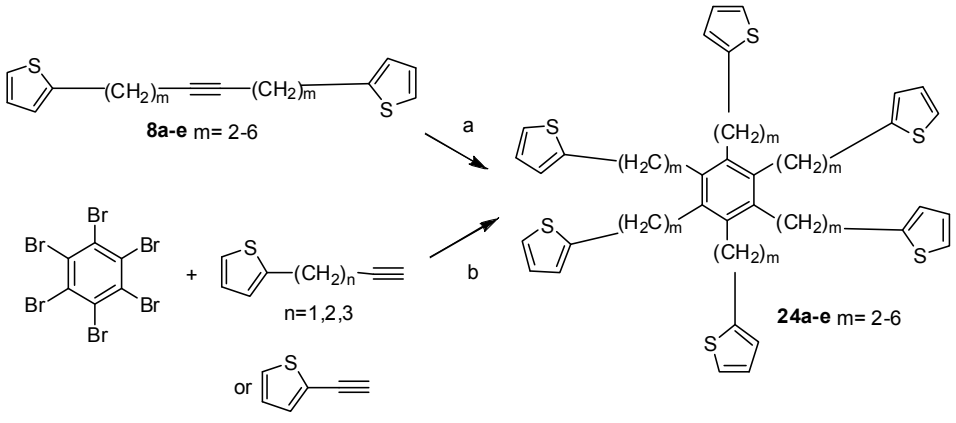


Figure 3-3:Proposed inverted discotic liquid crystals based on hexathiophenylalkyl substituted benzenes 24.

3.3 Synthesis of hexa(thiophenylalkyl)benzenes

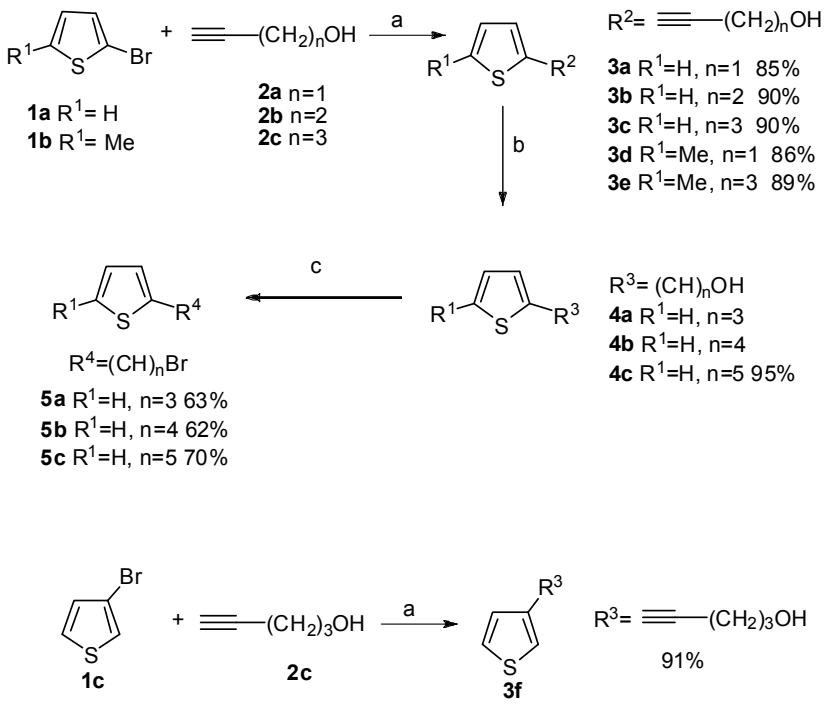
Two different approaches to hexa(thiophenylalkyl)benzenes **24** have been pursued here. The first approach relies on the [2+2+2] cylcotrimerization of di(thiophenylalkyl) substituted acetylenes **8** as final step whereas the second approach requires a hexa-Sonogashira reaction as key and final step (Scheme 3.1). Both approaches have their shortcomings and compounds **24** have not yet been successfully prepared. In the following I will describe the different synthetic pathways I have tested and conclude with possible alternative pathways that may be more successful but could not be tested because of time constrains.



Scheme 3.1: Typical synthetic route to prepare hexa(thiophenylalkyl) substituted benzene derivatives 24a-e. a) [2+2+2] cylcotrimerization of di(thiophenylalkyl) substituted acetylenes 8a-e and b) hexa-Sonogashira reaction followed by hydrogenation of alkyne groups to generate the final products 24a-e.

3.4 Approach via [2+2+2] cylcotrimerization of di(thiophenylalkyl) substituted acetylenes 8

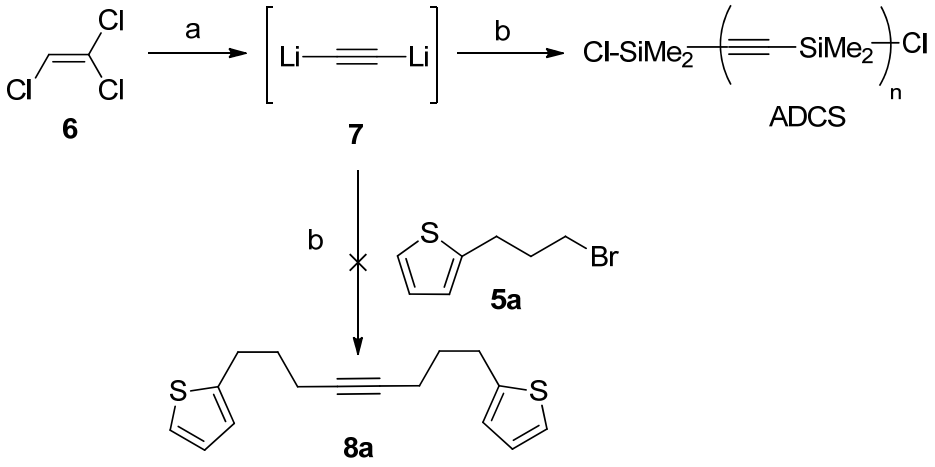
Synthesis of the di(thiophenylalkyl) substituted acetylenes **8** was not as straightforward as expected and several different approaches have been explored (Schemes 3.2-9). The first attempt was based on a dialkylation of acetylene with bromoalkyl thiophenes. Bromoalkyl thiophenes **5** with alkyl spacers of 3-5 methylene groups were prepared in 3 steps and overall yields of about 55% as outlined in Scheme 1. Bromothiophene **1** was reacted to compounds **3** by Sonogashira coupling with commercially available terminal alkynols **2** in excellent yields, which were subsequently hydrogenated to the hydoxyalkyl thiophenes **4** in quantitative yields. Lower yielding was the final conversion of the alkyl alcohol to the alkyl bromide with PBr_3 in about 70% yield after purification. Conversion to the bromide could also be performed with the crude hydrogenation products in 63% yield overall. In fact, only compound **4c** was obtained as analytically pure sample to determine the yield of this step.



Scheme 3.2: Synthesis of bromoalkyl thiophenes 5. Reaction conditions: a. $PdCl_2(PPh_3)_2$, CuI, $[CH_3(CH_2)_{15}]_4NCl$, aq. 2-ethanolamine, THF, 60 °C, 14 hrs.[5] b. H_2, 10% Pd/C, MeOH, rt, 4 days; [5] c. PBr_3, THF, 0°C-rt, 5 hrs. Yields for 5a and 5b are based on two reactions.

Compound **5a** was used for testing the dialkylation of acetylene to generate 1,8-di(thiophen-2-yl)oct-4-yne **8a**, the required precursor for the final [2+2+2] cyclotrimerization. Dilithi

um acetylene was chosen as nucleophilic acetylene species and generated in situ by the reaction of 1,1,2-trichloroethene with *n*BuLi (Scheme 3).[18] The formation of dilithium acetylene was confirmed by trapping it with dimethyldichlorosilane to form acetylenic dimethylchlorosilane (ADCS).[18] However, addition of **5a** did not generate **8a** but unreacted **5a** was recovered after quenching although different solvents and reaction temperatures were tested (Table 3.1).

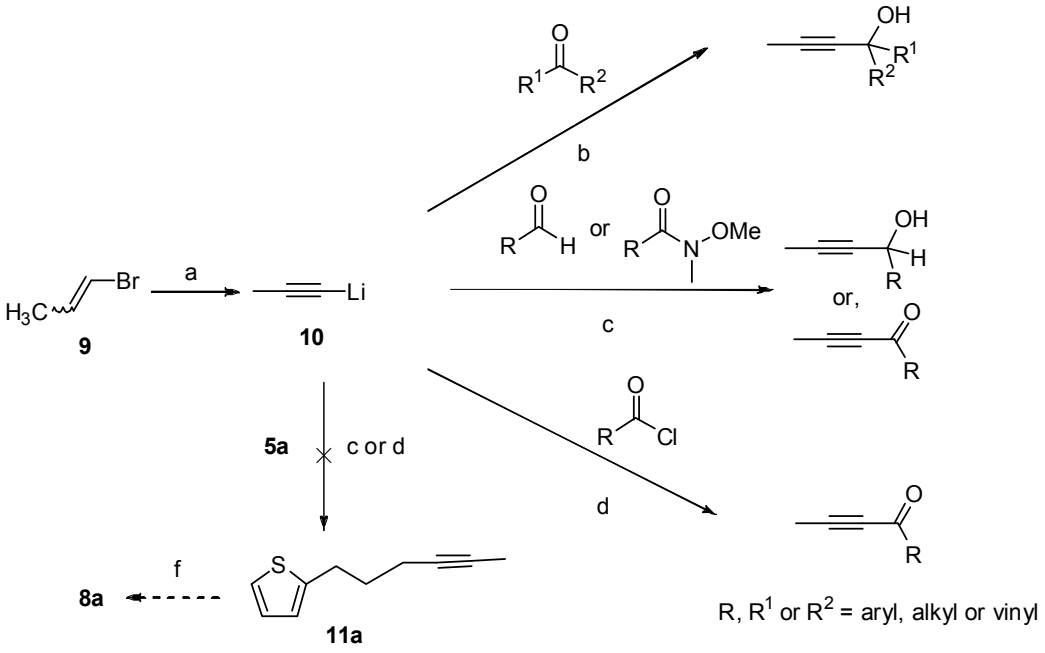


Scheme 3.3: Confirmation of the formation of dilithium acetylene by trapping it with dimethyldichlorosilane to generate acetylenic dimethylchlorosilane (ADCS) and reaction scheme to prepare 1, 8-di(thiophen-2-yl)oct-4-yne 8a *via* dilithium acetylide reaction with 2.2 eq. of 5a.; Reaction conditions: a. 3 equiv. *n*BuLi, 1:1 Et_2O : THF, -78°C-rt, 12 hrs. b. 4 equiv. Me_2SiCl_2, Et_2O, 0 °C- rt, 8 hrs . [18]

Table 3.1: Different conditions that were tested for the synthesis of 1,8-di(thiophen-2-yl)oct-4-yne

	a				b				
entry	nBuLi (equiv.)	Temp (°C)	Solvent	Time(hrs)	5a (equiv.)	HMPA (equiv.)	Temp (°C)	Time (hrs)	outcome
1	3	-78 - rt	THF	12	2.2	0	0-rt	8	Recovered **5a**
2	3	0 - rt	THF	8	2.2	0	0-rt	15	Recovered **5a**
3	3	rt	THF	12	2.2	2.2	0-rt	15	Decomposition of **5a**
4	3	10	THF	12	2.2	2.2	10-rt	15	Recovered **5a**
5	3	-78	1:1 Et_2O/THF	12	2.2	0	0-rt	15	Recovered **5a**
6	3	0	1:1 Et_2O/THF	10	2.2	2.2	0-rt	15	Decomposition of **5a**
7	3	rt	1:1 Et_2O/THF	8	2.2	2.2	0-rt	15	Decomposition of **5a**
8	3	-78 - rt	1:1 Et_2O/THF	12	2.2	2.2	0-rt	15	Decomposition of **5a**
9	3	0 - rt	1:1 Et_2O/THF	8	2.2	0	0-rt	15	Recovered **5a**
10	3	rt	1:1 Et_2O/THF	12	2.2	0	rt	8	Recovered **5a**
11	3	10	1:1 Et_2O/THF	12	2.2	2.2	10-rt	8	Decomposition of **5a**

The second approach to convert compounds **5** to **8** involved the substitution of the bromide with propynyllithium and subsequent $(^tBuO)_3W{\equiv}CCMe_3$ catalyzed alkyne metathesis of the products.[19,20] Again 2-(3-bromopropyl)thiophene **5a** was used for testing the feasibility of this approach (Scheme 3.4).



Scheme 3.4: Attempted conversion of 2-(3-bromopropyl)thiophene 5a with in situ formed propynyllithium 10 and subsequent alkyne metathesis. Reaction conditions: a. nBuLi 2.2 equiv., THF, -78 °C, 2 hrs ; b. (1) $CeCl_3$, -78 °C, 1 h; (2) 1 h, -78-20 °C; (3) aqueous saturated NH_4Cl; c. (1) aldehyde or Weinreb amide, 1 h, -78-20 °C; (2) aqueous saturated NH_4Cl; d. (1) $ZnCl_2$, -20 °C, 15 min; (2) 5 mol % $Pd(PPh_3)_4$, 0 °C, 30 mins; (3) aqueous saturated NH_4Cl.[19] f. 10 mol% $(^tBuO)_3W{\equiv}CCMe_3$, toluene, 100 °C, 10 hrs.[20]

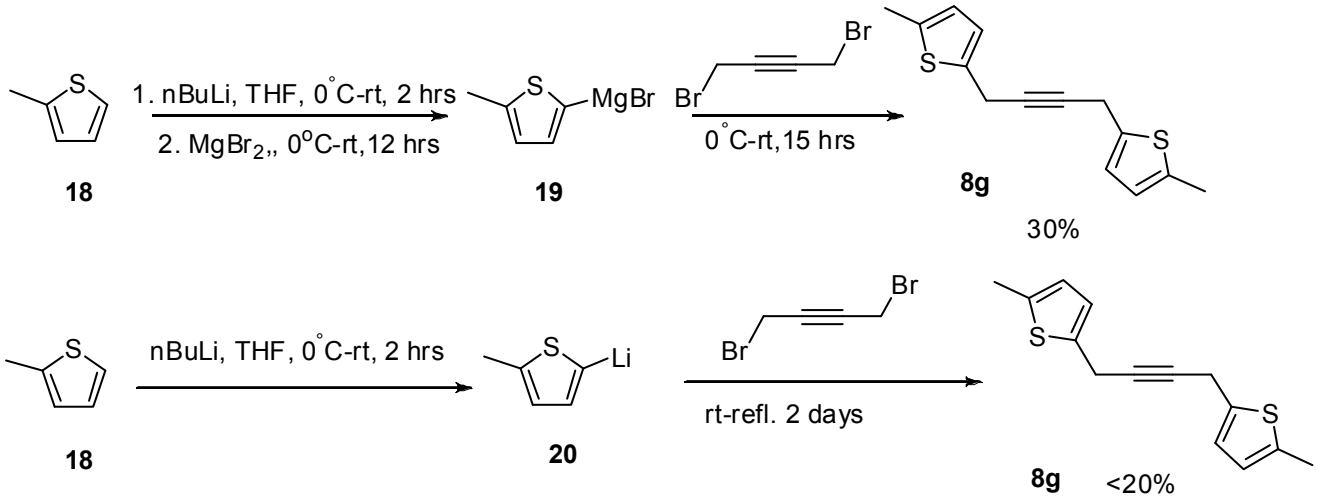
Propynyllithium **10** was prepared in situ by reacting 1-bromoprop-1-ene with nBuLi and the successful formation of **10** was confirmed by trapping it with benzaldehyde. Unfortunately, no reaction occurred with **5a** under the tested reaction conditions (Table 3.2). Successful reactions of propynyllithium with benzoyl chloride and cinnamoyl chloride have been reported if conducted in presence of zinc chloride and 5 mol % tetrakis(triphenylphosphine)palladium in THF at 0 °C.[19]

Table 3.2: Different conditions tested for the conversion of 5a with propynyllithium to form compound 11a.

a						c*				
Entry	1-bromoprop-1-ene (equiv.)	nBuLi (equiv.)	Temp (°C)	Solvent	Time (hrs)	5a (equiv.)	HMPA (equiv.)	Temp (°C)	Time (hrs)	outcome
1	1.55	2.2	-78	THF	2	1	0	-78 - rt	5	Decomposition of **5a**
2	1.55	2.2	0	THF	2	1	0	0 - rt	15	Recovered **5a**
3	1.55	2.2	rt	THF	2	1	0	rt	15	Recovered **5a**
4	1.55	2.2	-78	THF	2	1	1	-78 - rt	15	Decomposition of **5a**
5	1.55	2.2	0	THF	2	1	1	0 - rt	15	Decomposition of **5a**
6	1.55	2.2	rt	THF	2	1	1	rt	15	Decomposition of **5a**
7	1.55	2.2	-78	THF	2	d				Decomposition of **5a**
8	1.55	2.2	0	THF	2	d				Decomposition of **5a**

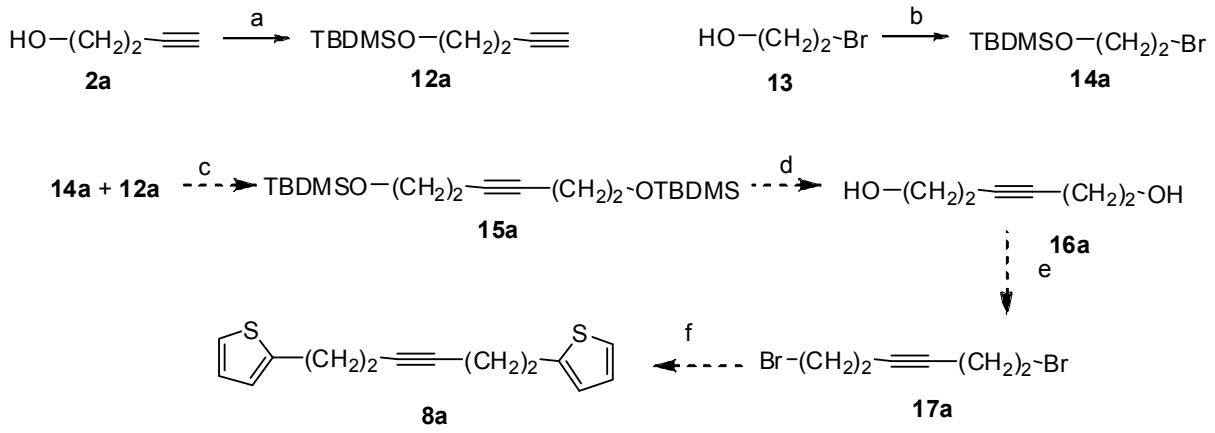
** reaction mixture was quenched with aqueous saturated NH_4Cl after completion; d. (1) $ZnCl_2$, -20 °C, 15 min; (2) 5 mol % $Pd(PPh_3)_4$, 5a (1 equiv.), 0 °C, 30 min; (3) aqueous saturated NH_4Cl.*

My next attempt involved the alkylation of thiophene as the last step. This possible pathway was tested with 2-methylthiophene to block the second reactive site of thiophene (Scheme 3.5). 2-Methylthiophene was converted into its magnesium bromide salt **19** and in situ reacted with 1,4-dibromobut-2-yne that was obtained from but-2-yne-1,4-diol by conversion with PBr_3 in 80% yield. The product **8g**, 1,4-bis(5-methylthiophen-2-yl)but-2-yne, was obtained albeit in low yields of 30-35% after purification. Reaction of the lithium salt of 2-methylthiophene with 1,4-dibromobut-2-yne generated **8g** in less than 20% yield. One should note here that both reactions (scheme 3.5) required extensive chromatographic separations for purification of **8g** from the crude reaction mixture.

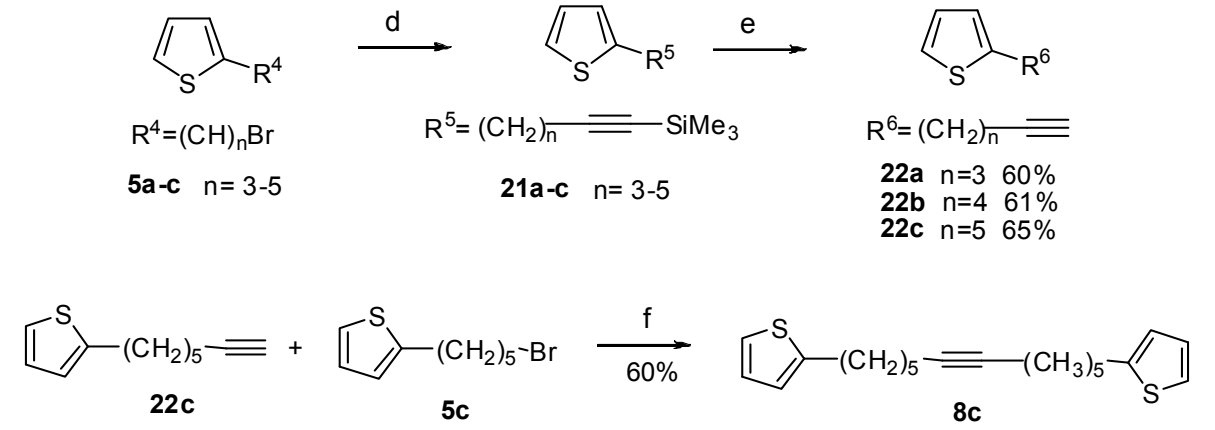


Scheme 3.5: Synthesis of 1, 4-bis(5-methylthiophen-2-yl)but-2-yne by substitution of 1,4-dibromobut-2-yne with thiophene metal salts.

Despite the relatively low yields of the final step I also attempted the synthesis of all other compounds **8**, which required the synthesis of the adequate dibromoalkynes (Scheme 3.6). The approach starts with the protection of the hydroxyl groups of commercially available alkynyl aclohols **2** and bromo alcohols **13** with *tert*-butyldimethylsilyl chloride. *tert*-Butyldimethylsilyl ether protected compounds **14a** and **12a** are coupled *via* the lithium acetylide to form the dialkylated acetylenes **15a**. Unfortunately, this coupling step generated compounds **15a** in less than 20% yield and required tedious chromatographic separations for purification. Thus, this approach was also dismissed and the following deprotection of the hydroxyl groups and their substitution with bromide were not conducted.

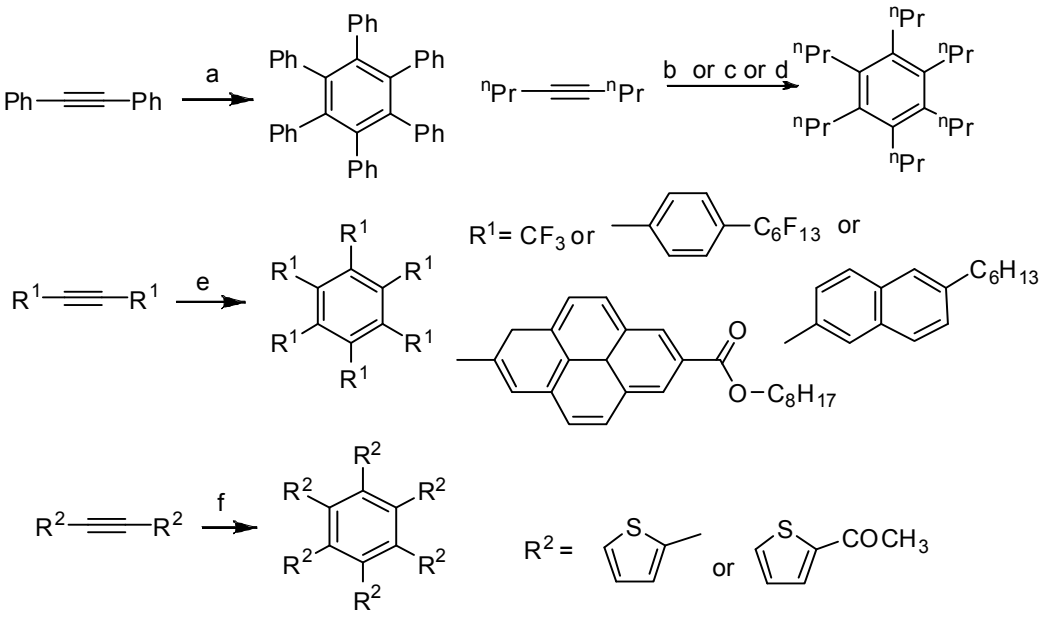


Scheme 3.6: Reaction conditions: a,b. TBDMSCl, imidazole, N,N-4-dimethylaminopyridine, DCM, rt., 3 hrs; c. BuLi, HMPA, 0 °C, d. TBAF, THF, rt.; e. PBr_3,THF, rt.; f. thiophene, nBuLi, Et_3N, $MgBr_2$, -78 °C.



Scheme 3.7: Reaction conditions: a. Trimethylsilylacetylene, *n*BuLi, HMPA, THF, -78 °C; e. K_2CO_3, MeOH, rt, 24 hrs f. *n*BuLi, HMPA, 0 °C, 2.5 days

Finally, the best working approach I found is presented in Scheme 9. Compounds **5a-c** were reacted with in-situ generated lithium trimethylsilyl acetylide to give compounds **21a-c** that were isolated as crude products and deprotected in methanolic potassium carbonate to afford compounds **22a-c** in fair yields. Coupling was tested only for compounds **21c** and **5c** to generate **8c** in 60% yield. One should note here that slightly less than one equivalent of *n*BuLi with respect to **21c** was used to avoid unreacted *n*BuLi that would react with thiophene and cause the formation of side products.



Scheme 3.8: Some representative examples of [2+2+2] cyclotrimerization of acetylene derivatives. Reaction conditions: a. Me_3SiCl, 10% Pd/C, THF, refl. 96 hrs;[21] b. 5 mol% $PdCl_2$, 3 equiv. $CuCl_2$, MeCN, rt, 10 hrs;[22] c. 5 mol% $PdCl_2$, 2 equiv. $CuCl_2$, 2 equiv. NaOAc, benzene/nBuOH (50:3), 40°C, 4 hrs;[23] d. 3 mol% $PdCl_2(PhCN)_2$, DME, 0°C - rt , 6 hrs;[24] e. 5 mol% $Co_2(CO)_8$, dioxane, reflux;[12] f. 8 mol% $RhCl_3 \cdot 3H_2O$, 30 mol % iPr_2NEt_3 , isopropanol, refl., 24 hrs.[14]

With sufficient amounts of compounds **8c** and **8g** in hand the final [2+2+2] cyclotrimerization to the hexa(thiophenylalkyl) substituted benzene derivatives was explored. Several different catalysts and conditions are known from the literature but many [2+2+2] cyclotrimerization were conducted with diaryl acetylenes and only a few with dialkyl acetylenes. Examples of previously reported [2+2+2] cyclotrimerization of acetylene derivatives are given in Scheme 3.8.

Unfortunately, all cyclization conditions I tested were unsuccessful for the trimerization of compounds **8c** or **8g**.

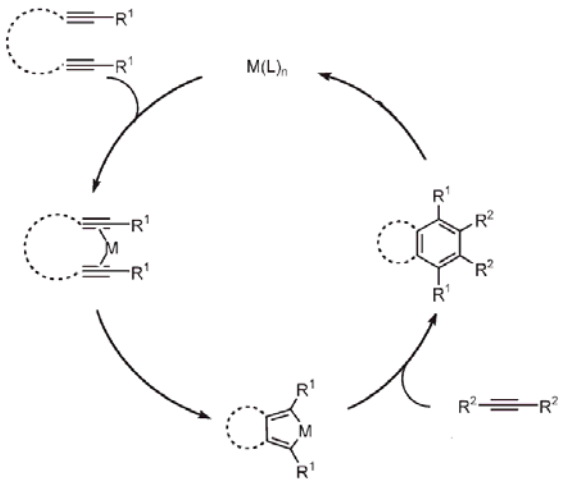
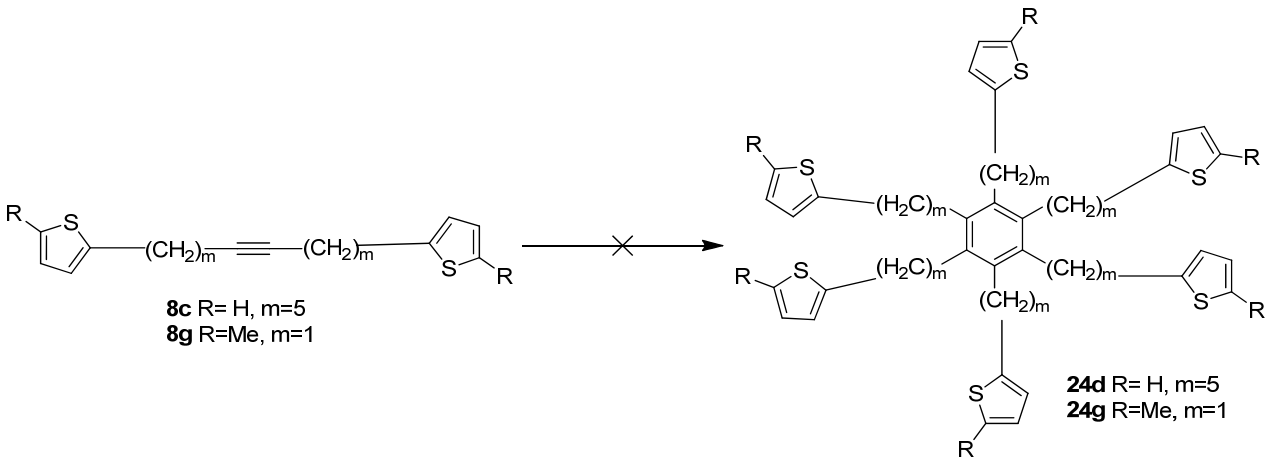


Figure 3-4: General reaction mechanism for metal catalyzed [2+2+2] cycloadditions of substituted acetylenes.[31]

A summary of the tested reactions is given in Table 3.3. Starting materials were recovered in about 85% yields for entries 1 to 4 while the starting material completely decomposed in entries 5 and 6 after 120 hrs. Products **24** were not identified by proton and carbon NMR in any of the crude reaction mixtures.

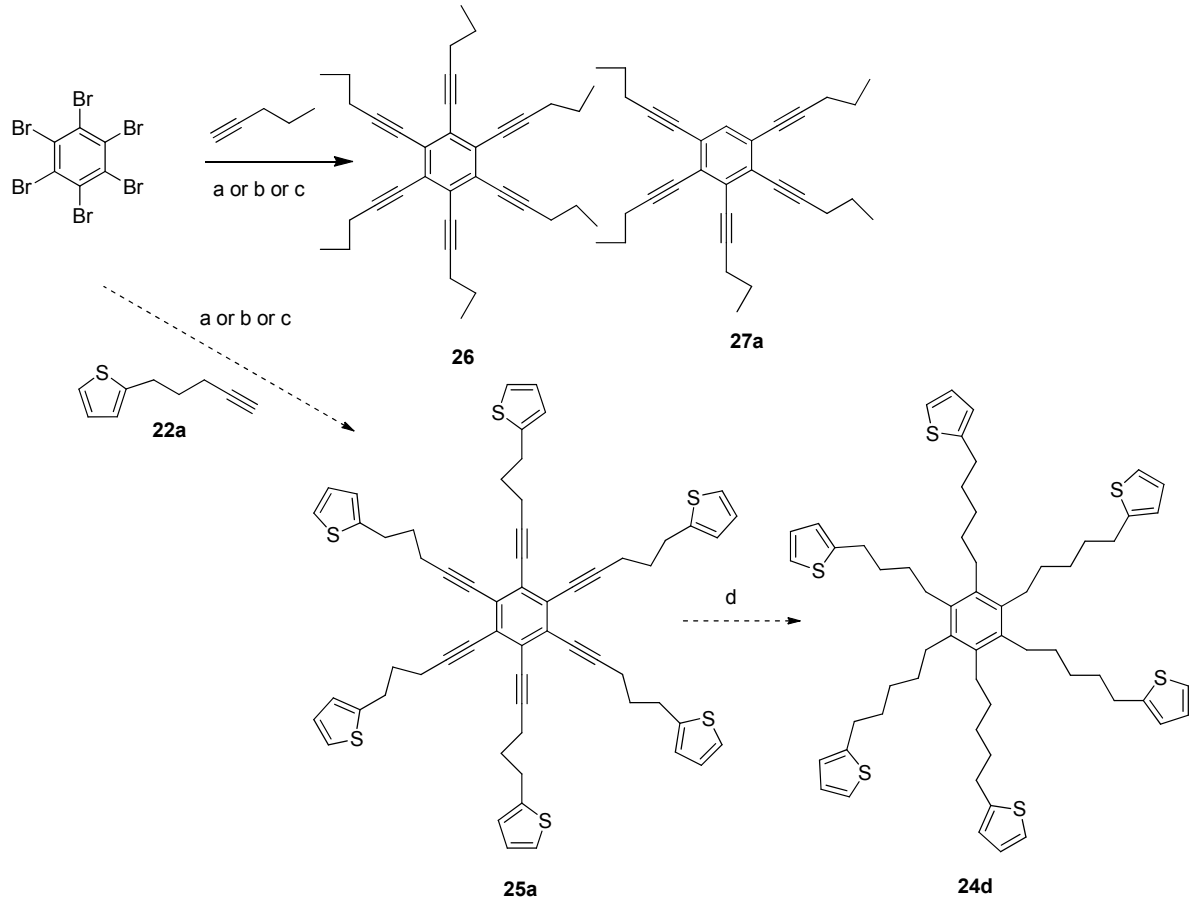


Scheme 3.9: Attempted cyclizations of 8c and 8g.

Table 3.3: Tested reaction conditions for the trimerization of compounds 8c and 8g.

Entry	reagent	solvent	Temp °C	Reaction time(hrs)
1[21]	Me_3SiCl, 10% Pd/C	THF	refl.	120
2[22]	5 mol% $PdCl_2$, 3 eq. $CuCl_2$	MeCN	rt	120
3[23]	5 mol % $PdCl_2$, 2eq.$CuCl_2$, 2 eq. NaOAc	benzene:nBuOH (50:3)	40	120
4[24]	3 mol% $PdCl_2(PhCN)_2$	DME	rt	120
5[12]	5 mol% $Co_2(CO)_8$	dioxane	refl.	120
6[10]	$RhCl_3 \cdot 3H_2O$, iPr_2NEt_3	isopropanol	refl.	120

The second approach to compounds **24** is based on a hexa Sonogashira coupling involving the 2-(alkyn-1-yl)thiophene derivatives **22** prepared in Scheme 10 followed by hydrogenation of the six acetylene groups (Scheme 3.10). Hexa Sonogashira reactions with hexabromo benzene have been reported but the yields were only 30%.[26-29] Since a separation of the hexa-substituted product from penta- and tetra-substituted side products is expected to be very tedious the viability of this approach was tested by coupling 4-pentyne to hexabromo benzene. Three different reaction conditions were tested for the hexa Sonogashira couplings and reaction times up to 10 days. All conversions generated product mixtures that contained the hexa-substituted product in less than 10% yield. Typical side-products were penta- and tetra-subtituted benzene derivatives that had the remaining bromine atoms replaced by H. Optimization of the reaction conditions may increase the product yield to 30% but the required complex chromatographic purification discouraged us from continuing this path.



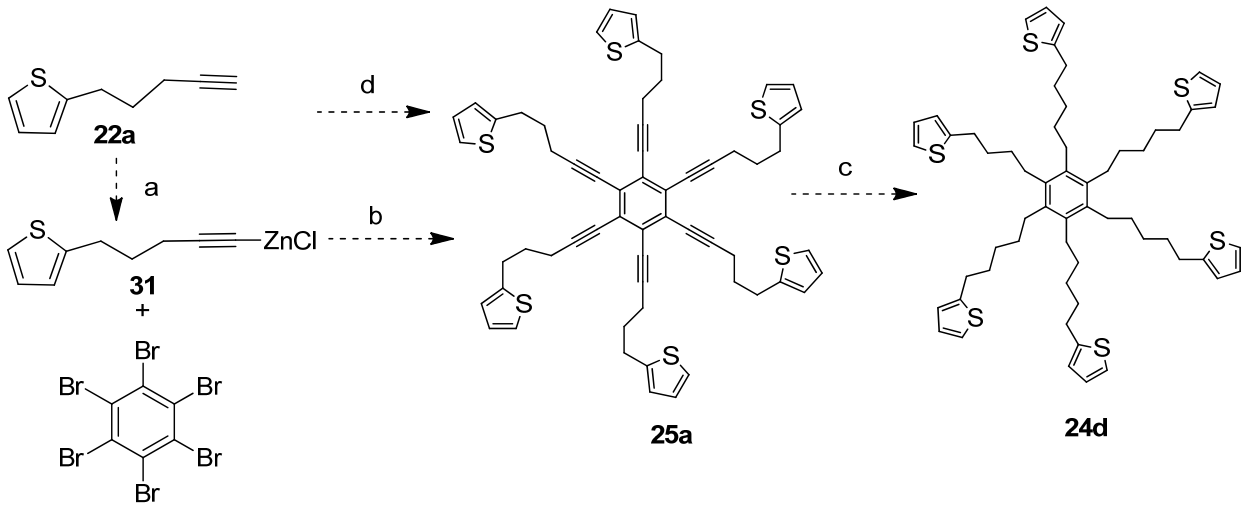
Scheme 3.10: Hexa Sonogashira reactions of hexabromo benzene with 4pentyne or 22a. Reaction conditions: a: $PdCl_2(PPh_3)_2$, CuI, $[CH_3(CH_2)_{15}]_4NCl$, aq. 2-ethanolamine, THF, 60 °C , b: Pd $(PPh_3)_4$, Et_3N, CuI, THF, refl.; c: $PdCl_2(PPh_3)_2$,CuI, $(i\text{Pr})_2NH$, THF:toluene, refl. d: H_2, 10% Pd/C, EtOAc, rt.[17, 26-29]

3.5 Outlook and Conclusions

The main road blocks for the preparation of hexa(thiophenylalkyl)benzenes **24** are the [2+2+2] cyclotrimerization of the first approach and the hexa Sonogoshira coupling to hexabromo benzene in the second approach. Initial difficulties with the synthesis of the precursor di(thiophenylalkyl)acetylenes **8** have been overcome but the yields of some of the steps must certainly be improved if larger scale preparations are necessary.

Many other catalysts (e. g. CpCo-η^4-cyclooctadiene complex)[25] could be tested for the [2+2+2] cyclotrimerization but it is unclear to us what changes to the catalyst system may be most promising. In

contrast, not all reported cross-coupling conditions for the hexa Sonogashira reaction with hexabromo benzene have yet been tested by us because of time constrains. For example the catalyst system 4 mol% $PdCl_2(CH_3CN)_2$ and 8 mol% X-Phos has been successfully employed in hexa Sonogoshira coupling reactions.[27]



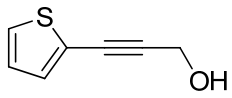
Scheme 3.11: Proposed synthesis of 24d Reaction conditions: a. nBuLi, $ZnCl_2$; b. $Pd(PPh_3)_4$, Et_3N, CuI, THF, refl. c. H_2, 10% Pd/C, EtOAc, rt. ; d. 4 mol % $PdCl_2(CH_3CN)_2$, 8 mol % X-Phos, 3 mol CuI , (iPr)$_2$ HN, dioxane, 80°C.

Another reported synthetic route to hexa-alkynyl substituted benzenes uses the zinc chloride salts of acetylenes and their $Pd(PPh_3)_4$ catalyzed cross-coupling to hexabromo benzene generates the hexa-substituted product in a reasonable yield of 60%.[29] An example synthetic pathway for the preparation of **24d** is given in Scheme 3.11

3.6 Experimental

3.6.1 Preparation of (thiophen-2-yl) alkyn-1-ols (3a-f)

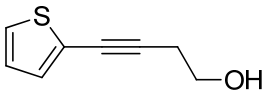
To a 50 mL of round bottom flask equipped with a magnetic stirring bar, 2-bromothiophene (0.3 mL, 490 mg, 3 mmol), $PdCl_2$ $(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (38 mg, 0.2 mmol) and hexadecyltrimethylammonium chloride (64 mg, 0.2 mmol) were added in 15 mL of THF under nitrogen atmosphere. To this mixture the alkynyl alcohol (2 mmol) and 0.5 M aqueous solution of 2-ethanolamine (8 mL) were added. The resulting mixture was heated at 60 °C for 20 hrs. This reaction mixture was cooled to room temperature and 50 mL water was added. The aqueous layer was extracted with dichloromethane (3 x 50 mL) and the combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the organic layer under vacuum gave the crude product that was purified by column chromatography on silica gel using 1:4 ethyl acetate:hexanes as eluent to yield compounds **3a** as viscous yellow liquid.



3-(thiophen-2-yl) prop-2-yn-1-ol **3a** (234 mg, 85%) as a viscous yellow liquid

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.8 (br, 1H), 4.51 (s, 1H), 6.96-6.99 (m, 1H), 7.21-7.27 (m, 2H)

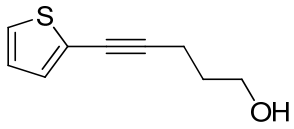
^{13}C-NMR (300 MHz, $CDCl_3$, δ): 61.10, 76.1, 85.88, 123.87, 125.31, 127.20, 129.87.



4-(thiophen-2-yl)but-3-yn-1-ol (**3b**) (274 mg, 90%) was prepared in a similar fashion to the synthesis of 3a using 3-butyn-1-ol (0.15 mL, 140 mg, 2 mmol).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.7 (br, 1H), 2.72 (t, J=6.23 Hz, 2H), 3.82 (t, J=6.23 Hz, 2H), 6.94-6.97 (m, 1H), 7.16-7.22 (m, 2H)

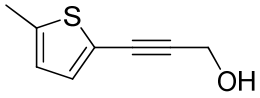
^{13}C-NMR (300 MHz, $CDCl_3$, δ): 23.23, 61.13, 76, 85.88, 123.87, 125.31, 127.20, 129.87.



5-(thiophen-2-yl) pent-4-yn-1-ol (3c) (300 mg, 90%) was prepared in a similar fashion to the synthesis of 3a using 4-pentyn-1-ol (0.1 mL, 168 mg, 2 mmol).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.66 (br, 1H), 1.86 (p, J=3.87 Hz, 2H), 2.56 (t, J=4.18 Hz, 2H), 3.81(t, J=3.69 Hz, 2H), 6.93-6.95 (m, 1H), 7.06 (dd, J =3.05 & 13.53 Hz, 2H).

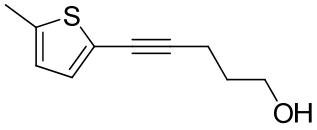
^{13}C-NMR (300 MHz, $CDCl_3$, δ): 16.30, 16.73, 31.29, 61, 76, 93.51, 123.93, 126.18, 126.90, 131.22.



3-(5-methylthiophen-2-yl)prop-2-yn-1-ol(3d) (260 mg , 86%) was prepared in a similar fashion to the synthesis of 3a using 2-bromo-5-methylthiophene (0.34 mL,533 mg ,3 mmol) and propargylic alcohol (0.11 mL,112 mg,2 mmol) .

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.61 (br, 1H), 2.46 (s, 3H), 4.5(s, 2H), 6.63 (s, 1H), 7.02 (d, J=3.3 Hz, 1H).

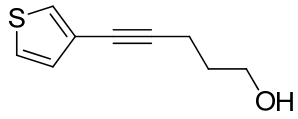
^{13}C-NMR (300 MHz, $CDCl_3$, δ): 16.37, 31.38, 61.89, 74.72, 92.54, 121.46, 125.10, 131.43, 140.90.



5-(5-methylthiophen-2-yl) pent-4-yn-1-ol (3e) (320 mg, 89%) was prepared in a similar fashion to the synthesis of 3a using 2-bromo-5-methylthiophene (0.34 mL, 533 mg, 3 mmol).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.86 (p, J=6.58 Hz, 2H), 2.44 (s, 3H), 2.56 (t, J= 3.46 Hz, 2H), 3.80 (t, J=3.53 Hz, 2H), 6.58 (d, J=3.40 Hz, 1H), 6.92 (d, J=3.45 Hz, 1H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 15.45, 16.37, 31.38, 61.89, 74.72, 92.54, 121.46, 125.10, 131.43, 140.90.



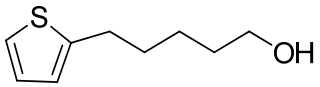
5-(thiophen-3-yl) pent-4-yn-1-ol (3f) (302 mg, 91%) was prepared in a similar fashion to the synthesis of 3a using 3-bromothiphene (0.3 mL, 326 mg, 3 mmol).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.7 (br, 1H), 1.85 (t, J=3.59 Hz, 2H), 2.52 (t, J= 3.49 Hz, 2H), 3.80 (t, J= 1.33 Hz, 2H), 7.06 (d, J=2.97 Hz, 1H), 7.23 (t, J=1.278 Hz, 1H), 7.35 (d, J= 1.60 Hz, 1H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 15.85, 16.23, 31.23, 61.58, 75.81, 88.81, 122.39, 122.98, 128.14, 129.84.

3.6.2 Synthesis of 5-(thiophen-2-yl) alkane-1-ol (4c)

To a solution of 5-(thiophen-2-yl) pent-4-yn-1-ol 3c (664 mg, 4 mmol) in 100 mL MeOH, 10 wt% Pd/C was added. Then this solution was kept stirring for 4 days under hydrogen atmosphere. The reaction mixture was passed through a Celite pad and concentrated in vacuo. The residue was further purified by column of silica gel using 1:5 (Ethyl acetate: Hexanes) as an eluent to afford 5-(thiophen-2-yl) pentan-1-ol as yellow liquid (647 mg, 95%).

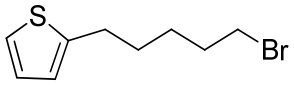


^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.41-1.49 (m, 3H), 1.57-1.64 (m, 2H), 1.67-1.75 (m, 2H), 2.85 (t, J=7.62 Hz, 2H), 3.65 (t, J=6.53 Hz, 2H), 6.78 (d, J=2.78 Hz, 1H), 6.92 (t, J= 4.92 Hz, 1H), 7.11 (d, J=5.03, 1H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 25.45, 30.23, 30.35, 32.60, 62.93, 119.94, 125.18, 128.24, 142.89.

3.6.3 Synthesis of 2-(5-bromopentyl)thiophene(5c)

To a 100mL dichloromethane solution of 5-(thiophen-2-yl)pentan-1-ol (680 mg, 4 mmol) , PBr_3 (0.6 mL, 1.624 g, 6 mmol) was added at 0°C in drop wise manner under nitrogen atmosphere. The reaction mixture was allowed to reach room temperate slowly and kept stirring for 5 hrs under nitrogen atmosphere. This mixture was slowly poured into 100 mL ice cold water and 5(M) sodium bicarbonate solution added to neutralize it, finally extracted with dichloromethane (3 X 75 mL).The combined organic layer was dried over anhydrous magnesium sulfate and dried under reduced pressure. The residue was further purified by column of silica gel using 1:5 (Ethyl acetate: Hexanes) as an eluent to afford 2-(5-bromopentyl)thiophene as yellow liquid (653 mg, 70%).

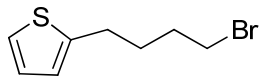


^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.44-1.57 (m, 2H), 1.72 (p, J= 7.22 Hz, 2H), 1.9 (p, J= 6.80 Hz, 2H), 2.85 (t, J= 7.59 Hz, 2H), 3.44 (t, J= 6.80 Hz, 2H), 6.79-6.80 (m, 1H), 6.91-6.94 (m, 1H), 7.11-7.13(m, 1H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 27.71, 29.79, 31, 32.61, 33.74, 123.02, 124.20, 126.79, 145.20.

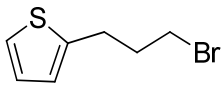
3.6.4 Synthesis of 2-(4-bromobutyl)thiophene (5b) and 2-(3-bromopropyl)thiophene (5a)

To a solution of 4-(thiophen-2-yl)but-3-yn-1-ol (609 mg, 4 mmol) in 100 mL MeOH, 10 wt% Pd/C was added. Then this solution was kept stirring for 4 days under hydrogen atmosphere. The reaction mixture was passed through a Celite pad and concentrated in vacuo. The residue was used for bromination without purification .To the 100 mL dichloromethane solution of the residue, PBr_3 (0.6 mL, 1.624 g, 6 mmol) was added at 0 °C in drop wise manner under nitrogen atmosphere. The reaction mixture was allowed to reach room temperate slowly and kept stirring for 5 hrs under nitrogen atmosphere. This mixture was slowly poured into 100 mL ice cold water and 5 M sodium bicarbonate solution added to neutralize it, finally extracted with dichloromethane (3 X 75 mL).The combined organic layer was dried over anhydrous magnesium sulfate and dried under reduced pressure. The residue was further purified by column of silica gel using 1:4 (Ethyl acetate: Hexanes) as an eluent to afford 2-(4-bromobutyl)thiophene (543 mg, 62%).



^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.8-1.94 (m, 4H), 2.88 (t, J= 7.12 Hz, 2H), 3.42 (t, J= 2.65 Hz, 2H), 6.80 (s, 1H), 6.91-6.94 (m, 1H), 7.13 (d, J= 4.08, 1H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 29.07, 30.24, 32.09, 33.39, 123.18, 126.84, 144.63.



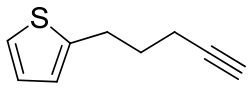
2-(3-bromopropyl)thiophene (**5a**) (517 mg, 63%) was prepared in similar fashion to the synthesis of 5b using 3-(thiophen-2-yl)prop-2-yn-1-ol 3a (553 mg, 4 mmol) .

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.23 (p, J=6.5 Hz, 2H), 3.03 (t, J= 7.22 Hz, 2H), 3.43 (t, J= 6.8 Hz, 2H), 6.8 (d, J= 3.1 Hz, 1H), 6.90-6.93 (m, 1H), 7.15 (d, J= 4 Hz, 1H).

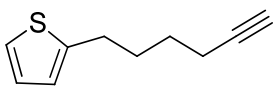
^{13}C-NMR (300 MHz, $CDCl_3$, δ): 31.04, 32.61, 34.38, 123.56, 125,126.97, 143.08.

3.6.5 Synthesis of 2-(alkyn-1-yl)thiophene (22a-c)

To a stirred solution of trimethylsilylacetylene (0.47 mL, 323 mg, 3.3 mmol) in 50 mL THF, 1.6 (M) nBuLi in hexanes (1.87 mL , 3 mmol) was added in dropwise manner at -78°C under nitrogen atmosphere. The mixture was kept stirring at -78°C for 1.5 hrs under nitrogen atmosphere .To it the solution of 5a (615 mg, 3 mmol) in hexamethylphosphoramide (0.6 mL, 537 mg, 3 mmol) was added drop wise at -78°C under nitrogen atmosphere. The mixture was then allowed to warm up to room temperature slowly and kept stirring for 6 hrs. The solvent was removed from the reaction mixture under reduced pressure. To the 50 mL methanolic solution of residue, Potassium carbonate (553 mg, 4mmol) was added and stirred for 2hrs under nitrogen atmosphere at room temperature. The reaction mixture was passed through a Celite pad and 100 mL water was added. Finally the mixture was extracted with diethyl ether (3 X 75 mL).The combined organic layer was dried over anhydrous magnesium sulfate and dried under reduced pressure. The residue was further purified by column of silica gel using 1:4 (ethyl acetate / hexanes) as an eluent to afford 2-(pent-4-yn-1-yl)thiophene (270 mg, 60%).



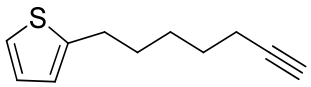
^{13}C-NMR (300 MHz, $CDCl_3$, δ): 17.78, 28.71, 30.38, 68.98, 83.87, 123.27, 124.63, 126.87, 144.23.



2-(hex-5-yn-1-yl)thiophene (**22b**) (300 mg, 61%) was prepared in a similar fashion to the synthesis of **22a** using 5b (657 mg, 3 mmol).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.55-1.66 (m, 2H), 1.79-1.84 (m, 2H), 1.96 (t, J=2.47 Hz, 1H), 2.23 (dt, J=2.51 & 6.99 Hz, 2H), 2.86 (t, J=7.32 Hz, 2H), 6.8 (s, 1H), 6.92 (t, J=3.44 Hz, 1H),7.12 (d, J=5.11 Hz, 1H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 18.37, 28.23, 29.79, 31.29, 68.269, 84.53, 122.85, 124.04, 126.69, 145.47.



2-(hept-6-yn-1-yl)thiophene (**22c**) (331 mg, 65%) was prepared in a similar fashion to the synthesis of 7a using 5c (700 mg, 3 mmol).

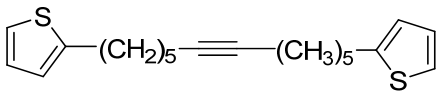
^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.44-1.60 (m, 4H), 1.66-1.73 (m, 2H), 1.95 (t, J=1.74 Hz, 1H), 2.20 (dt, J=2.38 & 6.81 Hz, 2H), 2.84 (t, J=7.65 Hz, 2H), 6.79 (d, J=2.67 Hz, 1H), 6.92 (t, J=3.58 Hz, 1H), 7.11 (d, J=5.10 Hz, 1H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 18.42, 25.98, 28.30, 29.85, 31.37, 68.34, 84.60, 122.92, 124.11, 126.76, 145.54.

3.6.6 Synthesis of 1, 12-di(thiophen-2-yl)dodec-6-yne (8c)

To stirred solution of 22c (588mg, 3.3 mmol) in 50 mL THF, 1.6 (M) nBuLi in hexanes (1.87 mL , 3 mmol) was added in dropwise manner at -78°C under nitrogen atmosphere. The mixture was kept stirring at -78°C for 1.5 hrs under nitrogen atmosphere .To it the solution of 5c (700 mg, 3 mmol) in Hexamethylphosphoramide (0.6 mL, 537 mg, 3 mmol) was added drop wise at -78°C under nitrogen atmosphere. The mixture was then allowed to warm up to room temperature slowly and kept stirring for 6 hrs. 100 mL water was added and the mixture was extracted with diethyl ether (3 X 75 mL).The

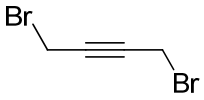
combined organic layer was dried over anhydrous magnesium sulfate and dried under reduced pressure. The residue was further purified by column of silica gel using 1:4 (Ethyl acetate: Hexanes) as an eluent to afford 8c (594 mg, 60%).



^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.44-1.55 (m, 12H), 1.70 (p, J=7.2 Hz, 4H), 2.17 (t, J=4.8 Hz, 2H), 2.84 (t, J=7.5 Hz, 4H), 6.78 (d, J=3Hz, 1H), 6.92 (d, J=3.3Hz, 1H), 7.11 (dd , J=1.2 & 5.1 Hz, 1H).

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 18.78, 28.41, 28.93, 29.91, 31.42, 80.27, 122.89, 124.07, 126.75, 145.70.

3.6.7 Synthesis of 1, 4-dibromobut-2-yne

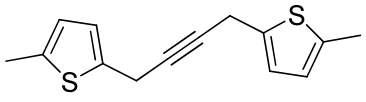


To a stirred solution of but-2-yne-1, 4-diol (860 mg, 10 mmol) in 100mL diethyl ether, PBr_3 (2.1 mL, 5.955 g, 22 mmol) was added drop wise at 0°C under nitrogen atmosphere. The reaction mixture was allowed to reach room temperature and stirred for 5 hrs. Then the mixture was slowly poured into 100 mL ice cold water and 5(M) sodium bicarbonate solution added to neutralize it, finally extracted with dichloromethane (3 X 75 mL).The combined organic layer was dried over anhydrous magnesium sulfate and dried under reduced pressure. The residue was further purified by column of silica gel using 1:4 (dichloromethane: Hexanes) as an eluent to afford 1, 4-dibromobut-2-yne (6) (1.695 g, 80%).

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 3.86 (s, 4H) which consistent with the reported value[30]

3.6.8 1, 4-bis (5-methylthiophen-2-yl) but-2-yne (8g)

To a stirred solution of 2-methylthiophene (1 mL, 982 mg, 10 mmol) in 50 mL of THF, 1.6 M nBuLi in hexanes was added drop-wise (7.5 mL, 12 mmol) at 0°C under nitrogen atmosphere. The mixture was allowed to reach room temperature and kept stirring for 2 hrs under nitrogen atmosphere. Then anhydrous magnesium dibromide (1.841 g, 10 mmol) was added to the reaction mixture portion wise at 0°C under nitrogen atmosphere and kept stirring for another 12 hrs after it reached room temperature. Finally reaction mixture was cooled to 0°C and 1, 4-dibromobut-2-yne (890 mg, 4.4 mmol) was added portion-wise. After stirring the reaction mixture for 15 hrs at room temperature, it was poured over 100 mL of water and extracted with dichloromethane (3 X 75 mL).The combined organic layer was dried over anhydrous magnesium sulfate and dried under reduced pressure. The residue was further purified by column of silica gel using 1:5 (dichloromethane: Hexanes) as an eluent to afford 8g (739 mg, 30%).



^{1}H-NMR (300 MHz, $CDCl_3$, δ): 2.45 (s, 6H), 3.71 (s, 4H), 6.57 (s, 2H), 6.74 (d, J=1.71 Hz, 2H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 15.432, 20.25, 79.16, 124.731, 124.804, 137.552, 138.542.

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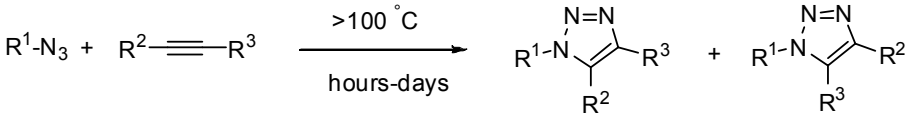
4 Chapter 4: Cross-Linking of Tetraazaporphyrins in Mesophases and at the Air-Water Interface by Click Chemistry

4.1 Background

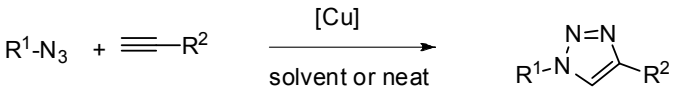
Huisgen and his co-workers were the first to realize the thermal 1,3-dipolar cycloaddition of azides and terminal or internal alkyne to 1,2,3-triazole derivatives.[6] However, the high activation energy of this reaction requires a high reaction temperature for longer periods of time to be synthetically useful and both 1,4- and 1,5-regioisomers are formed. In 2001 the groups of Medal[7] and Sharpless[8] independently reported the first examples of copper catalyzed azide alkyne cycloaddition (CuAAC) reactions that occur at substantially lower temperatures and faster rate and produce predominantly 1,4-adducts.

A. 1,3-Diploar cycloaddition of azides and alkynes



reactions are faster when R^2, R^3 are electron withdrawing gropus

B. Copper catalylzed cycloaddition of azides and alkynes (CuAAC)



C. Ruthenium catalylzed cycloaddition of azides and alkynes (RuAAC)

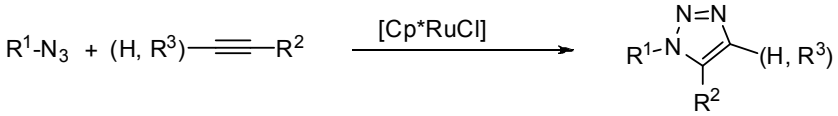


Figure 4-1 :Uncatalyzed and catalyzed 1,3-dipolar cycloadditions of azides and alkynes.[12]

CuAAC reactions are tolerant to most functional groups, proceed in high yields with few possible side-reactions, and form stable 1,2,3-triazole rings as linkers.[1-3] Their application in the synthesis and processing of self-organizing and self-assembling materials, however, has been limited to the synthesis of molecular building blocks and the modification of self-assembled monolayers[4] and Langmuir-Blodgett films.[5]

4.1.1 Mechanism of CuAAC based on DFT calculation

The mechanism of CuAAC reactions given in the Figure 4.2 was proposed by Sharpless *et al.* and is based on experimental studies and calculations at the Density Functional Theory (DFT) level. [9-11] The reaction cycle is initiated by the conversion of alkyne **1** to Cu(I) acetylide **2** by the displacement of a ligand (such as acetonitrile or water). In the following step exchange of one of the ligands with azide takes place to form copper-azide-acetylide complex **3** where azide attaches to the copper through the nitrogen next to the carbon. Cyclization to an unusual six-membered copper (III) metallacycle intermediate **4** occurs in the next step when the remote nitrogen of the azide in intermediate **3** is linked to the C-2 carbon of the alkyne.

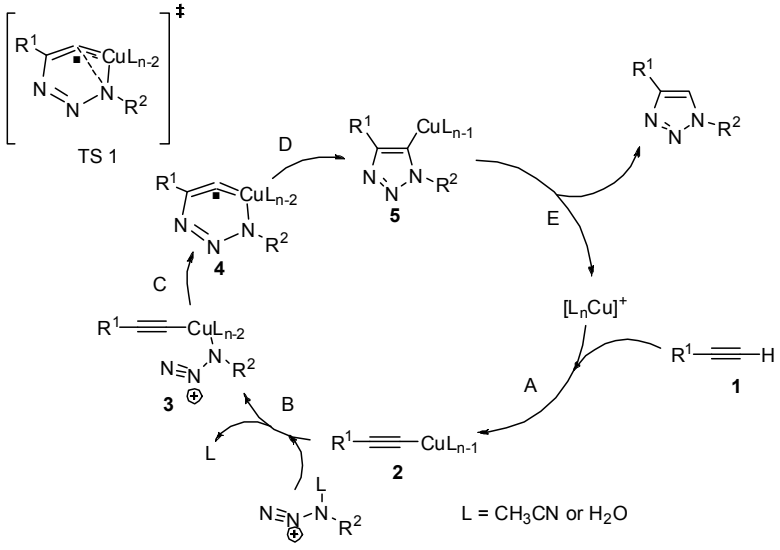


Figure 4-2: Proposed mechanism of Cu mediated azide-alkyne 1,3-dipolar cycloaddition (CuAAC).[9]

Five membered ring intermediate **5** is produced to release the distorted ring strain of complex **4** *via* TS 1. The reaction cycle completes with the protonation of complex **5** to give the desired triazole product.

4.1.2: Applications of CuAAC

CuAAC is a particularly powerful reaction for the assembly of complex building blocks such as the attachment of large dendrons to a rotaxane core,[13] the synthesis of oligomeric phthalocyanines,[14-16] and the attachment of dyes to polymers and carbon nanotubes.[17] The 1,2,3-triazole rings that result from the CuAAC may also benefit supramolecular properties, self-organization, and electronic properties of the product because 1,2,3-triazoles have a strong dipole and aromatic character and the ability to accept H-bonds. Calamitic, [18-20] polymeric,[21] and discotic [22-24] liquid crystals containing the 1,2,3-triazole motive have recently been reported.

Reviewed in the following is the application of 1, 3-dipolar cycloaddition of azides and alkynes, especially CuAAC, in the synthesis of complex dyes, the attachment of dyes to surfaces, polymers, and nanostructures, as well as the synthesis of liquid crystals. Current work by various research groups have established that CuAAC is a straightforward coupling reaction method to append a large selection of molecules (proteins, sugars, porphyrins, phthalocyanine, DNA) onto a diverse range of surfaces such as gold, graphite, and silicon.[25-40]

Yilmaz *et al*. prepared first of a kind tetratriazole-functionalized phthalocyanines quantitatively and efficiently using click chemistry.[41] Ikawa and his co-workers have prepared a water-soluble N-fused porphyrin-nona-arginine peptide conjugate (NFP-R9) *via* CuAAC method which has an enhanced ability to penetrate cells.[42]

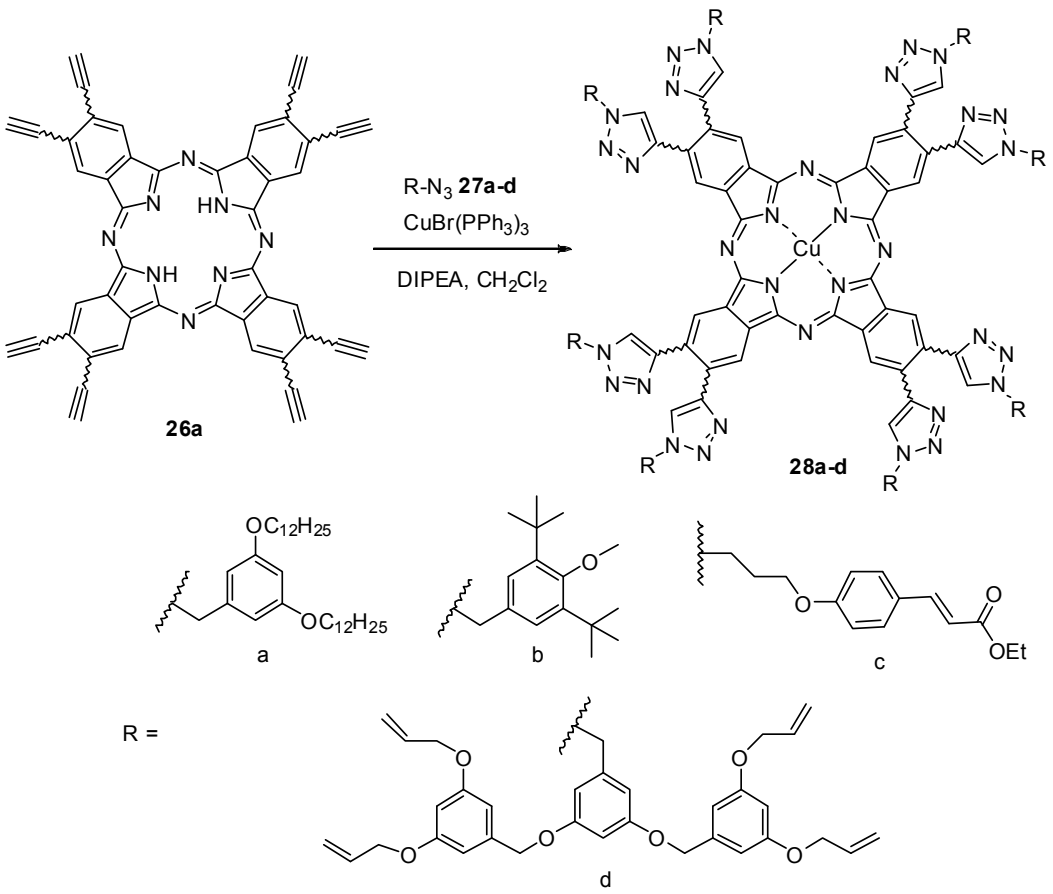


Figure 4-3: Alteration of symmetrically substituted phthalocyanines *via* multi click chemistry.[46]

CuAAC technique was also used to synthesize octatriazole-functionalized phthalocyanines in excellent yields, which are demonstrated to generate well-defined supramolecular structures when doped with zinc(II) triflate.[43] Yoshiyama and co-workers successfully used a double CuAAC methodology to prepare covalently connected binuclear phthalocyanines with both sterically demanding *tert*-Bu substituents or trifluoroethoxy groups with click spacers and investigated their clamshell properties.[44,45] Chen *et al.* functionally modified octaalkynyl Pc using click chemistry to prepare several Pc derivatives **28a-d** (Fig. 4.3) with different peripheral units on the macrocycle. These Pcs have been successfully used to fabricate solvent resistant Pc nanostructures *via* recently developed nano-imprint by melt processing (NIMP) technique.[46] Efficient attachment of Pcs to functionalized Single-Wall Carbon Nanotubes (SWNTs) *via* CuAAC

was reported by Bourgoin's group, which were applied as photoactive substances on ITO to generate photo-anodes.[47]

4.2 Synthesis of Tetraazaporphyrins (TAPs)

Tetraazaporphyrins (TAPs) belong to the general class of porphyrazines that are derivatives of porphyrins with methine bridges substituted by aza bridges. TAPs have all four methine bridges substitute by aza bridges similar to the more prominent phthalocyanines (Pcs) that also have benzene rings annelated to each of the four pyrrole groups of the porphyrin ring (Fig 4.4). Their opto-electronic and chemical properties are also similar to those of phtalocyanines because they are dominated by the meso-nitrogens in the macrocycle. In contrast, TAPs aggregate much less than phtalocyanines but similarly to porphyrins because of their smaller π-electron systems. TAPs have been tested as active materials in photoconductors,[53] gas sensors,[55] photovoltaic cells,[53] photodynamic therapeutics,[54] optical data storage devices,[55] and other commercially relevant applications. They are attractive compounds not only because of their high absorption coefficients in the visible range but also because of their often high thermal, chemical, and photochemical stability.[48-52]

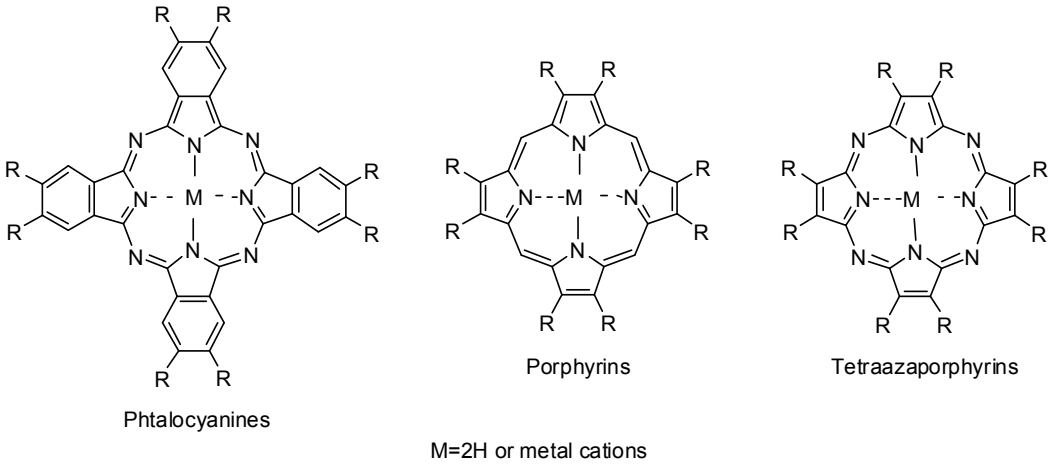


Figure 4-4: General structures of phthalocyanine, porphyrin and tetraazaporphyrin cores.

In 1937, Linstead and Cook first synthesized tetraazaporphyrins (TAPs) by reacting diphenylmaleodinitrile and anhydrous magnesium powder at 275 °C for 10 minutes to obtain the octaphenyl magnesium TAP almost quantitatively.[56] The same research group later found that maleodinitriles and their derivatives generate TAPs at substantially lower temperatures (90 °C) when refluxed in presence of magnesium *n*-propanolate in *n*-propanol. This procedure produces TAPs in yields of nearly 55% with respect to the maleodinitrile derivative. Removal of the Mg ion from the TAP core under acidic conditions (e.g. acetic acid or dilute hydrochloric acid) [57] gives access to the corresponding metal free TAPs, which can be subsequently metallated with many other metal ions. Linear polynitrile oligomers are the main side products of the magnesium *n*-propanolate method, [57,58,59] which agrees with the mechanism proposed by Oliver and Smith (Fig. 4.5). Formation of TAPs from maleodinitriles proceeds *via* reactive precursors that form oligomeric intermediates that subsequently condense to the magnesium ion templated cyclotetramer. The Mg(II) complex with two dimers is the proposed key intermediate.

Metal free TAPs are obtained by removing the Mg(II) ion in acidic solution and can be chelated with a wide variety of metal ions by exposing them to the desired metal salt solution. Several different elements, most commonly Cu, Zn, Co, and Ni, have been inserted into the central cavity of TAPs to fine tune their mesomorphism as well as the optoelectronic properties. The types of metals inserted in the cavity of TAPs also have tremendous impact on the liquid crystalline properties of the TAPs, in contrast to PCs where mesomorphism is little affected by the metallation.[56]

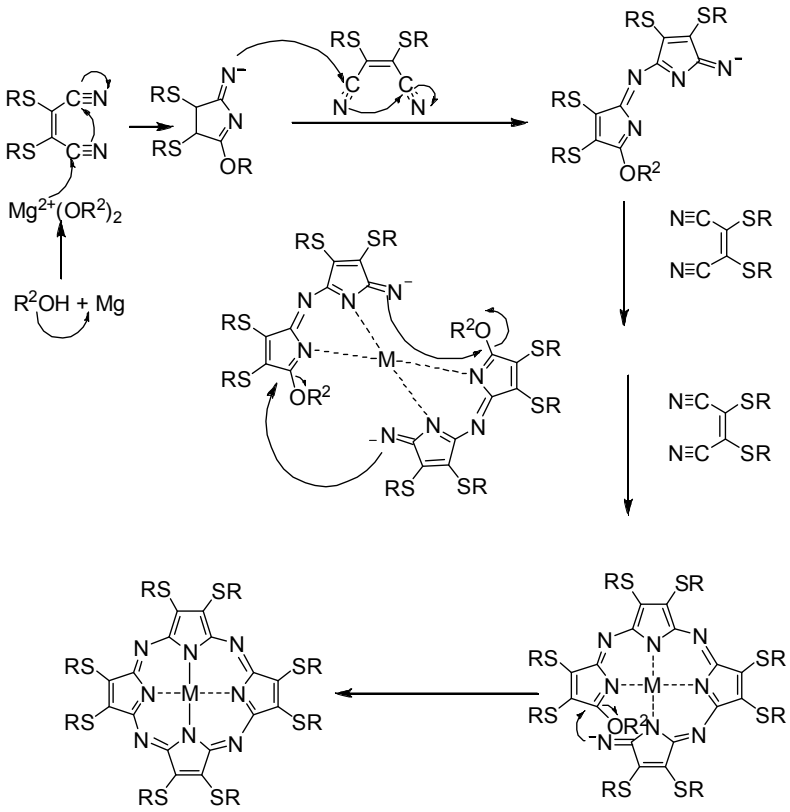
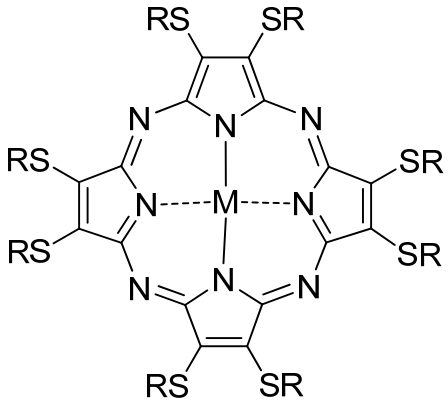


Figure 4-5: Proposed reaction mechanism for the formation of TAPs from maleodinitriles in the presence of magnesium *n*-propanolate.[59]

Metal-metal interactions significantly add to the co-facial interactions between mesomorphic TAPs and Pcs but the clearing temperatures (transition from liquid crystal to isotropic liquid phase) of the metal-free Pcs are often already above their decomposition temperatures so that the stabilizing influence of a metal ion cannot be studied based on transition temperatures. Most metal-free TAPs are not mesomorphic but their metallated analogues display columnar mesophases over wide temperature ranges. Pcs have a higher propensity to form columnar mesomorphism than TAPs because their π-electron system is larger, which increases π-π stacking interactions. However, the less strongly stacking and aggregating TAPs are better suited for studying the influences of metal ions and different functionalized side-chains on columnar mesomorphism.[58,60.]

In 1990 Doppelt and co-workers reported the first mesogenic TAPs and studied the mesomorphism of a series of metallated octakis(octylthio)tetraazaporphyrins. All of them exhibit hexagonal columnar mesophases,[61] which was later confirmed by Morelli's studies on copper TAPs.[62] The octathioether derivatives of TAPs appeared to be versatile core structures for discotics as the large polarizable sulfur atoms near the core enhance intra-columnar and inter-molecular stacking interactions[63,64] and the thioether linkage provided flexibility for the attachment of different side-chains.

Different examples of reported octakis(alkylthio)tetraazaporphyrin derivatives are shown in the Fig. 4.6. Studies on octakis(alkylthio)tetraazaporphyrins **18**[63] reveal that all metallated TAPs show mesomorphism whereas most metal-free TAPs do not except for the homologues with butyl and hexyl chains. The most stable columnar mesophases are formed by the copper and cobalt complexes. Vibrational and electronic spectral studies suggest that axial interactions between metal ions and sulfur atoms of neighboring macrocycles may alos contribute to intermolecular stacking interactions espeically in the solid phase.[65] Unexpectedly, compounds **18** form monolayer and multilayer Langmuir-Blodgett (LB) films although their amphiphilic character is weak.[66]



[63]**18** .R = C_nH_{2n+1}, n = 4, 6-10, 12
M = 2H, Co, Ni, Cu, Zn,

[67]**19** . R = $(CH_2CH_2O)_2CH_3$ or $(CH_2CH_2O)_3CH_3$
M = 2H, Co, Ni, Cu, Zn,

[68]**20**. R = $CH_2(CH_2)_nCH{=}CH_2$, n=1-3
M= 2H, Co, Ni, Cu

Figure 4-6:Examples of different octakis(octylthio)tetraazaporphyrins.

Our group studied the mesomorphism and Langmuir-Blodgett properties of octathioether TAPs containing oligo(oxyethylene) side-chains **19**.[67] Their mesomorphism is comparable to their alkyl chain analogues but compounds **19** form more stable Langmuir and Langmuir-Blodgett films. All metal-free and Zn(II) complexes are not mesomorphic while all other TAPs **19** display hexagonal columnar mesophases. In alkenyl(sulfanyl)TAPs **20**[68] introduction of terminal double bonds lessens the thermal range in which they exhibit mesomorphism compared to their saturated chain analogues. This trend is prominent in metal free, Cu, and Ni complexes and weaker in cobalt complex.

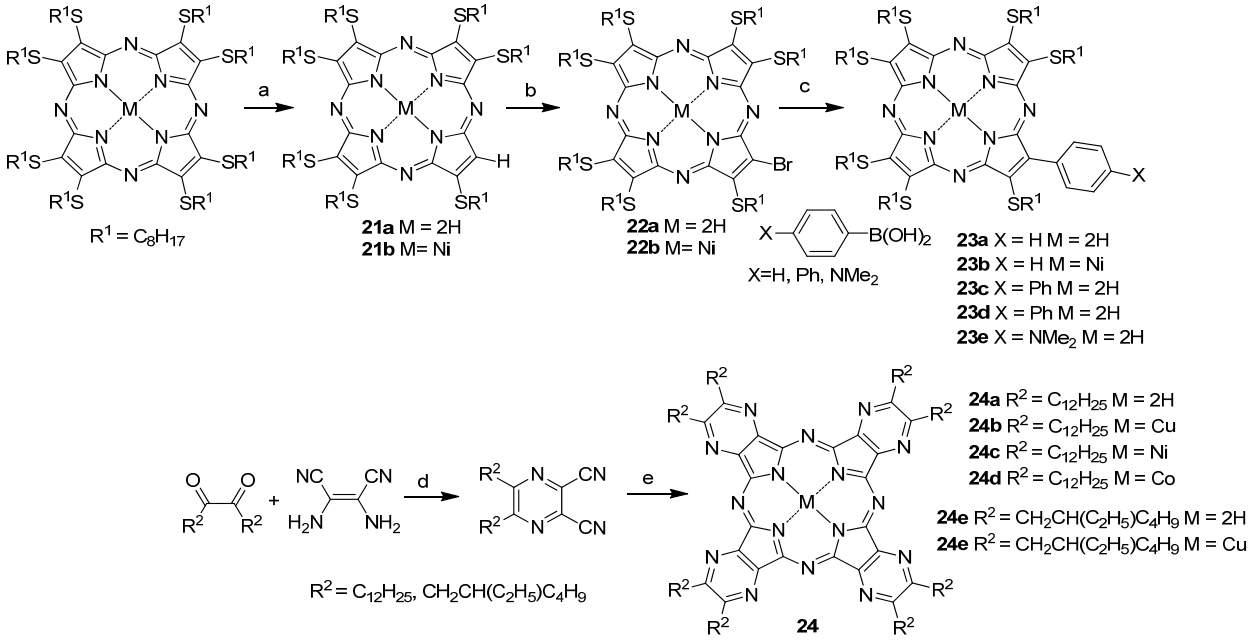
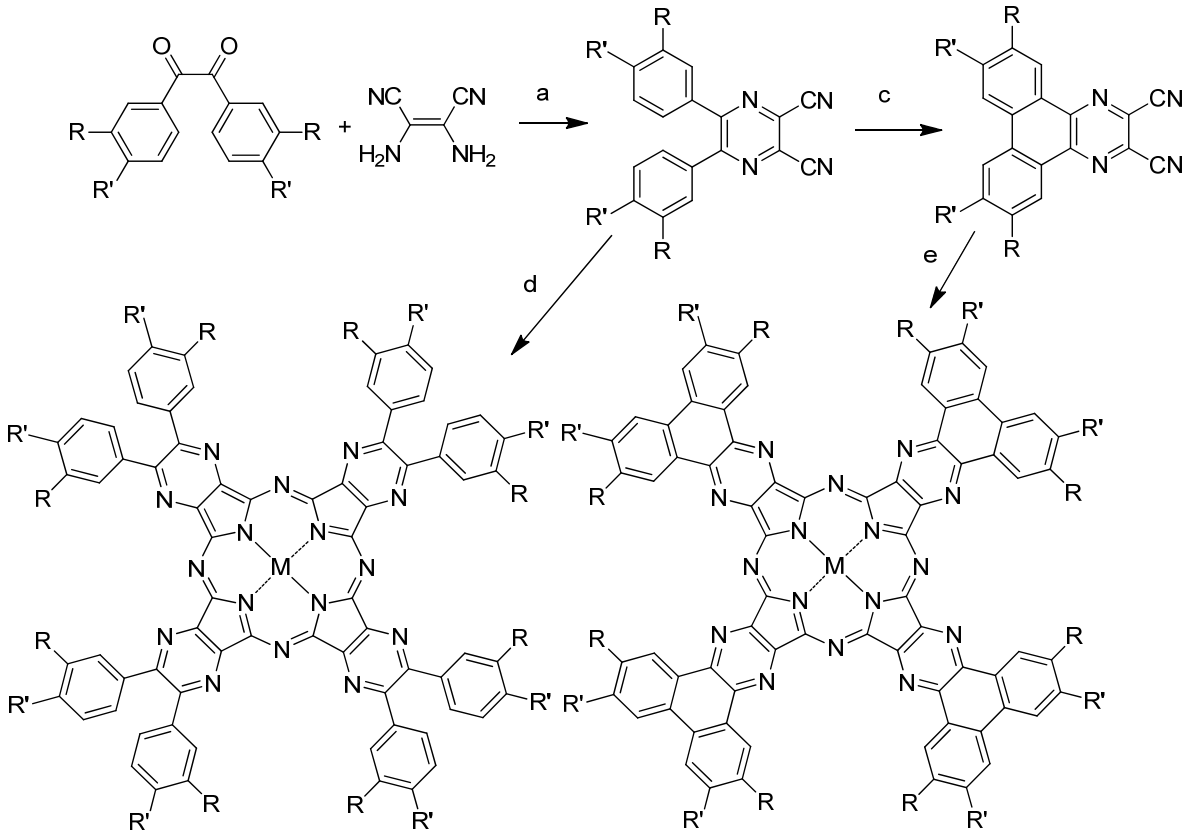


Figure 4-7: Preparation of unsymmetrically substituted TAPs 21a-b, 22a-b and 23a-e and tetrapyrazino TAPs 24a-e. Reaction conditions: a.$CrCl_2$, trichlorobenzene, n-BuOH, 190 °C, 7 hrs; b. NBS, rt., $CHCl_3$, 15 mins; c. $Pd(PPh_3)_4$, toluene, DMF, K_2CO_3; d. AcOH; e. MX_2, DBU, n-$C_5H_{11}OH$.

Several unsymmetrical TAPs **21a-b**, **22a-b** and **23a-e** [69] where one thioether group is substituted by hydrogen, bromide, or aryl groups, respectively, have been reported to exhibit

mesomorphism except for **23e**. Ohta *et al.* prepared octaaza PCs **24a-e**[70] that form rectangular columnar mesophases as well as their octaphenyl derivatives **25a-k**, which can be converted to tetra-diazatriphenylene annulated TAPs **26a-f** that display tetragonal columnar mesophases (Fig.4.7 and 4.8).[71-73]



25a R = $OC_{10}H_{21}$, R' = H M = Cu, **25g** R = OC_8H_{17}, R' = OC_8H_{17} M = Ni
25b R = $OC_{12}H_{25}$, R' = H M = Cu, **25h** R = $OC_{10}H_{21}$, R' = $OC_{10}H_{21}$ M = Cu
25c R = $OC_{10}H_{21}$, R' = H M = Ni, **25i** R = $OC_{10}H_{21}$, R' = $OC_{10}H_{21}$ M = Ni
25d R = $OC_{12}H_{25}$, R' = H M = Ni, **25j** R = $OC_{12}H_{25}$, R' = $OC_{12}H_{25}$ M = Cu
25e R = $OC_{10}H_{21}$, R' = H M = Cu, **25k** R = $OC_{12}H_{25}$, R' = $OC_{12}H_{25}$ M = Ni
25f R = OC_8H_{17}, R' = OC_8H_{17} M = Cu

26a R = R' = C_8H_{17} M = Cu
26b R = R' = $OC_{10}H_{21}$ M = Cu
26c R = R' = $OC_{12}H_{25}$ M = Cu
26d R = R' = $OC_{10}H_{21}$ M = Ni
26e R = R' = $OC_{12}H_{25}$ M = Cu
26f R = R' = $OC_{14}H_{29}$ M = Cu

Figure 4-8: Preparation of octaphenyl tetrapyrazino TAPs 25 and triphenylene TAPs 26. Reaction conditions: a. AcOH; b. MX_2, DBU, n-$C_5H_{11}OH$; c. VOF_3, BF_3/ Et_2O, CH_2Cl_2, rt., 45 mins; d. MCl_2, DBU, 2 methylbutan-2-ol, 72 hrs.

4.3 UV/VIS studies of TAPs

Metal free and metallated TAPs can be easily differentiated by their characteristic UV/VIS spectra. The metallated TAPs have a higher symmetry (D_{4h} symmetry) than their metal-free counterparts (D_{2h} symmetry) and exhibit one weak and one intense absorption at around 670 nm denoted as "Q-Bands". "Q-Bands" of metal-free TAPs split into two weak and two intense peaks at about710 nm and 650 nm because of their lower symmetry. [61]

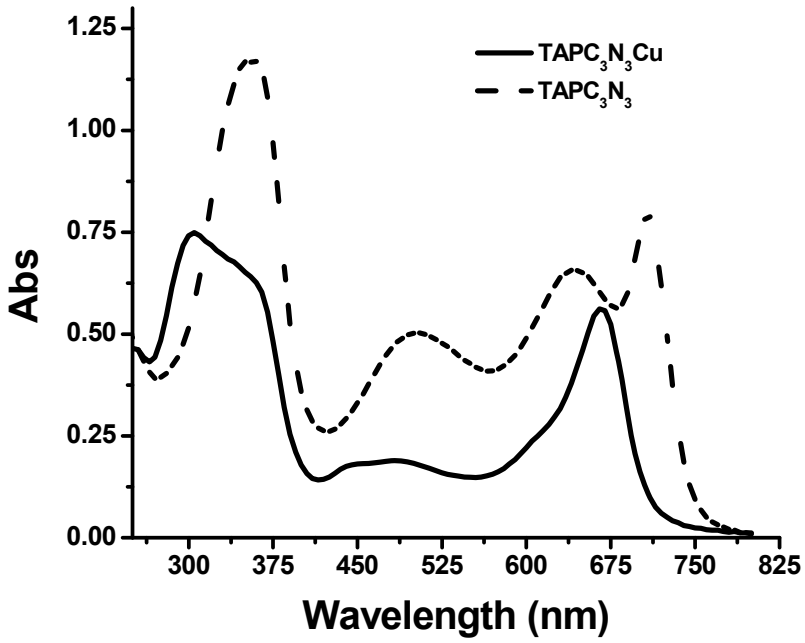
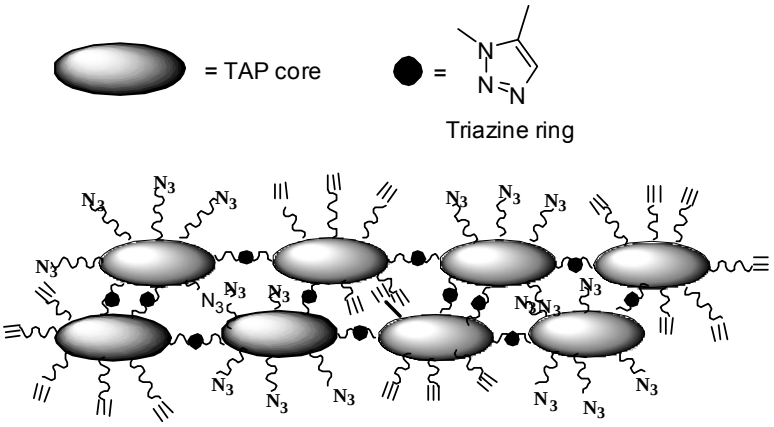


Figure 4-9: Representative UV-VIS spectra of a copper metallated (solid) and a metal-free TAP (dashed).

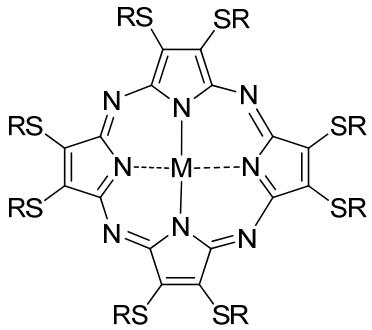
Absorptions common to metal-free and metallated TAPs are their Soret-Bands at 350 nm and a weaker absorption at 530 nm that is characteristic of all octathio-substituted TAPs (Fig. 4.9). Schaeffer and Gouterman used extended Hückel calculations to determine in detail what orbitals are involved in the electronic transitions of TAPs.[74,75]

4.4 Cross-linking of Discotic Tetraazaporphyrin Dyes in Two and Three Dimensions by "click" Chemistry

Reported here is the synthesis and mesomorphism of discotic tetraazaporphyrins (TAPs) that are octa-substituted with either terminal alkylazide or terminal alkynyl groups. 1:1 Mixtures of these compounds could be cross-linked by thermally activated [3+2] cycloaddition in a hexagonal columnar mesophase and in Langmuir monolayers *via* CuAAC. The Langmuir and Langmuir-Blodgett work was performed by Mohamed Ahmida and Hi Taing and only a few results are presented here to complete the description of the properties of these compounds. Both, CuAAC in Langmuir films and AAC in mesophases are unprecedented to the best of our knowledge. We also show for the first time that azide groups withstand the reaction conditions for the preparation of TAPs.



A



16aH: M = H; R = $(CH_2)_3N_3$ **16aCu**: M = Cu; R = $(CH_2)_3N_3$

16bH: M = H; R = $(CH_2)_6N_3$ **16bCu**: M = Cu; R = $(CH_2)_6N_3$

16cH: M = H; R = $(CH_2)_9N_3$ **16cCu**: M = Cu; R = $(CH_2)_9N_3$

17aH: M = H; R = $(CH_2)_3$—≡ **17aCu**: M = Cu; R = $(CH_2)_3$—≡

17bH: M = H; R = $(CH_2)_6$—≡ **17bCu**: M = Cu; R = $(CH_2)_6$—≡

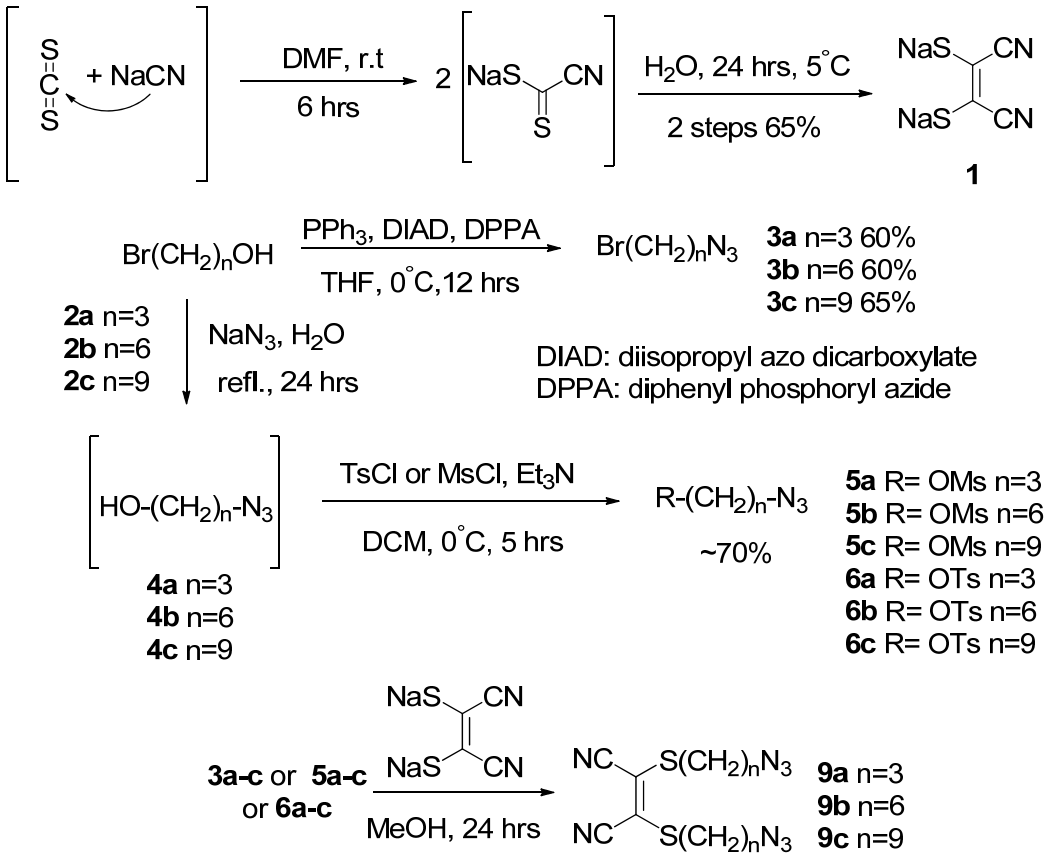
17cH: M = H; R = $(CH_2)_9$—≡ **17cCu**: M = Cu; R = $(CH_2)_9$—≡

Figure 4-10: Cross-linking of TAPs 16 and 17 by CuAAC in two dimensions (A) and structures of all synthesized TAPs.

4.5 Synthesis of TAPs

4.5.1 Synthesis of Maleodinitrile Derivatives

The starting material, disodium 1,2-dicyanoethylene-1,2-dithiolate **1** was synthesized from sodium cyanide and carbon disulfide in DMF following a literature procedure by Davidson and Holm. Its formation in 65% yield is in line with previously reported yields and verified by ^{13}C-NMR and IR spectroscopy.



Scheme 4.1: Synthesis of Maleodinitrile Derivatives 9a-c.

Adequate purification of **1** by several recrystalizations from water was indispensable to extend its shelf life to several months. Samples of **1** are best stored in a freezer under inert atmosphere in an amber container because it is temperature and light sensitive.

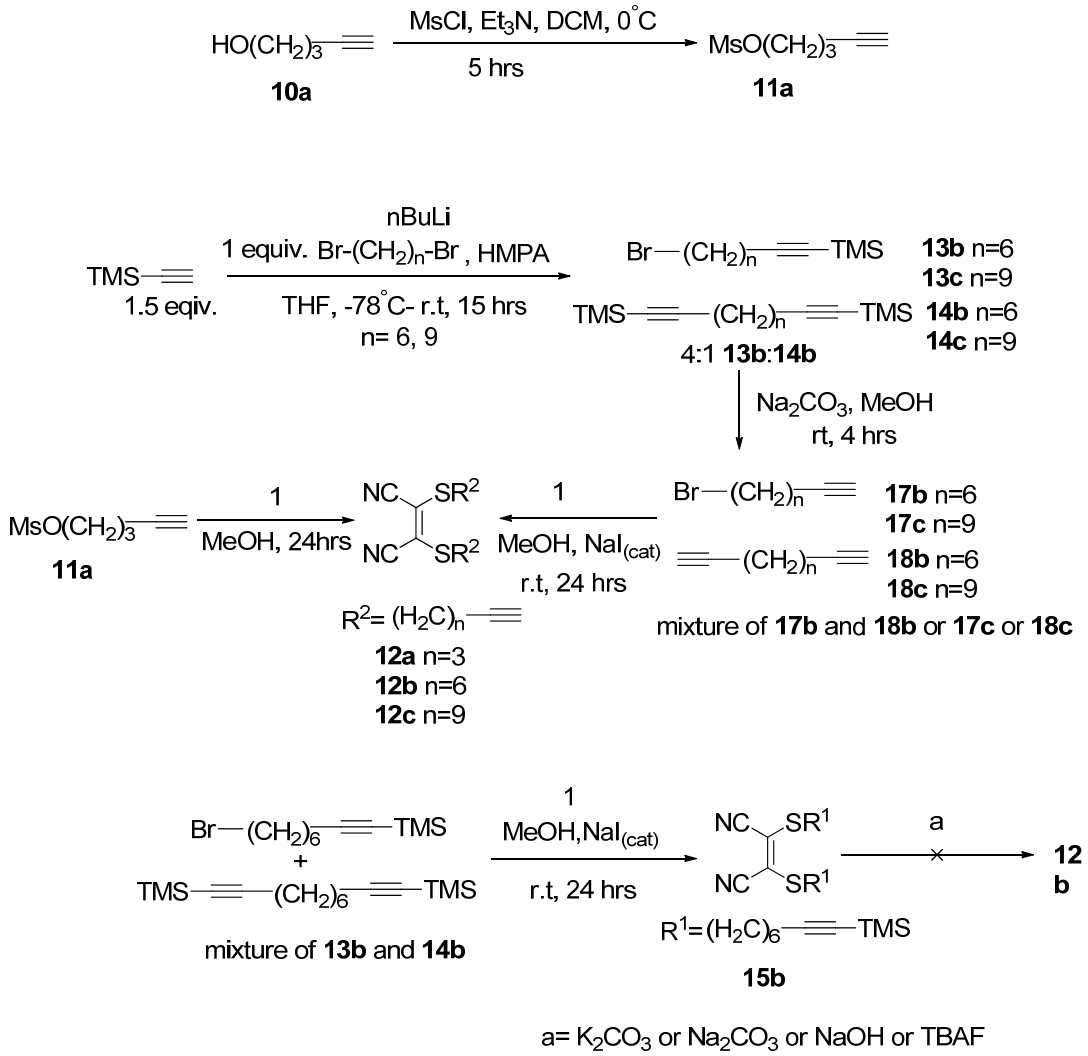
In order to prepare the required side chains we have followed different methodologies that are discussed in the following. Alkanes with terminal bromine and azide groups were prepared in one step from commercially available bromoalkanols **2**. The Mitsunobu-type reaction conditions generate the bromo-alkyl azides **3** in 60-65% yield.

We also tested a 2-step approach that uses less expensive reagents, may give higher yields overall, and introduces more reactive leaving groups for the subsequent S_N2 reaction with

compound **1**. The same bromoalkanols **2** are first converted to azidoalkanols **4** by applying Sharpless conditions[76] and then the alcohol is converted into a leaving group by tosylation and mesylation. Chromatographic separation of tosyl alkyl azide **6** from excess tosyl chloride and tosyl alkyl azide mixture was found to be tedious. On the contrary purification of corresponding Mesyl derivative was easier. We have also tried another interesting method where dibromo alkyls **7** were subjected to react with sodium azide to generate the corresponding mono-azide **3** and di-azide **8** derivatives in high yields but the separation of mono-azides from di-azides was difficult because of their surprisingly similar physical properties (similar R_f values).

All alkyl azides react with **1** at room temperature to give thio alkyl substituted maleodinitriles **9** in yields of 60%. Bromo alkyl azides **3** reacted best with maleodinitrile **1** in methanolic solution and in presence of a catalytic amount of potassium iodide. Tosyl or mesyl alkyl azides **5** or **6** reacted faster with maleodinitrile **1** than their bromo analogues **3** and did not require potassium iodide as catalyst.

Side-chains with terminal acetylene groups and their maleodinitriles were also prepared by different approaches depending on the spacer length. Commercially available 4-pentyn-1-ol **10a** was converted to corresponding mesylate derivative **11a** using mesyl chloride. Subsequently, compound **11a** was reacted with maleodinitrile in MeOH to generate dialkylated maleodinitrile derivative **12a**.



Scheme 4.2: Synthesis of Maleodinitrile Derivatives 12a-c.

Di-bromononane and di-bromohexane were used as starting materials for the corresponding maleodinitriles **12b,c**. Dibromoalkanes were reacted with 1.5 equivalents of trimethylsilyl acetylene (TMSA) to generate both mono- and di-trimethylsilylacetylene (TMSA) substituted derivatives **13** and **14**. The relative amounts of **13** and **14** were calculated based on proton NMR data. Separation of compound **14** was not necessary as it does not react with disodium 1,2-dicyanoethylene-1,2-dithiolate **1** and the reaction of the mixture **13b**/**14b** with **1** cleanly forms **15b** except for unreacted **14b**. Surprisingly, the subsequent cleavage of the

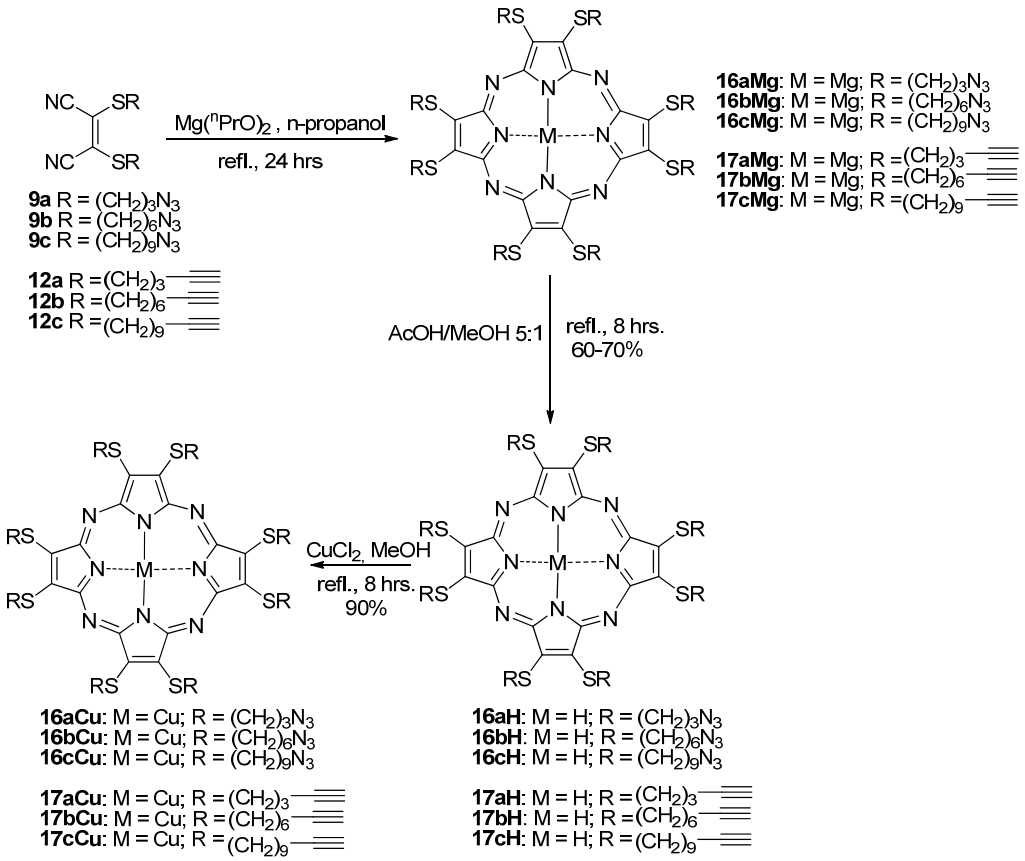
trimethyl silyl groups of **15b** was unsuccessful with commonly used methodologies, such as potassium carbonate, sodium carbonate, sodium hydroxide, and tetrabutyl ammonium fluoride, but resulted in decomposition of compound **15b**. Consequently, cleavage of the trimethyl silyl groups was conducted on mono- and di-trimethylsilylacetylene (TMSA) substituted derivative mixtures **13b,c** and **14b,c** to generate **17b,c** and **18b,c .** This mixture of **17** and **18** was reacted with maleoditrile to generate compounds **12b** or **12c** and unreacted **18b** or **18c**. Diacetylene derivatives **18b** or **18c** are easily removed from the mixture by evaporation in vacuum.

4.5.2 Synthesis of TAPs

Crude Mg chelated TAPs **16a-cMg** and **17a-cMg** were synthesized in typical yields of 60%-70% from maleodinitriles **9** and **12** by the Mg *n*-propanolate method described earlier (Scheme 4.3). Remarkably, neither the azide nor the acetylene groups are affected by the reaction conditions.

The generation of the TAP macrocycle was verified by UV/VIS spectroscopy and the presence of azide and acetylene functional groups was confirmed by IR spectroscopy of the crude reaction mixtures.

However, the Mg chelated TAPs were not further purified because of their high propensity to axially co-ordinate solvents and other Lewis bases to the central Mg^{2+} ion. Coordinated axial ligands obstruct π-π stacking and increase solubility but complicate purification and characterization, which is why the crude compounds were first dematellated before being purified and fully characterized.



Scheme 4.3: Synthesis of TAPs with azide and acetylene end-groups.

Demetallation of Mg chelated TAPs **16a-cMg** and **17a-cMg** was performed by heating them in methanolic acetic acid (5:1 acetic acid /MeOH) at 80 °C for about 8 hours. Progress of demetallation was monitored by UV/VIS absorption spectroscopy following the typical changes of the Q-bands (Fig. 4. 9). Purification of the crude products were acomplished by precipitation from acetone solutions by slow addition of methanol: water (2:1). Finally, chromatographic purification on silica gel gave analytically pure samples in overall yields of 30-35% starting from **9** and **12** respectively. Compounds **16a-cH** and **17a-cH** were characterized by ^{1}H-NMR, ^{13}C-NMR, EA and IR spectroscopy.

Incorporation of Cu^{2+} ion into the metal-free TAP was performed by exposing compounds **16a-cH** and **17a-cH** to methanolic solutions of copper acetate or copper chloride. Again UV/VIS

spectroscopy was used to monitor the progress of the metallation to compounds **16a-cCu** and **17a-cCu** by following the change of their characteristic Q band absorptions. The paramagnetic character of the Cu^{2+} ion did not allow for NMR studies on these samples but they were characterized by IR, UV/VIS spectroscopy and HRMS.

4.6 Mesomorphism and Click Chemistry studies of 16 and 17 TAPs.

The thermal stability of TAPs **16** and 1**7** is limited by the stability of their alkynyl and alkylazide chains and was studied by thermal gravimetric analysis under He. Least stable are TAPs 1**6aH** and 1**6aCu** containing azide groups and propyl spacers that decompose between 100-120 °C (onset temperature). All other azid and alkynyl substituted TAPs decompose between 140-160 °C, which is still significantly lower than the reported 240 °C for analogous octa-alkenyl substituted TAPs.[68] Only small and non-systematic differences in thermal stability are observed between metal-free and copper containing TAPs.All twelve TAPs were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) to probe their mesomorphism (Figure 4.12). TAPs 1**6aCu**, 1**6bCu**, 1**7aH**, and **17aCu** display columnar liquid crystal phases.

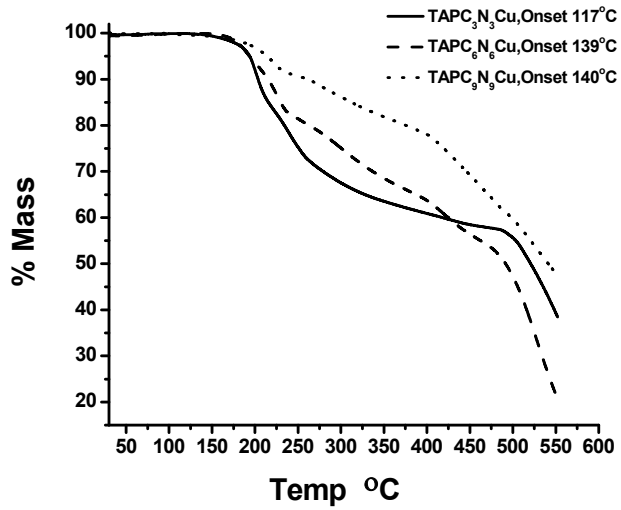


Figure 4-11:TGA graph of TAPs 16a-cCu.

All other TAPs form crystalline or columnar soft crystal phases, except for **16cH**, **16cCu** and **17bCu** that are amorphous soft solids and **17cH** and **17cCu** which are isotropic liquid. Clearly, the more stable mesophases are obtained with the shorter propyl rather than the hexyl or nonyl spacers.

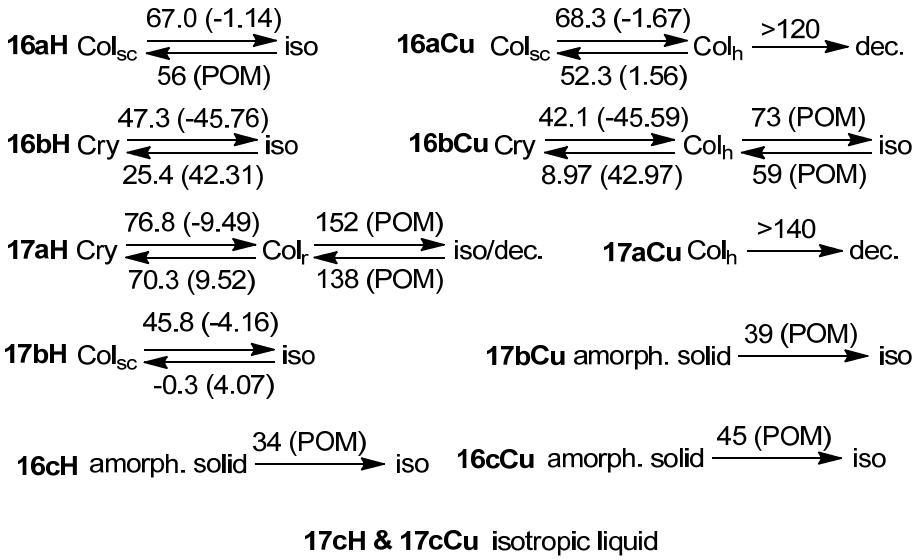


Figure 4-12: Phase behaviour of TAPs as determined by POM, DSC, and XRD. Transition temperatures are given in °C and enthalpies in kJ/mol. (POM) indicates that transition temperatures are obtained by POM and are not observed by DSC. Col_h and Col_r are columnar mesophases of hexagonal and rectangular symmetry, respectively, and soft crystal phase of columnar structure are designated as Col_{sc}.

A comparison with the reported mesomorphism of octa-alkenyl substituted TAPs[67] suggests that terminal alkyne and azide groups destabilize columnar mesophases more than terminal alkenes. Mesophases of azide TAPs **16** have the lowest temperature ranges, which is mainly a result of their higher propensity for crystallization and, for propyl spacers, their lower thermal stability in comparison to TAPs **17**. However, the obtained data do not conclusively determine whether columnar mesophases of TAPs are more destabilized by azide or alkyne groups.

Langmuir films (L-films) of a 1:1 mixture of TAPs **16bH** and **17aH** were chosen for the cross-linking by CuAAC because the macrocycles seem to adopt a more face-on orientation at low surface pressures based on the calculated area per molecule of about 240 $Å^2$. A face-on orientation of the macrocycle is expected to bring more azide and alkyne groups in contact with the catalyst in the aqueous subphase than an edge-on orientation.

L-films of the 1:1 mixture on an aqueous solution of copper(II) acetate and sodium ascorbate became insoluble in organic solvents after about 1 hour. Progress of the cross-linking is monitored by the decrease in surface pressure at a constant area and the point at which the surface pressure remained constant was interpreted as the completion of the CuAAC reaction (after about 190 min).

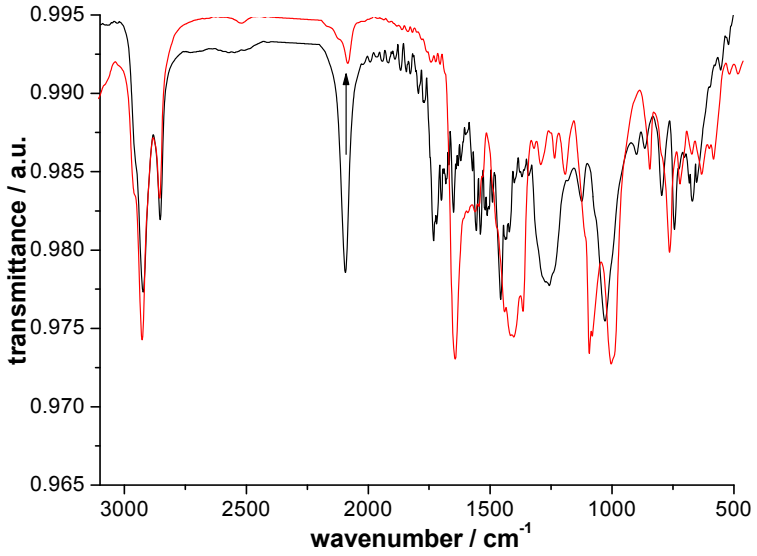


Figure 4-13: IR (film on KBr) of a 1:1 mixture of TAPs 16bH and 17aH (black) and of the same mixture as Langmuir film after cross-linking by CuAAC (0.638 x 10^{-3} M copper (II) acetate and 1.92 x 10^{-3} M sodium ascorbate) for 200 minutes (red) and transfer onto a KBr disk. The progress of CuAAC is monitored by the decrease of the N_3 and C≡C stretching absorptions at 2100 cm^{-1} (arrow) and no further change was observed for reaction times long than 200 minutes. All L film work was performed by Mohamed M. Ahmida

The occurrence of CuAAC and its completion is independently confirmed by IR measurements of transferred L-films that show a large decrease of the overlapping azide/alkyne absorptions with time but not a complete disappearance (Fig. 4.13). A conversion of only a fraction of all azide and alkyne groups is reasonable because some azide and alkyne groups will not be able to reach each other once the molecules are locked into place after the first groups have reacted (Fig. 4.14). In fact, it is surprising that about 78% seem to react based on the relative integrations of the azide/alkyne absorptions at 2100 cm^{-1} by using the C-H stretching absorptions as internal reference.

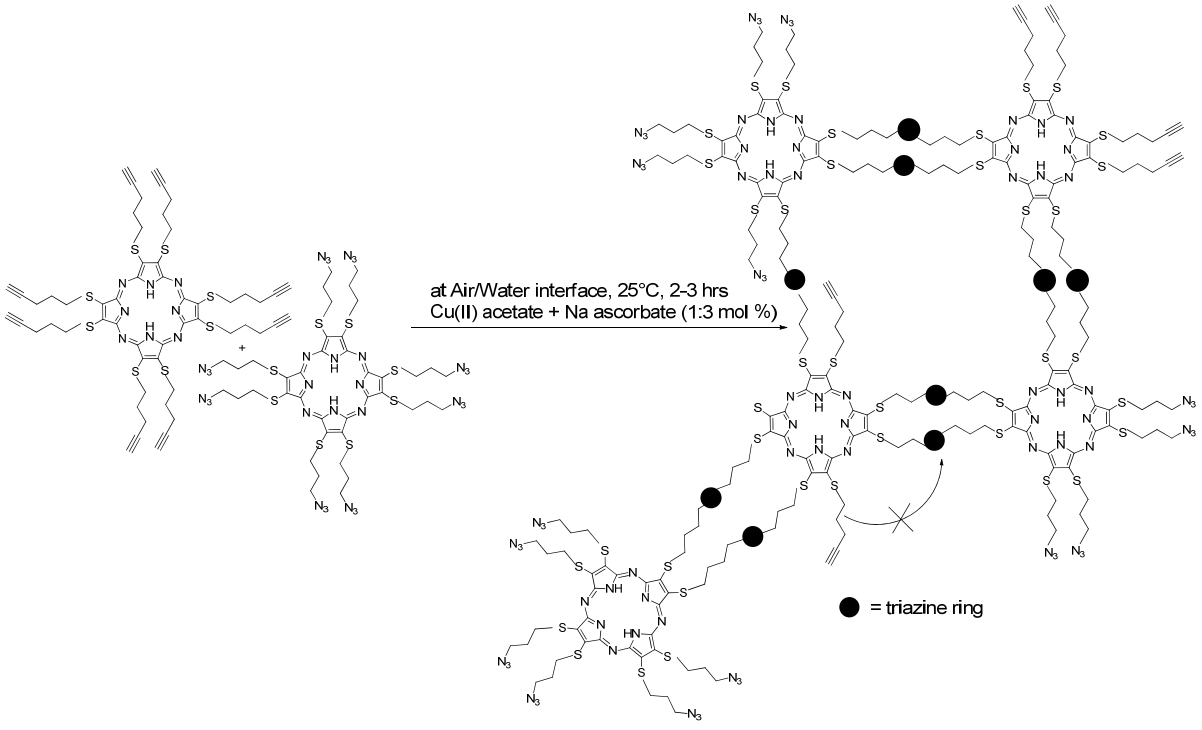


Figure 4-14: Cartoon of cross linking patterns of octa-azide and -acetylene TAPs in a Langmuir Film.

Solutions of any 1:1 mixture of azide TAPs **16** and alkyne TAPs **17** can be cross-linked by standard CuAAC to give amorphous dye polymers but more intriguing is their cross-linking in columnar mesophases without the use of a copper catalyst.

A 1:1 mixture of 1**6aCu** and **17aCu** displays a Col_h phase at 65 °C and was kept at that temperature for 3 days. IR spectroscopy is used to monitor the progress of azide-alkyne cycloaddition (Fig. 4.15)

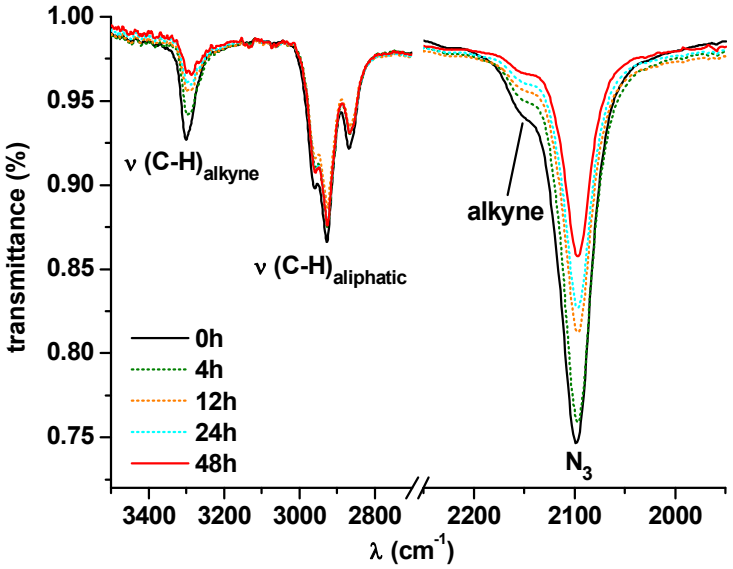


Figure 4-15: IR spectra of a 1:1 mixture of TAPs 16aCu and 17aCu as thin film on a KBr disk after heat treatment at 65 ºC for specific periods of time. No further change was observed for heat treatments longer than 48 hrs.

while powder XRD measurements confirm the stability of the Col_h phase during the cross-linking process (Fig. 4.16).

Again the decrease of the combined azide/alkyne absorption peak was monitored by IR that continued for 40-48 hours until its area was reduced by about 60%. This was 18% less the reduction that was obtained for an L-film but solubility tests showed that the material is already rendered insoluble in organic solvents after 24 hours. Unexpectedly, the cross-linking process did not significantly affect the columnar mesophase, as evidenced by XRD, despite the formation of relatively bulky and polar triazole rings.

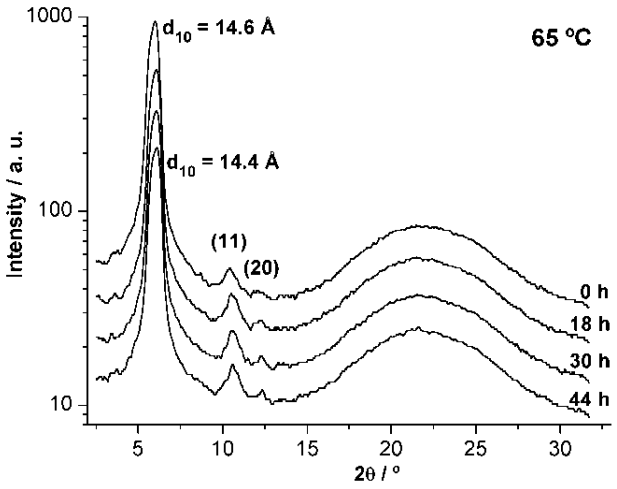


Figure 4-16: Powder XRD patterns of a 1:1 mixture of 16aCu and 17aCu at 65 °C over 44 hours. The y-axis has been shifted for clarity.

What is observed is a small decrease in intensity of the (10) reflection and its gradual shift to smaller lattice spacings by 0.2 Å over 44 hours. The former change indicates a small decrease in columnar packing order while the latter change is explained with the expected shrinkage of the intercolumnar packing distance during cross-linking.

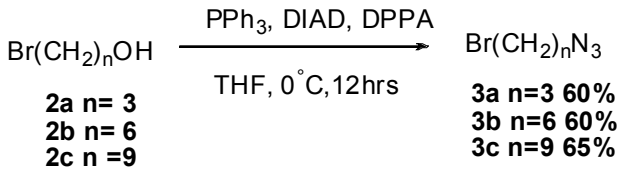
4.7 Conclusions

Described are the synthesis and properties of two new sets of TAPs that contain either eight alkylazide or eight alkynyl groups. Their thermal stability is at least 80 °C lower than for analogous alkenyl substituted TAPs and decreases with decreasing spacer length. Only few of the TAPs with shorter alkyl spacers display columnar mesophases but, surprisingly, include the metal-free derivative **17aH**. Mixtures of azide and alkyne TAPs can be cross-linked *via* CuAAC in Langmuir films and as thin films to generate insoluble polymers. It is also shown that a 1:1 mixture of a discotic TAPs **16aCu** and **17aCu** can be cross-linked by thermally activated azide-alkyne cycloaddition in their columnar mesophases and without significantly affecting the

hexagonal columnar mesophase. However, more systematic studies are required to probe the full scopes of thermally activated and CuAAC catalyzed cross-linking of these materials in thin films and mesophases.

4.8 Experimental

4.8.1 Synthesis of 1-bromoalkylazides 3a, 3b and 3c



PPh_3 (7.2 g, 27.5 mmol) were added to a stirred solution of 3-bromo-1-propanol (2.26 mL, 3.475 g, 25 mmol) or 6-bromo-1-hexanol (3.27 mL, 4.527 g, 25 mmol) or 9-bromo-1-nonanol (5.578 g, 25 mmol) in 100 mL of THF under nitrogen. The solution was stirred for 15 minutes at 0°C before diisopropylazodicarboxylate (DIAD) (6 mL, 5.560 g, 27.5 mmol) was added dropwise followed by dropwise addition of diphenylphosphorylazide (DPPA) (6.53 mL, 7.568 g, 27 mmol). The yellowish reaction mixture was allowed to warm up to room temperature and stirred for another 15 hrs. The mixture was concentrated to half of its volume before 40 mL of a 2:1 mixture of diethyl ether/hexane was added and the solution was kept at -8°C for an hour to precipitate out excess PPh_3 and generated $OPPh_3$. Removal of the precipitate by filtration was followed by a concentration of the organic layer in vacuum until a yellow viscous oil is obtained, which was further purified by flash chromatography on silica gel using ethyl acetate/hexane 1:4 as eluent to generate the pure product as a yellow oil.

1-Azido-3-bromo-propane (**3a)**: (2.45 g, 60%);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.10 (tt, J = 6.33 Hz, J = 6.20 Hz, 2H), 3.48 (m, 4H) ;

IR (cm^{-1}): 2932, 2856 (m,ν(C-H)), 2091 (s,ν(N_3));

MS [HR-CI]: Theoretical: 162.9745; Found: 162.9748 .

1-Azido-6-bromo-hexane (**3b)**: (3.08 g, 60%);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.44 (m, 4H) , 1.61 (m, 2H), 1.86 (m, 2H), 3.27 (t, J = 6.6 Hz, 2H), 3.40 (t, J = 6.6 Hz, 2H);

IR (cm^{-1}): 2935, 2871 (ν(C-H)), 2094 (ν(N_3));

MS [HR-CI]: Theoretical: 177.0153 [M - N_2]; Found: 177.0153 [M - N_2]$^{+}$.

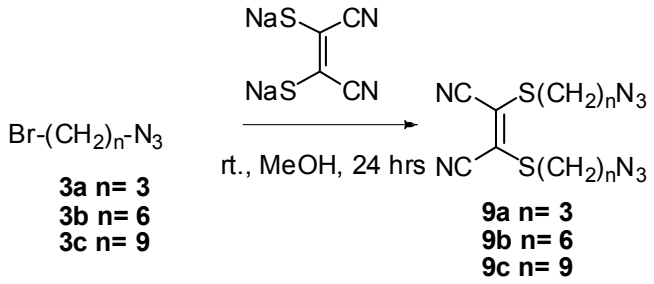
1-Azido-9-bromononane (**3c**): (4.032g, 65%)

^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.30-1.41 (m, 10H), 1.55-1.58 (m, 2H), 1.84(p, J=5.1Hz, 2H), 3.25(t, J=3.6Hz, 2H), 3.40 (t, J=3.9Hz, 2H)

^{13}C-NMR (300 MHz, $CDCl_3$, δ): 26.78, 28.21, 28.75, 28.92, 29.14, 29.37, 32.88, 34.12, 51.57.

MS [HR-CI]: Theoretical: 205.0592 [M - N_2]; Found: 205.0587 [M - N_2]$^{+}$.

4.8.2 Synthesis of 1,2-dicyano-1,2-bis(azido-alkylthio)ethylene (9a, 9b and 9c)



Compounds **3a** (2.445 g, 15 mmol) or **3b** (3.09 g, 15 mmol) or **3c** (3.72 g, 15 mmol) were added to a stirred solution of maleodinitrile **1** (1.3 g, 7 mmol) and NaI (105 mg, 0.7 mmol) in 50 mL of methanol at room temperature under nitrogen and the solution was stirred for 24 hrs. Methanol was evaporated under vacuum and the residue was extracted with dichloromethane (3 x 50 mL). The combined organic layers were concentrated under vacuum and passed through

a short column of silica gel using a 1:1 mixture of DCM/Hexanes as an eluent to generate the pure product as a viscous orange liquid.

cis-1,2-dicyano-1,2-bis(3-azido-propylthio)ethylene (**9a**): (1.51 g, 70%);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.99 (p, J = 6.74Hz, 4H), 3.21 (t, J = 7.07 Hz, 4H), 3.48 (t, J = 6.34 Hz, 4H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 29.11, 32.02, 49.39, 111.82, 121.15;

IR (cm^{-1}): 2928, 2855 (m, ν(C-H)), 2251 (m, ν(CN)), 2095 (s, ν(N_3)), 1647 (m, ν(C=C));

HR-MS (m/z) [CI]: Theoretical: 308.0628; Found: 308.0626.

cis-1,2-dicyano-1,2-bis(6-azido-hexylthio)ethylene (**9b**): (1.92 g, 65%);

^{1}H NMR (300 MHz, $CDCl_3$, δ):1.36 (m, 8H), 1.53 (m, 4H), 1.67 (m, 4 H), 3.05 (t, J = 7.2 Hz, 4H), 3.20 (t, J = 6.90 Hz, 4H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 27.49, 27.55, 28.81, 29.57, 34.69, 51.26, 112.05, 120.24;

IR (cm^{-1}): 2928, 2855 (m, ν (C-H)), 2259 (m, ν (CN)), 2095 (s, ν (N_3)), 1643 (m, ν (C=C);

HR-MS (m/z) [CI]: Theoretical: 392.1561; Found: 392.1565.

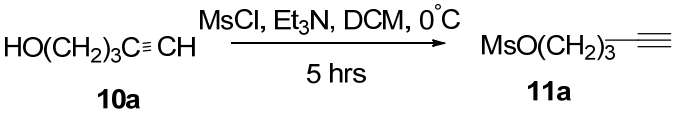
cis-1, 2-dicyano-1, 2-bis (9-azido-nonylthio) ethylene (**9c**): (2.068 g, 62%);

^{1}H NMR (300 MHz, $CDCl_3$, δ):1.35- 1.48 (m, 24H), 1.75 (p, J=7.2 Hz, 4H), 3.14 (t, J=7.5 Hz, 4H), 3.29 (t, J=6.9 Hz, 4H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 26.76, 28.88, 29.01, 29.20, 29.31, 29.49, 30.59, 35.37, 51.50, 140.71, 153.22.

HR-MS (m/z) [CI]: Theoretical: 476.2504; Found: 476.2516.

4.8.3 Synthesis of pent-4-yn-1-yl methanesulfonate (11a)



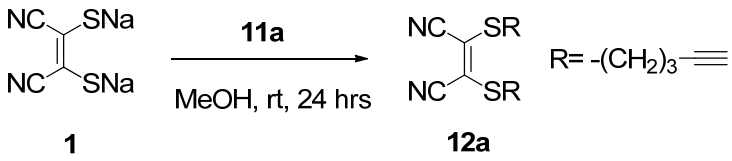
Methane sulfonyl chloride (1.87 mL, 2.750 g, 24 mmol) was added dropwise to a stirred solution of 4-pentyne-1-ol (1.84 mL, 1.680 g, 20 mmol) in 50 mL of diethyl ether and 5 mL triethyl amine was add at 0 ^{o}C under nitrogen. The reaction mixture was then allowed to warm to room temperature and stirred for another 5 hrs. Water was added to quench the reaction and HCl (1 M) was added dropwise to establish and maintain a pH of 7. The reaction mixture was extracted with H_2CCl_2 (3 x 50 mL) and the combined organic layers were washed with water (3 x 50 mL) and dried over anhydrous $MgSO_4$. The solution was concentrated and the pure product was obtained as a viscous brown liquid by solid phase extraction from silica with H_2CCl_2.

(2.9 g, 90%);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.95-1.99 (m, 3H), 2.35-2.39 (m, 2H), 3.04 (s, 3H), 4.37 (t, J= 6 Hz, 2H)

(consistent with reported values) [77]

4.8.4 Synthesis of 2,3-bis(pent-4-yn-1-ylthio)maleonitrile (12a)



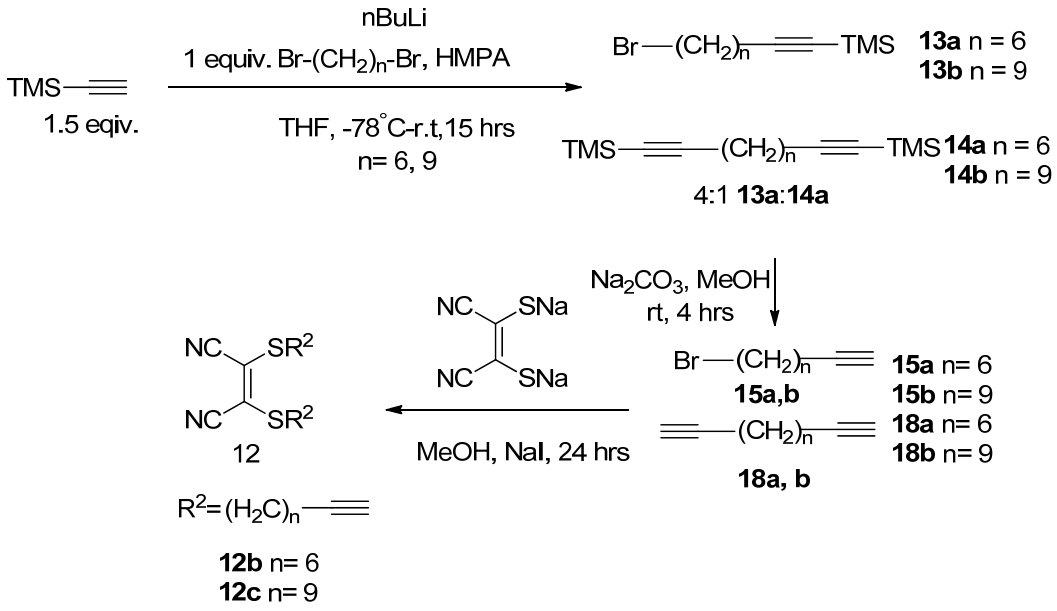
Pent-4-yn-1-yl methanesulfonate **11a** (2.6 g, 16 mmol) was added to a stirred solution of maleodinitrile **1** (1.3 g, 7 mmol) in 50 mL anhydrous methanol at room temperature and stirred for 24 hrs under nitrogen. MeOH was evaporated under vacuum and the residue was extracted with H_2CCl_2 (3 x 50 mL). The combined organic layers were concentrated under vacuum and passed through a column of silica gel using a 1:1 mixture of H_2CCl_2/hexanes) as eluent to generate the pure product as a viscous orange liquid.(1.25 g, 65 %);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.95 (p, J=3.3Hz, 4H), 2.024 (t, J= 2.7 Hz, 2H), 2.368 (dt, J= 3Hz, J= 6.75 Hz, 4H), 3.26 (t, J= 6Hz, 4H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 17.20, 28.44, 33.70, 70.18, 81.95, 111.95, 121.26.

HR-MS (m/z) [CI]: Theoretical: 274.0598; Found: 274.0591.

4.8.5 Synthesis of a mixture of (8-bromooct-1-yn-1-yl)trimethylsilane (13a) and 1,10-bis(trimethylsilyl)deca-1,9-diyne



*n*BuLi in hexane (1.6 M, 7.65 mL, 12.24 mmol) was added dropwise over a period of 5 min to a stirred solution of trimethyl silyl acetylene (1.44 mL, 1 g, 10.2 mmol) in 100 mL of THF at -78 ^{o}C under nitrogen. The resulting solution was stirred at -78 ^{o}C for 45 min before a solution of 1, 6-dibromohexane (1.07 mL, 1.7 g, 6.8 mmol) in hexamethyl phosphoramide (1.2 mL, 1.219 g, 6.8 mmol) was added dropwise at -78 ^{o}C.

The mixture was allowed to warm up to room temperature and stirred for another 5 hrs. It was then poured into 250 mL of water and extracted with H_2CCl_2 (3 x 100 mL) and the combined organic layers were dried over anhydrous $MgSO_4$ and finally passed through a short column of silica gel by using hexane as eluent.

The product is obtained in a 4:1 mixture of (8-bromooct-1-yn-1-yl)trimethylsilane **13a** and 1,10-bis(trimethylsilyl)deca-1,9-diyne based on ^{1}H-NMR analysis and was used for the next step without separation.(combined 1.260 g, 70%);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.130 (s), 1.36-1.47 (m), 1.86-1.88 (m), 2.18-2.24 (m, 6H), 3.39 (t, J= 6.9 Hz, 4H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 0.28, 18.43, 19.87, 27.40, 27.73, 27.95, 28.32, 28.44, 28.55, 32.61, 32.72, 33.76, 33.92, 84.47, 84.66, 107.42, 107.66.

4.8.6 Synthesis of 2,3-bis(oct-7-yn-1-ylthio)maleonitrile (12b)

A 4:1 mixture of (8-bromooct-1-yn-1-yl)trimethylsilane **13a** and 1,10-bis(trimethylsilyl)deca-1,9-diyne (1.191 g, 4.5 mmol) in 100 mL MeOH was treated with K_2CO_3 (1.105 g, 8 mmol) at room temperature and stirred for 5 hrs to remove the trimethylsilane groups. Excess of K_2CO_3 was precipitated at 0 ^{o}C and filtered off before a solution of maleodinitrile (280 mg, 1.5 mmol) and NaI (24 mg, 0.15 mmol) was added. The reaction mixture was stirred for another 24 hrs at room temperature, MeOH was evaporated, and the residue was suspended in 100 mL of H_2CCl_2. Precipitates were removed by filtration before the organic layer was concentrated and passed through a column of silica gel using a 4:1 mixture of H_2CCl_2 /hexanes) as an eluent to generate pure **12b** as a yellow liquid.

12b (774 mg, 60%)

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.46-1.47 (m, 12H), 1.74 (t, J=6. 6 Hz, 4H), 1.94 (t, J=2.7 Hz, 2H), 2.17-2.21 (m, 4H), 3.12 (t, J=7.2 Hz, 4H),

^{13}C-NMR ($CDCl_3$) δ: 18.38, 28.01, 28.11, 28.21, 29.83, 35.08, 68.56, 84.39, 112.18, 121.12.

HR-MS (m/z) [CI]: Theoretical: 358.1537; Found: 358.1543.

4.8.7 Synthesis of a mixture of 11-bromoundec-1-yne (15b) and trideca-1,12-diyne (18b)

*n*BuLi in hexane (1.6 M, 7.65 mL, 12.24 mmol) was added dropwise over a period of 5 min to a stirred solution of trimethyl silyl acetylene (1.44 mL, 1 g, 10.2 mmol) in 100 mL of THF at -78 ^{o}C under nitrogen. The resulting solution was stirred at -78 ^{o}C for 45 min before a solution of 1, 9-dibromononane (1.3 mL, 1.94 g, 6.8 mmol) in hexamethyl phosphoramide (1.2 mL, 1.219 g, 6.8 mmol) was added dropwise at -78 ^{o}C.

The mixture was allowed to warm up to room temperature and stirred for another 5 hrs. It was then poured into 250 mL of water and extracted with H_2CCl_2 (3 x 100 mL) and the combined organic layers were dried over anhydrous $MgSO_4$ and finally passed through a short column of silica gel by using hexane as eluent. Finally the crude liquid was dissolved in 100 mL MeOH and added K_2CO_3 (1.105 g, 8 mmol). The reaction mixture was stirred at room temperature for 5 hrs to remove the trimethylsilane groups. Excess of K_2CO_3 was precipitated at 0 ^{o}C and solvent was evaprated to get 2:1 mixture of **15b** and **18b.** (combined 1.101 g , 70%)

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.30 (broad), 1.39 (broad), 1.47- 1.54 (m) 1.85 (q, J= 6.9 Hz), 1.93 (t, J= 2.7 Hz), 2.17 (dt, J= 2.4 Hz & J= 6.6 Hz, 10H), 3.40 (t, J= 6.9 Hz, 4H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 18.43, 26.15, 28.18, 28.51, 28.74, 29.01, 29.06, 29.30, 29.36, 29.46, 29.68, 32.86, 33.98, 58.56, 68.08, 72.99, 84.79

4.8.8 Synthesis of 2,3-bis(undec-10-yn-1-ylthio)maleonitrile (12c)

2:1 mixture of **15b** and **18b** (1 g, 4.3 mmol) was added to a stirred solution of maleodinitrile **1** (240 mg, 1.3 mmol) and NaI (30 mg, 0.2 mmol) in 50 mL anhydrous methanol at room temperature and stirred for 24 hrs under nitrogen. MeOH was evaporated under vacuum and the residue was extracted with H_2CCl_2 (3 x 50 mL). The combined organic layers were concentrated under vacuum and passed through a column of silica gel using a 1:1 mixture of

H_2CCl_2/hexanes) as eluent to generate the pure product as a viscous orange liquid. (345 mg, 60 %);

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.29-1.45 (m, 24H), 1.75 (p, J= 6.9 Hz, 4H), 1.97 (t, J= 2.4 Hz, 2H), 2.12 (dt, J=2 Hz and J= 6.9 Hz, 4H), 3.14 (t, J= 7.2 Hz, 4H);

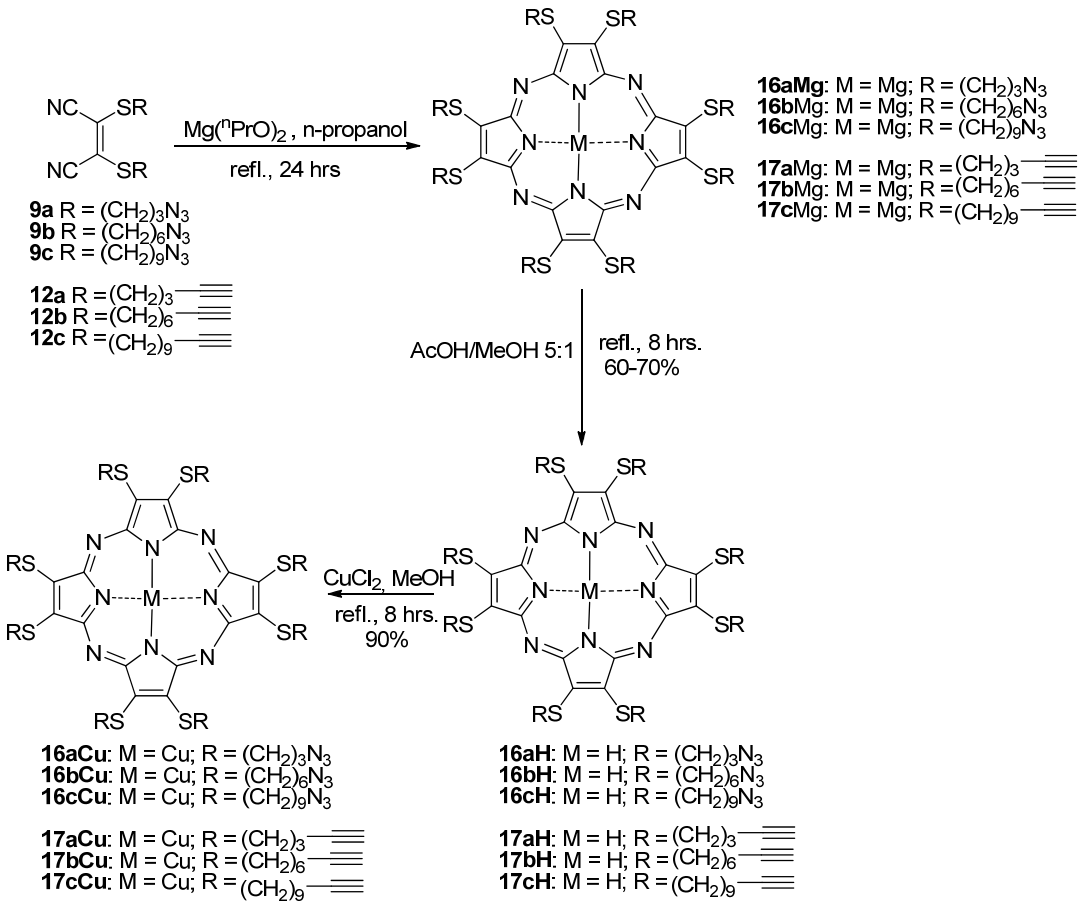
^{13}C-NMR ($CDCl_3$) δ: 18.43, 28.46, 28.70, 28.95, 29.00, 29.27, 29.76, 29.88, 35.11, 68.28, 84.75, 112.15, 121.05.

HR-MS (m/z) [Cl]: Theoretical: 442.2476; Found: 442.2485.

4.8.9 Synthesis of octa-azide and octa-acetylene TAPs (16aH, 16bH, 16cH, 17aH, 17bH and 17cH)

Mg powder (24.6 mg, 1 mmol) and 5 mg of iodine crystals were refluxed overnight in 50 mL of dry propan-1-ol under nitrogen until all Mg is reacted to Mg(II) propanolate. Maleodinitrile **9a** (1.54 g, 5 mmol) or **9b** (1.96 g, 5 mmol) or **9c** (2.383 g, 5 mmol) **12a** (1.372 g, 5 mmol) or **12b** (1.793 g, 5 mmol) or **12c** (2.213 g, 5 mmol) was added and the suspension was heated at reflux for another 24 hrs. The resulting greenish-blue suspension was cooled to room temperature, filtered and the filter residue was washed with methanol.

All alcohol extracts were combined, evaporated, and the residue Mg containing crude TAP was stirred in a mixture of 50 mL acetic acid and 10 mL methanol at 80 ^{o}C for 8 hrs to generate the metal-free TAP. Progress and completion of the demetallation was monitored by UV-VIS spectroscopy.



About 100 mL of water was added to the now purple solution and the product was extracted with H_2CCl_2 (3 x 100 mL), the combined organic layers were dried over anhydrous $MgSO_4$, and finally concentrated in vacuum. A partial purification was achieved by precipitation of the crude product from acetone solution by slow addition of a 2:1 mixture of methanol and water. The precipitated TAP was further purified by flash chromatography on silica gel using a 1:2 mixture of H_2CCl_2/hexane as eluent to generate the metal-free TAP as a deep purple solid.

2,3,7,8,12,13,17,18-octakis(azidopropylthio)-5,10,15,20-tetraazaporphyrin (**16aH**) (925 mg, 75%):

^{1}H NMR (300 MHz, $CDCl_3$, δ): -1.45 (s, 2H, NH), 2.18 (tt, J = 6.5 Hz, J = 7.0 Hz, 16H), 3.67 (t, J = 6.3 Hz, 16H), 4.19 (t, J = 6.6 Hz, 16H);

^{13}C NMR (300 MHz, $CDCl_3$, δ):29.21, 34.42, 49.21, 139.82, 151.15;

IR (cm^{-1}): 3290 (m,ν(N-H)), 2930 (m, ν(C-H)), 2098 (s, ν(N_3));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 344 (44 300), 513 (20 600), 651 (26 100), 712 (34200);

EA($C_{40}H_{48}N_{32}S_8$), Theoretical: 38.88 %C, 36.28 %N, 4.08 %H; Found: 39.22 %C, 36.00 %N 4.15 %H.

2,3,7,8,12,13,17,18-octakis(azidohexylthio)-5,10,15,20-tetraazaporphyrin (**16bH**) (1.255 g, 80%):

^{1}H NMR (300 MHz, $CDCl_3$, δ): -1.12 (s, 2H, NH), 1.31-1.45 (m, 16H), 1.47-1.71 (m, 32H), 1.88 (t, J = 6.9 Hz, 16H), 3.19 (t, J = 6.6 Hz, 16H), 4.09 (t, J = 6.9 Hz, 16H),

^{13}C NMR (300 MHz, $CDCl_3$, δ): 26.12, 28.63, 28.81, 29.72, 34.89, 49.86, 138.01, 149.93;

IR (cm^{-1}): 3285 (m, ν(N-H), inner core NH), 2932 (m, ν(C-H), CH_2), 2095 (s, ν(N_3), azide);

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 342 (44 100), 515 (20 500), 655 (26 200),714 (34 200);

EA ($C_{64}H_{96}N_{32}S_8$), Theoretical: 49.08 %C, 28.62 %N, 5.92 %H; Found: 48.80 %C, 28.30 %N, 6.24 %H.

2,3,7,8,12,13,17,18-octakis(azidononylthio)-5,10,15,20-tetraazaporphyrin (**16cH**) (1.545 g, 81%)

^{1}H NMR (300 MHz, $CDCl_3$, δ): -1.06 (s, 2H, NH), 1.28 (br, 64H), 1.59(br, 32H), 1.97(br, 16H), 3.20(br, 16H), 4.12(br, 16H);

^{13}C NMR (300 MHz, $CDCl_3$, δ): 26.71, 28.84, 28.96, 29.15, 29.26, 29.44, 30.54, 35.32, 51.45, 140.63, 153.43.

IR (cm^{-1}): 3283 (m,ν(N-H)), 2920 (m, ν(C-H)), 2100 (s, ν(N_3));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 344 (44 300), 510 (21 000), 651 (25 900), 713 (34115)

MS [HRMALDI] (m/z): Theoretical: 1908.0252 $[M+H]^+$; Found: 1908.0242.

2,3,7,8,12,13,17,18-octakis(pent-4-yn-1-ylthio)-5,10,15,20-tetraazaporphyrin (**17aH**) (770 mg, 70%):

^{1}H NMR (300 MHz, $CDCl_3$, δ):-1.30 (s, 2H, NH), 1.90 (s, 8H), 2.08 (p, J= 6.9 Hz, 16H), 2.52 (t, J = 2.1 Hz, 16H), 4.18 (t, J = 7.2 Hz, 16H),

^{13}C NMR (300 MHz, $CDCl_3$, δ): 17.72, 29.28, 34.00, 69.33, 83.43, 140.59, 153.35.

IR (cm^{-1}): 3290 (s,ν(C-H) alkyne), (w,ν(N-H), inner core NH), 2850, 2917, 2934 (m, ν(C-H), CH_2), 2115 (w, ν(C≡C));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 355 (43090), 565 (18940), 645 (26470), 710 (34200)

MS [HRMALDI] (m/z): Theoretical: 1099.2625 $[M+H]^+$; Found: 1099.2646.

2,3,7,8,12,13,17,18-octakis(oct-7-yn-1-ylthio)-5,10,15,20-tetraazaporphyrin (**17bH**) (1.005 g, 70%):

^{1}H NMR (300 MHz, $CDCl_3$, δ):-1.13 (s, 2H), 1.38-1.72 (m, 48H), 1.79-1.96 (m, 24H), 2.04-2.19 (m 16H), 4.08 (t, J=7.2 Hz, 16H);

^{13}C NMR (300 MHz, $CDCl_3$, δ):18.37, 28.39, 28.45, 29.75, 30.41, 35.24, 68.26, 84.49, 140.63, 153.2;

IR (cm^{-1}): 3290 (s, ν(C-H) alkyne), ν(N-H), inner core NH), 2854, 2930 (m, ν(C-H), CH_2), 2115 (w, ν(C≡C))

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 355 (43030), 562 (19091), 642 (26060), 710 (33333)

MS [HRMALDI] (m/z): Theoretical: 1435.6384 $[M+H]^+$; Found: 1435.6380.

2,3,7,8,12,13,17,18-octakis(undeca-10-yn-1-ylthio)-5,10,15,20-tetraazaporphyrin (**17cH**) (1.241 g, 70%)

^{1}H NMR (300 MHz, $CDCl_3$, δ): -1.09 (s, 2H), 1.28 -1.62 (m, 96H), 1.91 (br, 24H), 2.13 (br, 16H), 4.12 (br, 16H)

^{13}C NMR (300 MHz, $CDCl_3$, δ): 18.44, 23.03, 23.81, 28.13, 28.76, 29.07, 29.25, 30.42, 33.58, 68.2, 84.81, 132.52, 167.78.

IR (cm^{-1}): 3300 (s,ν(C-H) alkyne), (w,ν(N-H), inner core NH), 2845, 2920, 2933 (m, ν(C-H), CH_2), 2113 (w, ν(C≡C));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 360 (43100), 565 (18965), 645 (26500), 712 (34200).

4.8.10 Synthesis of octa-azide and octa-acetylene copper TAPs (16aCu, 16bCu, 16cCu 17aCu, 17bCu and 17cCu)

Metal-free TAP **16aH** (617 mg, 0.5 mmol) or 1**6bH** (785mg,0.5mmol),or 6c (954mg, 0.5 mmol) 1**7aH** (550mg, 0.5mmol), or **17bH** (718mg, 0.5mmol) or **17cH** (886mg, 0.5mmol) was stirred in a solution of anhydrous copper(II) chloride (108 mg, 0.8 mmol) in 50 mL methanol at reflux for 8 hrs. Progress and completion of copper metallation was monitored by UV-VIS spectroscopy. Aqueous 5% ammonium chloride (100mL) was added and the TAP was extracted with H_2CCl_2 (3 x 100mL). The combined organic layers were extracted with water (2 x 100mL), dried over anhydrous $MgSO_4$, and concentrated. The crude product was further purified by flash chromatography on silica gel using a 1:2 mixture of H_2CCl_2/hexane as eluent to generate the copper TAP as a deep blue solid.

2,3,7,8,12,13,17,18-octakis(azidopropylthio)-5,10,15,20-tetraazaporphyrinato-copper(**16aCu**) (519 mg, 80%):

IR (cm^{-1}): 2849, 2917, 2957 (m, ν(C-H), CH_2), 2093 (s, ν(N_3), azide);

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 362 (21820), 500 (7576), 667 (30606);

2,3,7,8,12,13,17,18-octakis(azidohexylthio)-5,10,15,20-tetraazaporphyrinato-copper(**16bCu**) (653 mg, 81%),

IR (cm^{-1}): 2853, 2929, (m, ν(C-H), CH_2), 2094 (s, ν(N_3), azide);

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 365 (21970), 505 (7758), 670 (30667);

MS [HRMALDI] (m/z): Theoretical: 1632.5635 $[M+H]^+$; Found: 1632.5630.

2,3,7,8,12,13,17,18-octakis(azidononylthio)-5,10,15,20-tetraazaporphyrinato-copper(**16cCu**) (788 mg, 80%),

IR (cm^{-1}): 2851, 2915, 2960 (m, ν(C-H), CH_2), 2090 (s, ν(N_3), azide);

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 365 (24857), 504 (8354), 670 (30616);

MS [HRMALDI] (m/z): Theoretical: 1968.9391 $[M+H]^+$; Found: 1968.9329.

2,3,7,8,12,13,17,18-octakis(pent-4-yn-1-ylthio)-5,10,15,20-tetraazaporphyrinato-copper (**17aCu**) (464 mg, 80%):

IR (cm^{-1}): 3295, 3353 (s,ν(C-H) alkyne), 2853, 2930(s, ν(C-H), CH_2), 2116 (w, ν(C≡C));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 360 (25151), 500 (8667), 665 (29090);

MS [HRMALDI] (m/z): Theoretical: 1160.1767 $[M+H]^+$; Found: 1160.1754.

2,3,7,8,12,13,17,18-octakis(oct-7-yn-1-ylthio)-5,10,15,20-tetraazaporphyrinato-copper(**17bCu**) (600 mg, 80%):

IR (cm^{-1}): 3300, 3352 (s, ν(C-H) alkyne), 2853, 2930(s, ν(C-H), CH_2), 2117 (w, ν(C≡C));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 365 (24850), 503 (8364), 670 (30606);

MS [HRMALDI] (m/z): Theoretical: 1496.5523 $[M+H]^+$; Found: 1496.5552.

2,3,7,8,12,13,17,18-octakis(undeca-10-yn-1-ylthio)-5,10,15,20-tetraazaporphyrinato-copper(**17cCu**) (726mg, 82%)

IR (cm^{-1}): 3300, 3350 (s, ν(C-H) alkyne), 2850, 2928 (s, ν(C-H), CH_2), 2110 (w, ν(C≡C));

UV/VIS (λ max in nm) THF, (ε / dm^3 mol^{-1} cm^{-1}): 365 (21975), 505 (7760), 670 (30655)

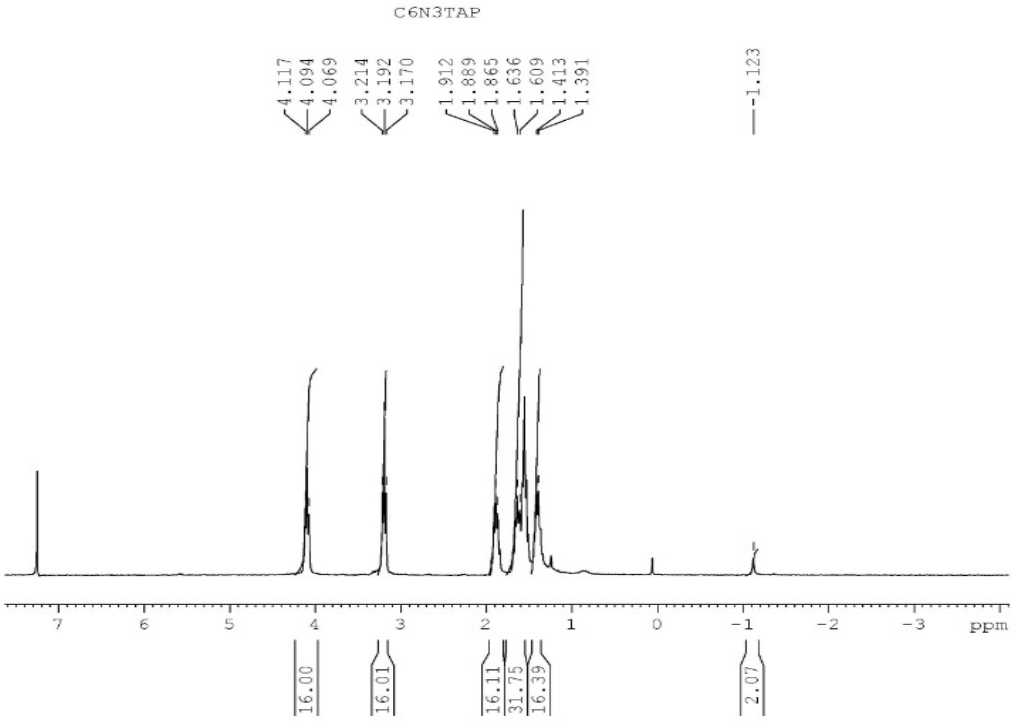


Figure 4-17: ^{1}H-NMR of 16bH (in $CDCl_3$).

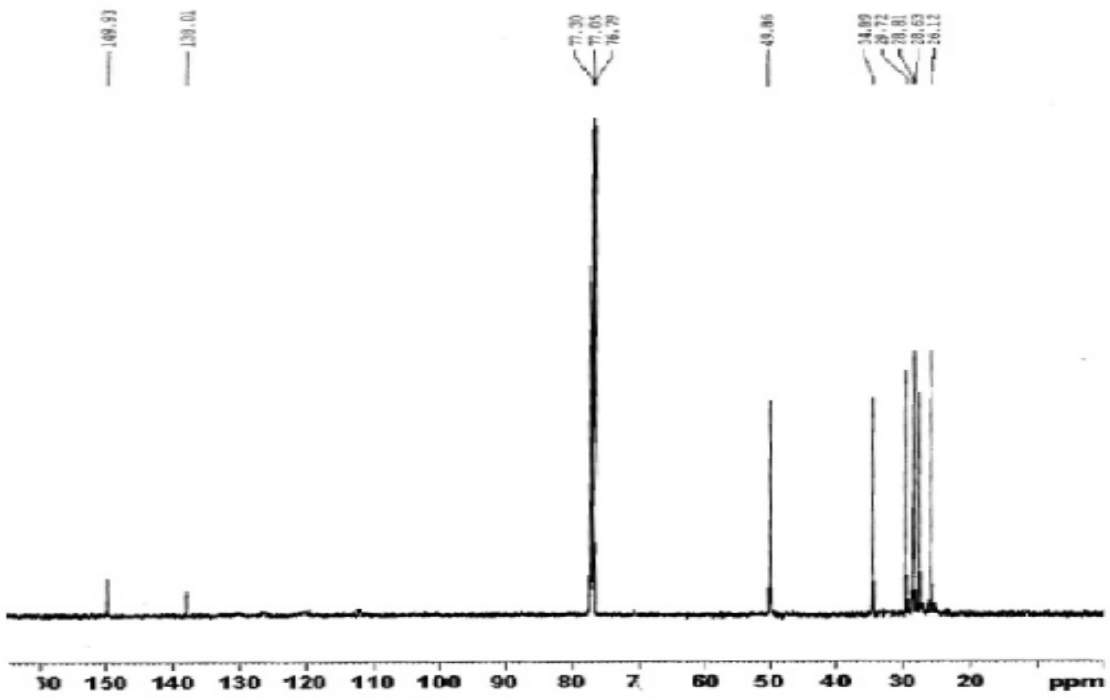


Figure 4-18: ^{13}C-NMR of 16bH (in $CDCl_3$).

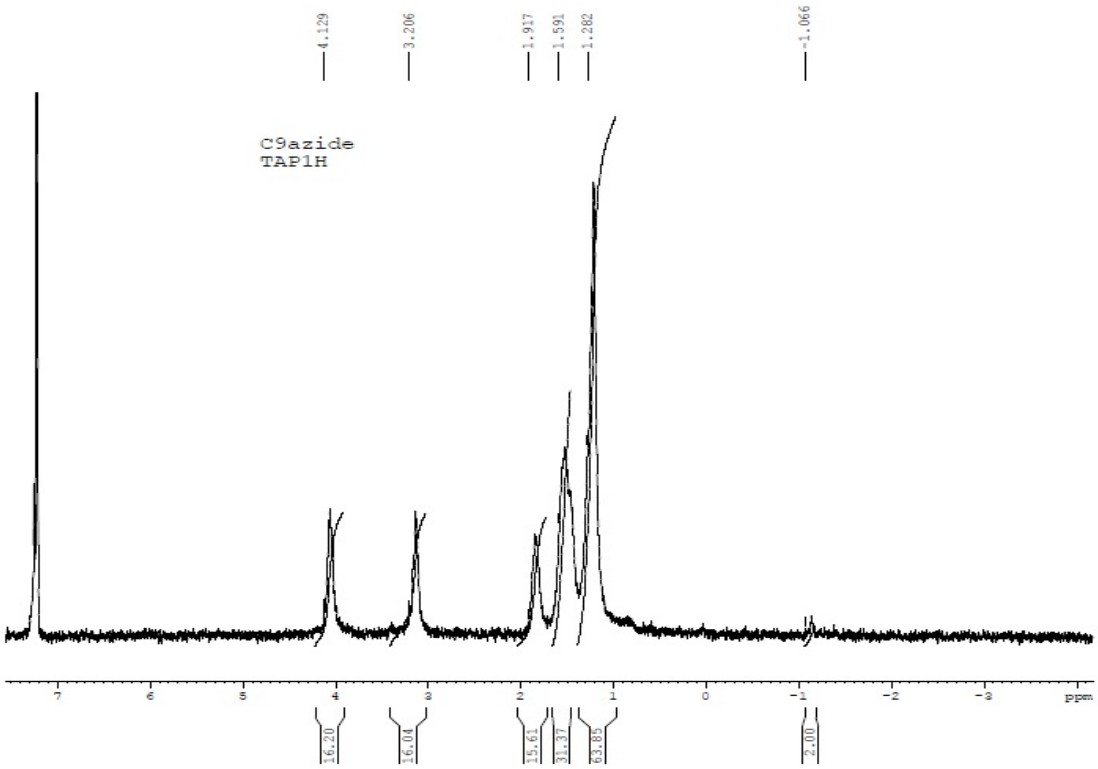


Figure 4-19: ^{1}H-NMR of 16cH (in $CDCl_3$).

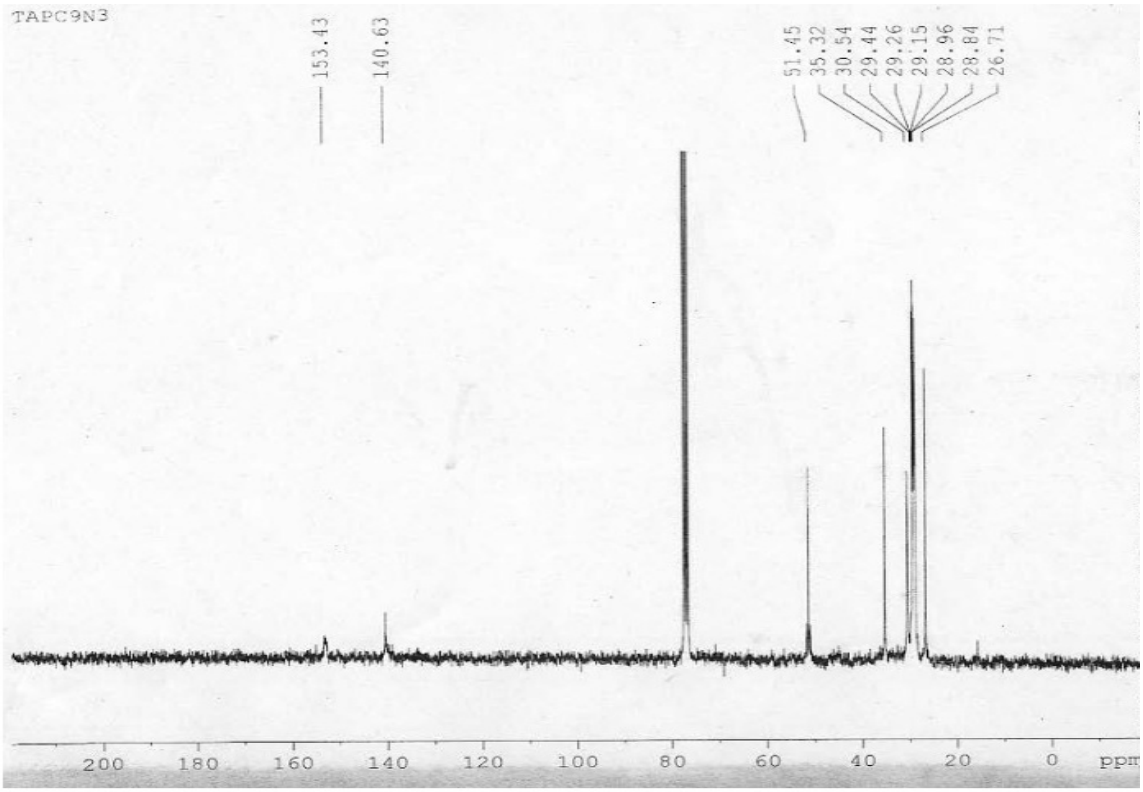


Figure 4-20: ^{13}C-NMR of 16cH (in $CDCl_3$).

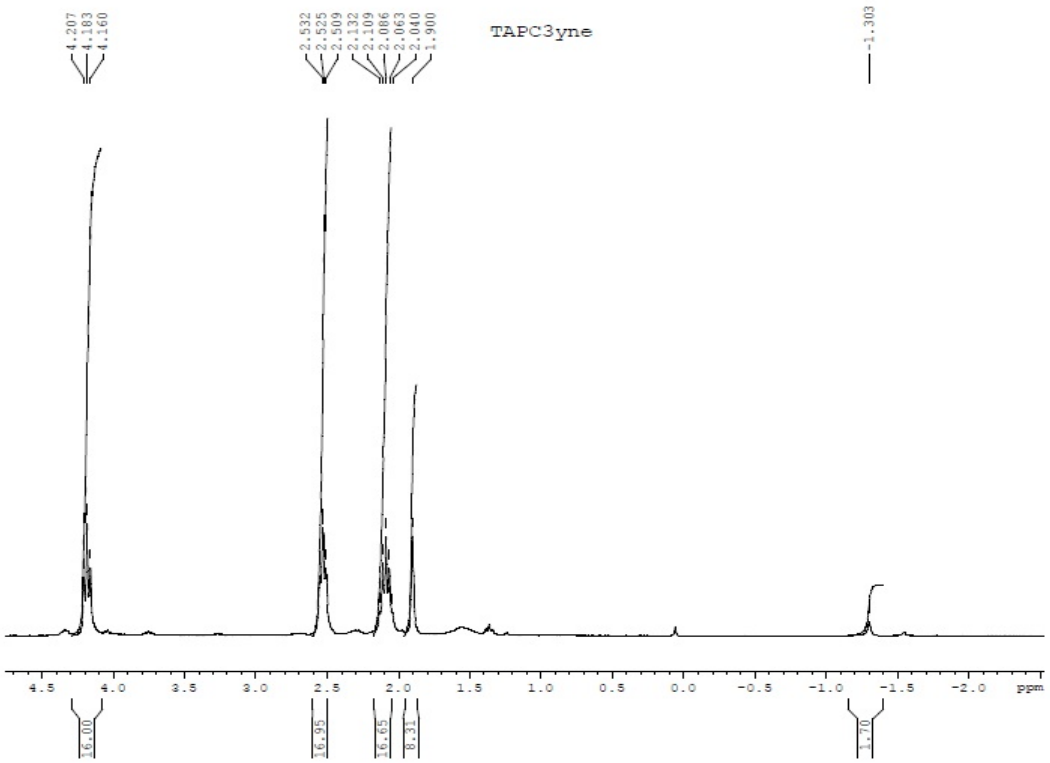


Figure 4-21:^{1}H-NMR of 17aH (in $CDCl_3$).

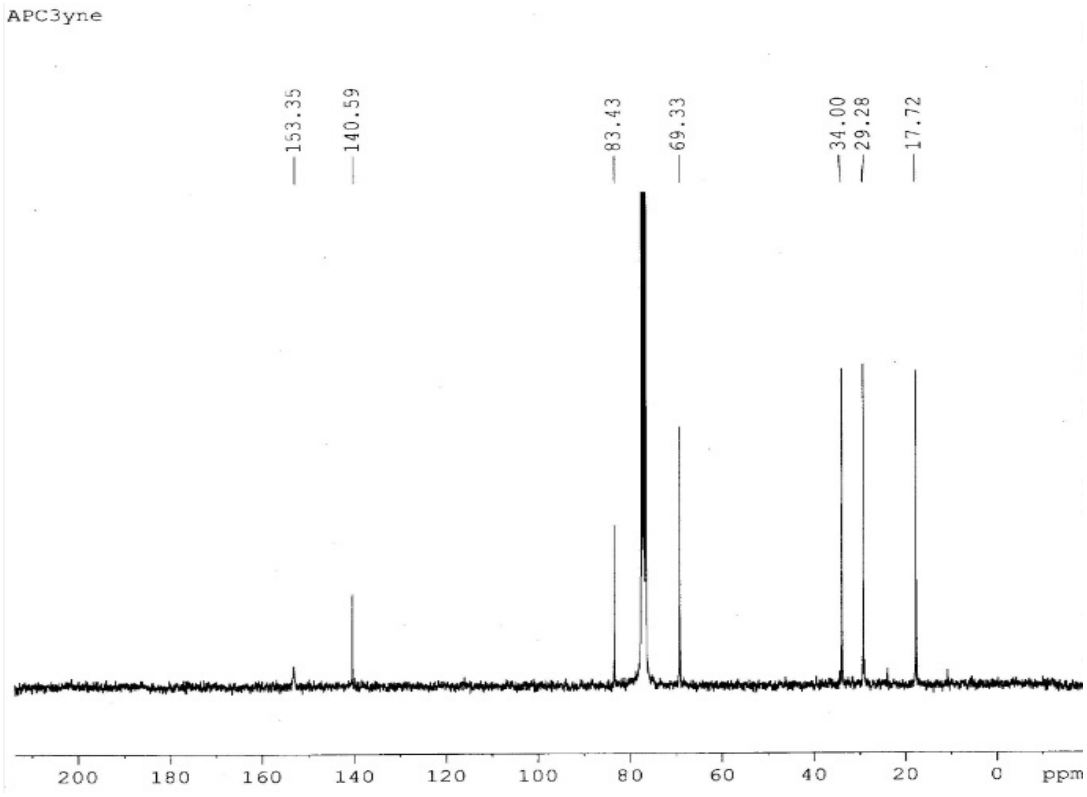


Figure 4-22: ^{13}C-NMR of 17aH (in $CDCl_3$).

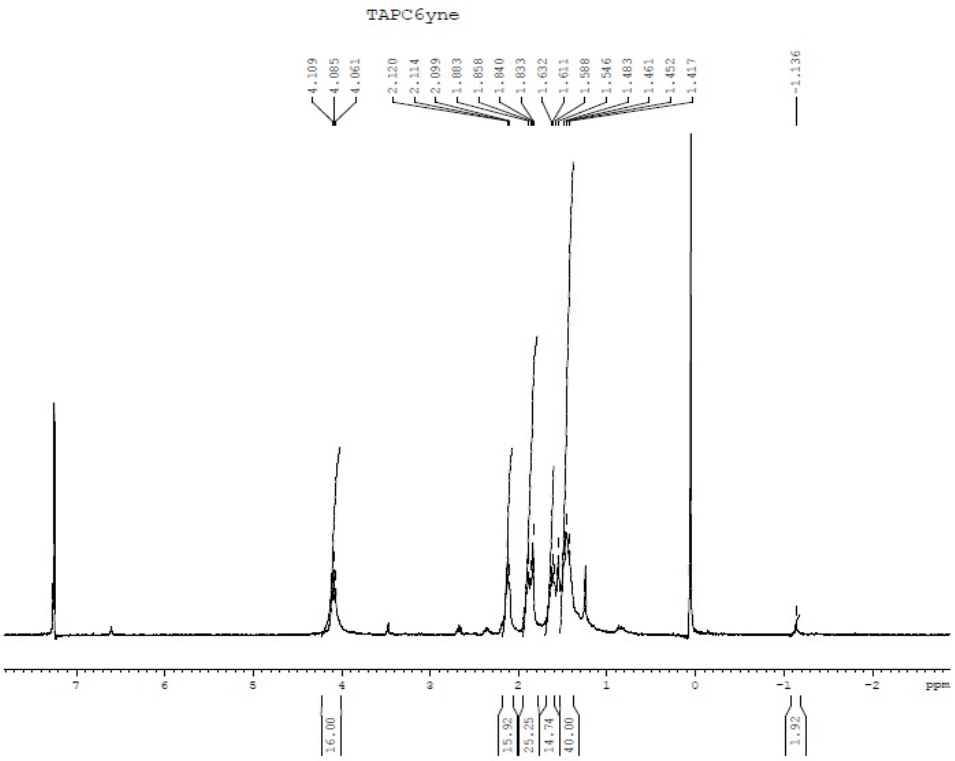


Figure 4-23: ^{1}H-NMR of 17bH (in $CDCl_3$).

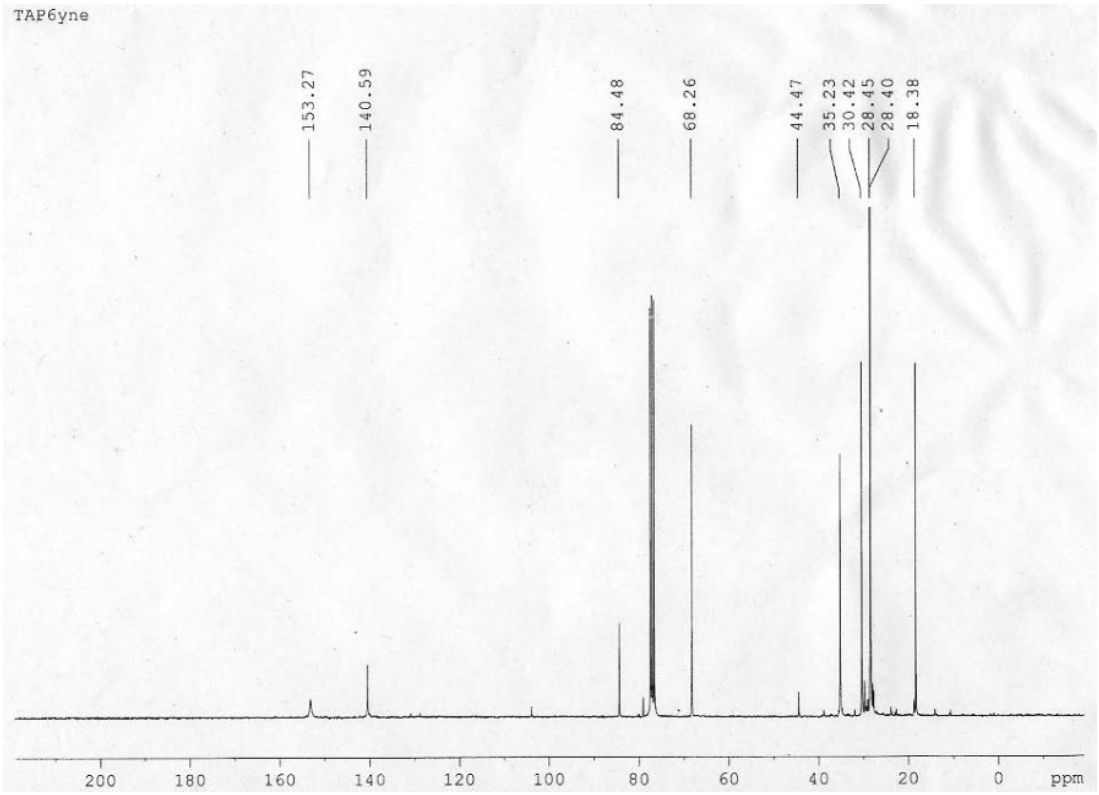


Figure 4-24: ^{13}C-NMR of 17bH (in $CDCl_3$).

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5 Chapter 5: Chromonics and Ionic Discotic Liquid Crystals

5.1 Overview

Most known discotic liquid crystals (DLCs) are neutral compounds that show thermotropic mesomorphism and in some cases also lyotropic mesomorphism in organic solvents. The number of reported ionic discotic liquid crystals is small and most of them display conventional thermotropic columnar mesophases when substituted with aliphatic side-chains. However, a special class of these compounds only exhibit lyotropic mesomorphism and was given the name chromonics because their lyotropic mesophases differ from those of surfactants. Chromonics do not have a critical micelle concentration and do not form micellar, lamellar, cubic and cylindrical structures typically found in surfactant solutions depending on concentration and temperature.[1-5] Instead, chromonics aggregate into columnar stacks and the lengths of these stacks increases continuously with increasing concentration.

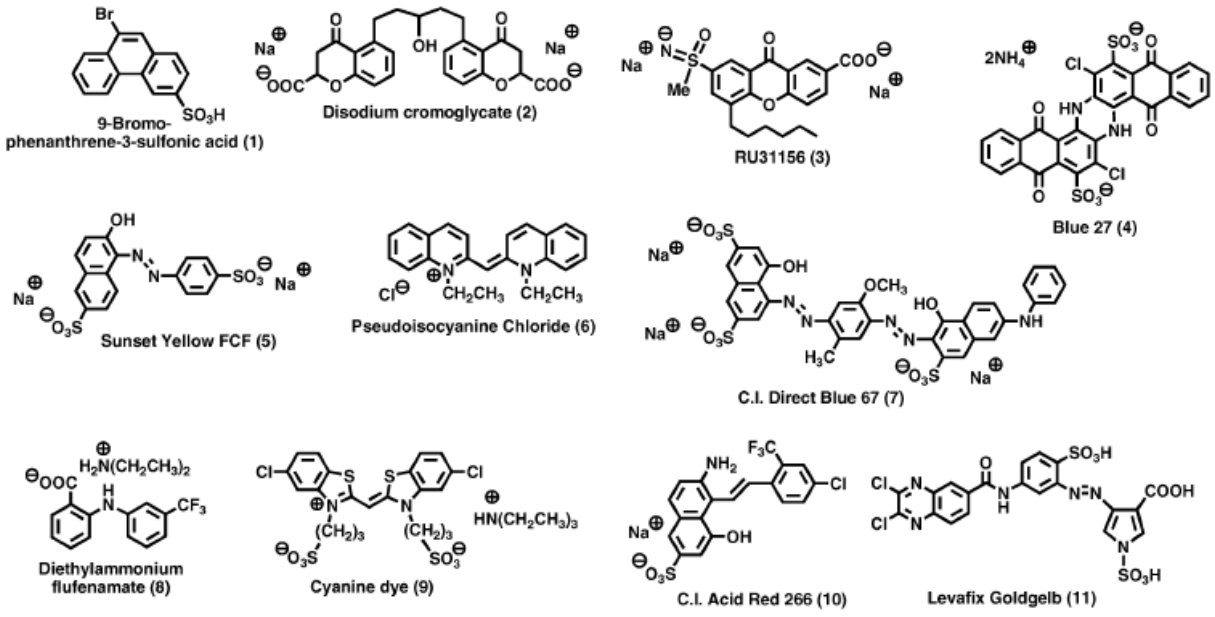


Figure 5-1: Examples of known chromonic molecules [5]

Molecules that form chromonic phases have ionic or easily ionizable groups (e.g. sulfonic acid) directly attached to a rigid aromatic core (Fig. 5.1). The overall shape of chromonics is either plank- or disc-like and may consist of several linked rigid cores. Due to this unique structure they are effectively insoluble in water in one dimension, which drives the formation of face-to-face stacks. These stacks can have only orientational order to generate a nematic lyotropic phase (N-phase) or they self-organize into higher ordered hexagonal columnar phase (M-phase).[3,4] Both, N- and M-phases are illustrated in Fig. 2 but more complex structures than shown in Fig. 5.2 have also been proposed for certain chromonic phases but many aspects of chromonics have remained little explored, mainly because a commercially important application for chromonic mesophases has not yet been found. Chromonics have been successfully tested in various biosensors, optical compensators, micro patterned polarizing elements, and photoinduced liquid crystalline gratings.[1-4]

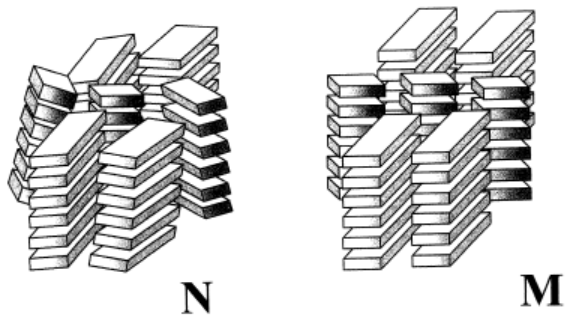


Figure 5-2: N and M phases of chromonics.[3]

Most chromonic molecules contain no flexible side-chains or an insufficient number and length of side-chains for the introduction of thermotropic mesophases but the formation of chromonic mesophases is not limited to charged compounds. Some neutral polyaromatics have also been reported to display chromonic phases.[3] Hydrogen bonding and dipolar interactions seem to play a vital role in their self-organization but their chromonic mesomorphism has not been studied in much detail.

Ionic DLCs that form thermotropic mesophases usually have ionic groups that are peripherally attached to the central aromatic core *via* aliphatic spacers or contain aliphatic side-chains in addition to ionic groups (Fig. 5.3). Molecules that contain more than one ionic group are generally denoted as polyionic DLCs. Incorporation of aliphatic spacers for the attachment of ionic groups and/or aliphatic side-chains significantly lowers the melting points of ionic DLCs, which is essential for the introduction of thermotropic mesomorphism. Ionic DLCs that show thermotropic columnar mesomorphism include compounds based on crown ethers,[7] tricycloquinazoline,[8] 3,5-diaryl-1,2-dithiolium,[9] 2,4,6-triarylpyrylium,[10,11] and 2,4,6-triarylpyridinium moieties. Some of these compounds also form lyotropic columnar mesophases in aqueous solutions, which appear to have the same properties as chromonic N and M mesophases. In general, the mesomorphism of ionic DLCs is controlled by the type of core structure, the type, number, and length of attached side- and spacer-chains, the types of ionic groups, and the types of counter ions. Only few of the many synthetic options have yet been explored.

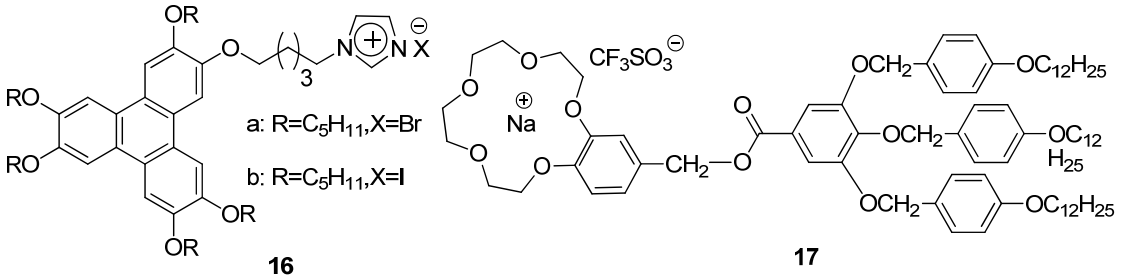


Figure 5-3:Examples of ionic discotic liquid crystals: 16) triphenylene-substituted imidazolium salts; [6] 17) benzo-15-crown-5 benzoate(6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxabenzocyclopenta-decen-2-ylmethyl 3, 4, 5-tris(p-dodecyloxybenzyl-oxy)benzoate) is complexed with $NaCF_3SO_3$ to form a mesophase;[7]

A possible application of ionic DLCs is their use as ion conductors that are important components, for example, in living cells and in batteries. Especially Kato's group has developed novel ionic liquid crystals that display 1-dimensional ion transport upon uniaxial alignment.[12-15] Some of their dendritic or

wedge shaped ionic liquid crystals are shown in Fig. 5.4. These compounds self-organize into helical columnar stacks because of their wedge shape and microphase segregation between ionic head groups and aliphatic side-chains. Consequently, they should not be categorized as ionic DLCs but as ionic liquid crystals that form columnar mesophases. Several examples on the incorporation of ionic DLCs into supramolecular structures dictated by electrostatic interactions have been reported.

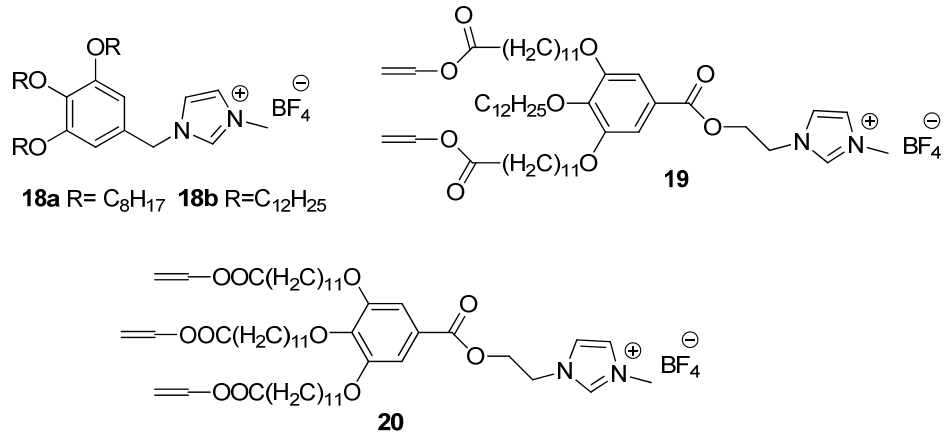


Figure 5-4: Ionic liquid crystals that form thermotropic mesophases of columnar structure [12-15]

For example, Müllen and co-workers have processed ionic DLCs together with polyelectrolytes. They have also demonstrated that ionic DLCs are amenable to electrostatic layer-by-layer deposition. [16, 17]

5.2 Objective

The objective of this project is the expansion of previous work by Scott Dufour (Eichhorn group) on tetraazaporphyrins (TAPs) containing eight carboxylic acid groups by preparing TAPs with eight basic or cationic groups and studying especially the properties of 1:1 mixtures of acidic and basic or anionic and cationic TAPs (Fig. 5.5). A combination of TAPs **15a** and **14a** or TAPs **14b** and **15b** is expected to enhance self-organization into novel lyotropic columnar mesophases in aqueous solution. The pure TAPs may also show thermotropic mesomorphism if the aliphatic spacer is sufficiently long. Other interesting

possibilities of processing these compounds is their surface coating by electrostatic layer-by-layer deposition or by alternating deposition of acidic and basic TAPs as LB monolayers.

We have chosen the TAP core because of its well documented attractive chemical and physical properties, which we have already discussed in Chapter 4. Shown here is the preparation of octa-substituted metallated and metal-free TAPs that contain imidazole or methyl imidazolium terminal groups, which are linked to the central TAP core *via* alkyl spacers of different chain lengths.

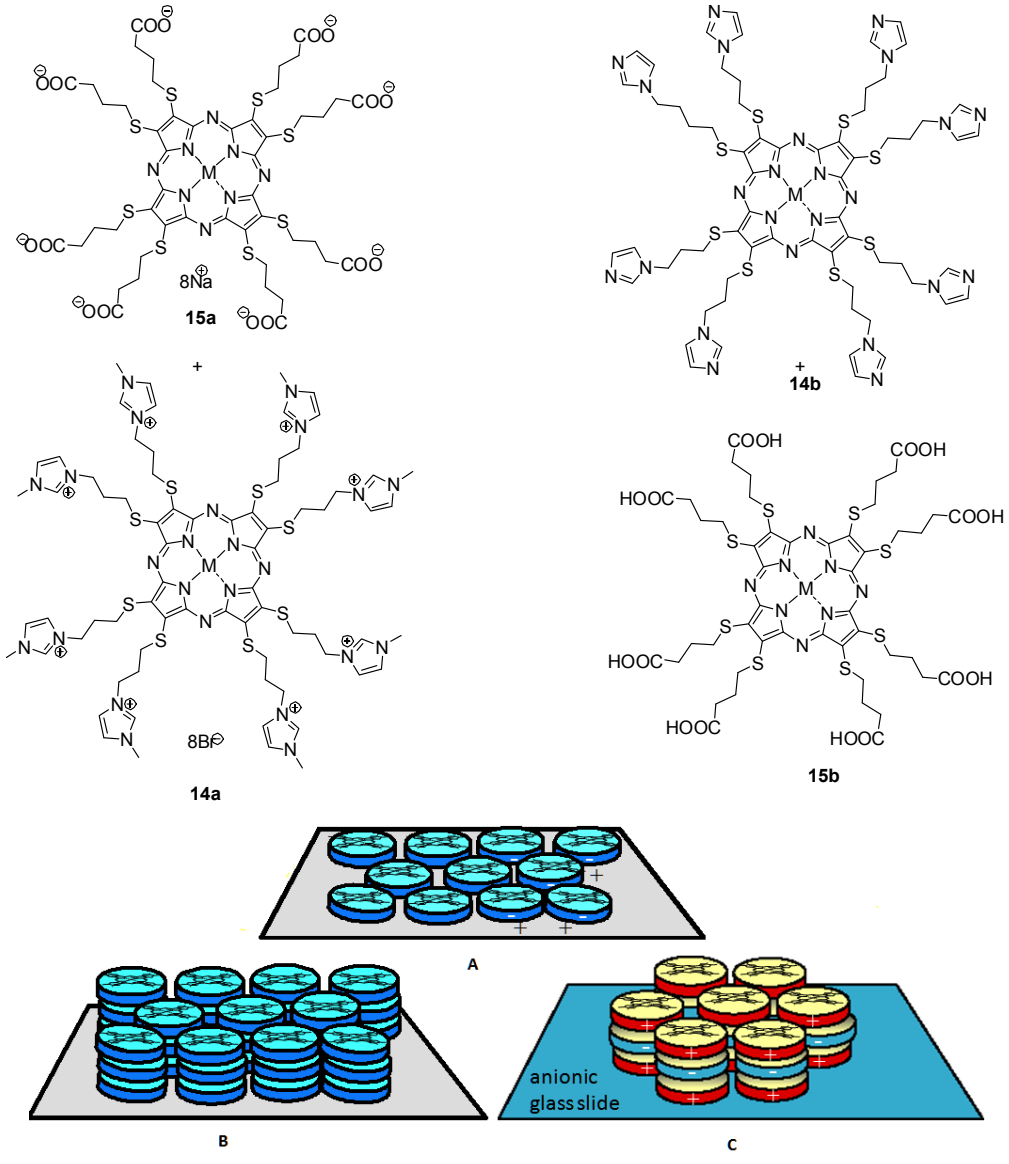


Figure 5-5: Electrostatic and LB Deposition of Polyionic TAPs. Cartoons of A. formation of monolayers B. alternating deposition of acidic and basic TAPs (15b and 14b) by LB monolayers. C. electrostatic layer-by-layer deposition by combination of TAPs 15a and 14a or TAPs 14b and 15b.

A weak base (imidazole) and weak acid (carboxylic acid) was deliberately chosen because the average number of attached charges per TAP molecule can be controlled by simply varying the pH, which can be beneficial for electrostatic depositions as well as LB deposition.

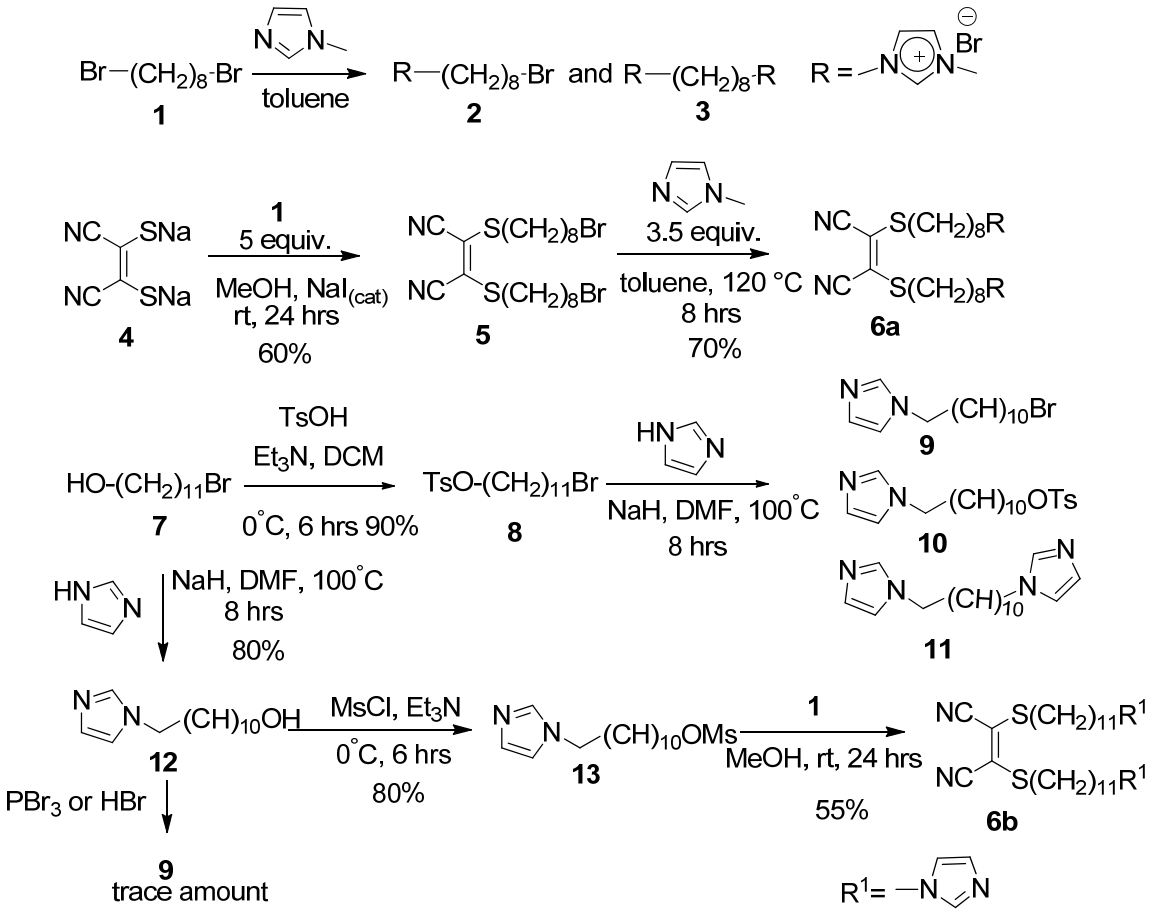
5.3 Synthesis of octaimidazolium TAPs

5.3.1 Synthesis of (Z)-3,3'-(((1,2-dicyanoethene-1,2-diyl)bis(sulfanediyl))bis(octane-8,1-diyl))bis(1-methyl-1H-imidazol-3-ium) bromide 6a and 2,3-bis((11-(1H-imidazol-1-yl)undecyl)thio)maleonitrile 6b

To synthesize the required side chain, we refluxed the mixture of excess dibromooctane **1** and methyl imidazole in toluene but unfortunately this reaction yielded inseparable gelatinous liquid mixture of **2** and **3**.

Following a different synthetic route, a methanolic solution of maleodinitrile **4** was added drop wise to a solution of 1,8-dibromooctane **3** in methanol to ensure an excess amount of **3** at all times (typically five equivalent with respect to maleodinitrile). Excess **3** was easily separated from product **5** by column chromatography using hexane as an eluent. Subsequently compound **5** was refluxed with 3.5 equivalent of methyl imidazole in toluene to give compound **6a**.

To prepare 2,3-bis((11-(1H-imidazol-1-yl)undecyl)thio)maleonitrile **6b,** the hydroxyl group of 11-bromoundecan-1-ol **7** was converted to the corresponding tosylate derivative **8** and then substituted with imidazole in presence of sodium hydride in DMF to obtain compound **10**. Unfortunately, both the tosylate and the bromide appear to have similar reactivity towards the sodium imidazolate salt compounds **9** and **11** are generated as side products. (Scheme 5.1)



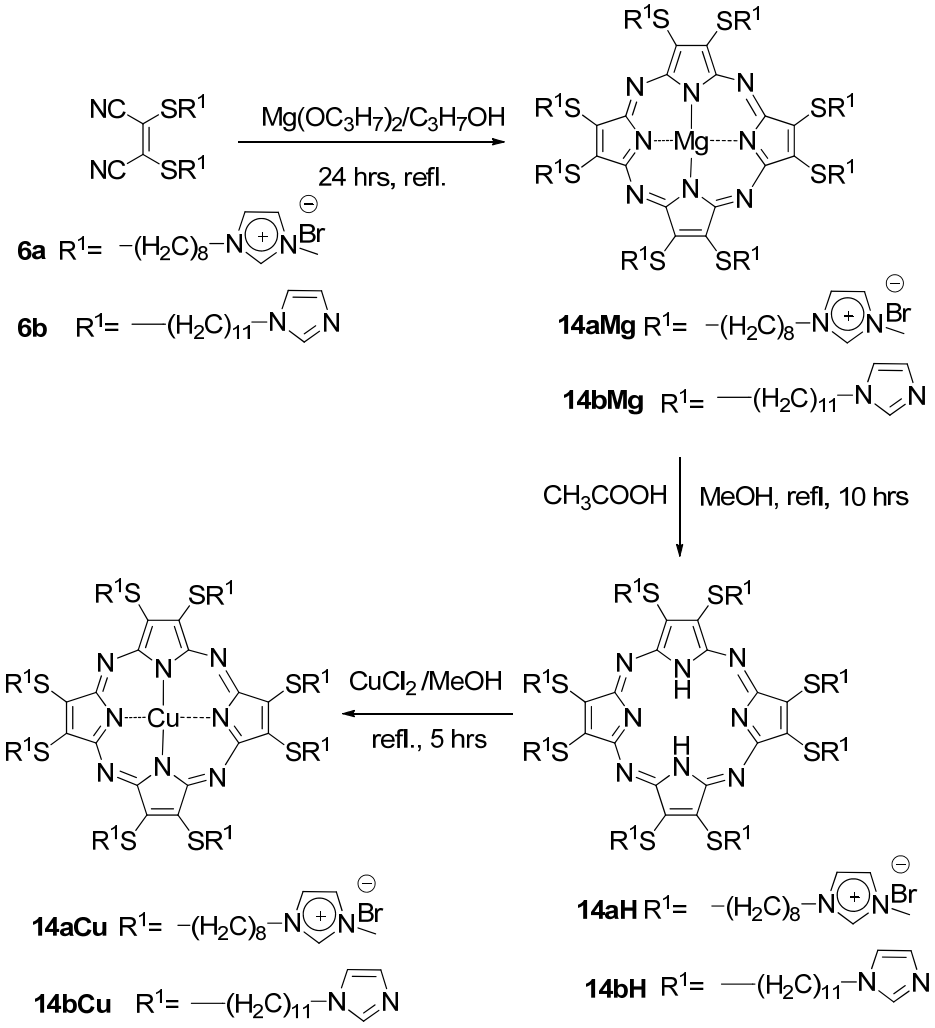
Scheme 5.1: Reaction of methyl imidazole with dibromo octane.

A better synthetic route starts with the alkylation of imidazole with 11-bromoundecan-1-ol **7** to afford compound **12** in 80% yield. The subsequent bromination of the hydxoyl group of **12** only afforded less than 10 % yield of the brominated derivative **9** but mesylation with 0.9 equivalents of methanesulfonyl chloride (MsCl) with respect to **12** generated compound **13** in 80% yield. Excess amount of MsCl was avoided to not mesylate the second N of imidazole. Finally, compound **13** was reacted with maleodinitrile **4** to give compound **6b** in 55% yield.

5.4 Synthesis of octa imidazole TAPs

Cyclo tetramerization of compounds **6a** and **6b** in magnesium propanolate/propanol successfully generated the corresponding MgTAP derivatives. Demetallation and metallation with Cu(II) were

conducted by following the same methods as described for octaazide and octaacetylene TAP derivatives in Chapter 4.



Scheme 5.2: Preparation of octa imidazole and imidazolium TAPs.

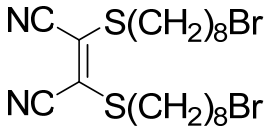
5.5 Conclusions and Future Work:

Cyclization to TAPs was successful for both maleodinitrile derivatives **6a** and **6b** containing methylimidazolium (cationic) and imidazolium (neutral) terminal groups, respectively. The formation of the TAP ring is unequivocally confirmed by its characteristic UV-VIS spectra but purification and characterization of these TAPs has not been completed. Chromatographic purification is complicated by

the low solubility of both **14a** and **14b** in common solvents and solution NMR spectra have not been conclusive because of substantial signal broadening due to strong aggregation at room temperature and at elevated temperature (60°C). Both, purification and characterization will have to be successfully completed before materials properties can be reasonably investigated.

5.6 Experimental

5.6.1 Synthesis of 2,3-bis((8-bromooctyl)thio)maleonitrile 5



5

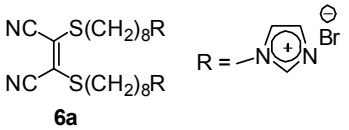
To stirred solution of 1, 8-dibromooctane (4.95 mL, 7.304 g, 26.85 mmol) and NaI (402 mg, 2.65 mmol) in 100mL of MeOH, maleodinitrile (1 g, 5.37 mmol) in 10mL MeOH was added at 0.5 mL per minute at ambient temperature. After the addition of Maleodinitrile was complete, the reaction mixture was kept stirring at ambient temperature for 24 hrs. MeOH was removed under reduced pressure, 100mL dicholoromethane was added and mixture was filtered. Dichloromethane solution was concentrated and passed through silica gel column using dichloromethane: Hexanes (1:1) mixture as an eluent to give 2,3-bis((8-bromooctyl)thio)maleonitrile **5** (1.690 g, 60%) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$, δ):1.2-1.5 (m, 16H), 1.71 (p, J=7.8Hz, 4H), 1.86 (p, J=6.9Hz, 4H), 3.12 (p, J=6.9Hz, 4H), 3.41(t, J=6.9Hz, 4H)

^{13}C NMR (300 MHz, $CDCl_3$, δ): 26.76, 28.88, 29.20, 29.31, 29.49, 30.59, 35.37, 51.50, 140.71, 153.22.

MS [HRCI] (m/z): Theoretical: 522.0374; Found: 522.0392.

5.6.2 Synthesis of (Z)-3,3'-(((1,2-dicyanoethene-1,2-diyl)bis(sulfanediyl))bis(octane-8,1-diyl))bis(1-methyl-4,5-dihydro-1H-imidazol-3-ium) bromide 6a



6a

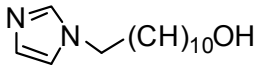
To stirred solution of 2, 3-bis ((8-bromooctyl)thio)maleonitrile (1.6 g, 2.86 mmol) in 100 mL toluene 1-methyl imidazole (0.8 mL, 822 mg, 10 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 8 hrs. (Z)-3,3'-(((1,2-dicyanoethene-1,2-diyl)bis(sulfanediyl))bis(octane-8,1-diyl))bis(1-methyl-4,5-dihydro-1H-imidazol-3-ium) bromide was phase separated from the toluene solution.The toulene layer was decanted and crude **6** was washed with toluene (3 X 20 mL) to get pure (Z)-3,3'-(((1,2-dicyanoethene-1,2-diyl)bis(sulfanediyl))bis(octane-8,1-diyl))bis(1-methyl-4,5-dihydro-1H-imidazol-3-ium) bromide **6a** (1.486 g ,70%) as a thick yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.10-1.34 (m, 20H), 1.61-1.63 (m, 4H), 1.76-1.78 (m, 4H), 3.84 (s, 6H), 4.14 (t , J=7.2Hz, 4H), 7.70 (s, 2H), 7.76 (s, 2H), 9.12 (s, 2H)

^{13}C NMR (300 MHz, $CDCl_3$, δ): 25.89, 28.21, 28.66, 29.68, 30.00, 29.83, 34.78, 36.27, 49.23, 112.89, 121.34, 122.77, 124.12, 136.99.

MS [HR-MALDI] (m/z): Theoretical: 507.2249; Found: 507.2250.

5.6.3 Synthesis of 11-(1H-imidazol-1-yl)undecan-1-ol 12



12

To a stirred solution of imidazole (1 g, 14.69 mmol) in 100mL DMF, 60% NaH in mineral oil (588 mg, 14.69 mmol) was added at room temperature under nitrogen atmosphere. The mixture was kept stirring until it became clear. To this 11-bromoundecan-1-ol (3.015 g, 12mmol) in 10 mL DMF was added drop wise under nitrogen atmosphere and mixture was heated to 100^0C for 8 hrs. The mixture was treated with 10% Na_2C0_3 (200 mL) and extracted with ethyl acetate (3 X 100 mL), combined organic layer was washed with water(3 X 100 mL) ,dried using anhydrous $MgSO_4$,concentrated under vacuum . Crude

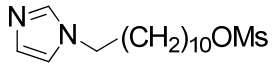
product was passed through neutral alumina column using dicholormethane:hexanes (1:1) mixture to get pure 11-(1H-imidazol-1-yl)undecan-1-ol **12** (2.288 g, 80%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.29-1.39 (m, 14H), 1.58 (t, J= 7.2 Hz, 1H), 1.77-1.81 (m, 4H), 3.66 (t, J= 6.6 Hz, 2H), 3.95 (t, J= 6.9 Hz, 2H), 6.93 (s, 1H), 7.08 (s, 1H), 7.49 (s, 1H).

^{13}C NMR (300 MHz, $CDCl_3$, δ):19.68, 25.80, 26.55, 29.04, 29.41, 29.54, 31.12, 32.90, 40.12, 47.15, 63.10, 118.90, 129.45, 137.22.

MS [HRCI] (m/z): Theoretical: 238.2045; Found: 238.2052.

5.6.4 Synthesis of 11-(1H-imidazol-1-yl)undecyl methanesulfonate 13



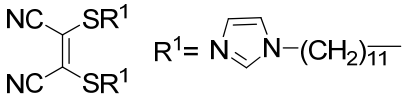
13

To a stirred solution of 11-(1H-imidazol-1-yl)undecan-1-ol (1.907 g, 8 mmol) and triethylamine (2.09 mL, 1.518 g, 15 mmol) in 100 mL diethyl ether at 0^{o}C under nitrogen atmosphere, Methanesulfonyl chloride (0.56 mL, 823 mg, 7.2 mmol) was added drop wise. The mixture was kept stirring for 5hrs at 0^{o}C. To this mixture 100 mL water was added followed by dropwise addition of 5(M) HCl solution to make pH~7. The mixture was extracted with ethylacetate (3 X 100 mL); combined organic layer was dried using $MgSO_4$, concentrated under reduced pressure. The crude product was purified by flash chromatography on neutral alumina using dichloromethane:hexanes (1:1) mixture to give 11-(1H-imidazol-1-yl)undecyl methanesulfonate **13** (2.051 g, 90%) as a white solid .

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.37-1.39 (m, 6H), 1.70-1.78 (m, 12H), 3.01 (s, 3H), 3.94 (t, J=6Hz, 2H), 4.22 (t, J=6.6Hz, 2H), 6.92 (s, 1H), 7.08 (s, 1H), 7.55 (s, 1H)

^{13}C NMR (300 MHz, $CDCl_3$, δ): 22.71, 25.83, 26.02, 28.91, 29.23, 29.70, 30.19, 30.19, 30.28, 39.61, 46.08, 62.62, 122.15, 122.47, 137.27.

5.6.5 Synthesis of 2,3-bis((11-(1H-imidazol-1-yl)undecyl)thio)maleonitrile 6b



6b

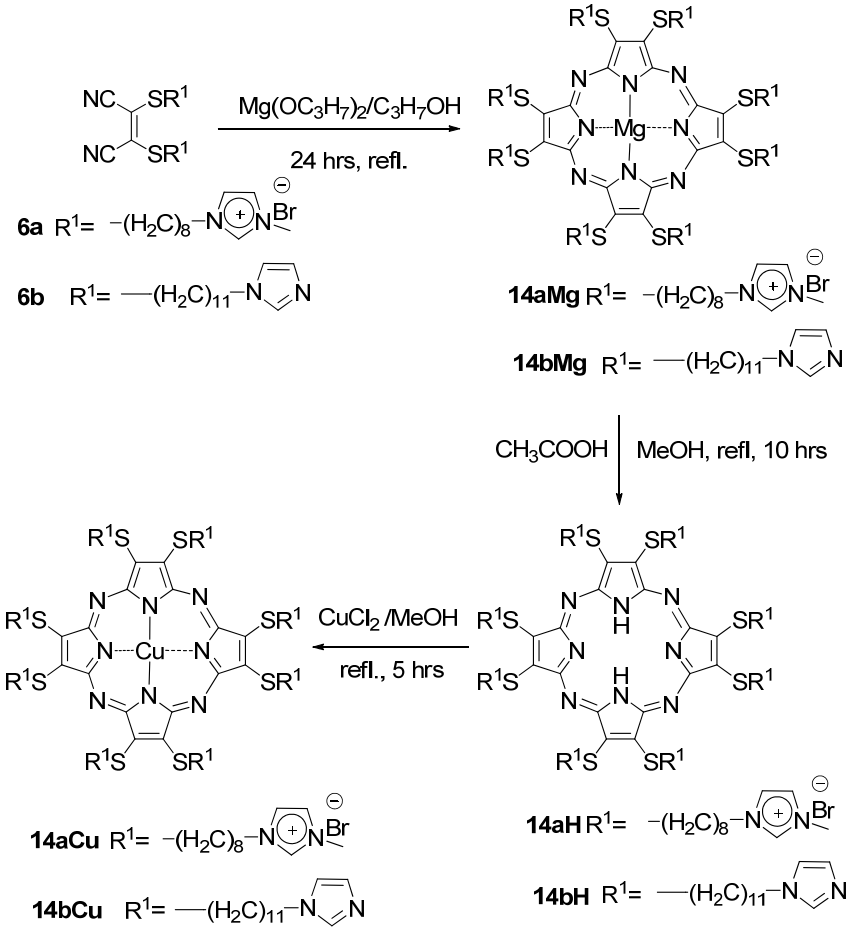
To a stirred solution of 11-(1H-imidazol-1-yl)undecyl methanesulfonate (2 g, 6.32 mmol) in 100 mL of MeOH, maleodinitrile (558 mg, 3 mmol) was added under nitrogen atmosphere at room temperature. The mixture was kept stirring for 15 hrs. The MeOH was removed under vacuum; 100 mL dichloromethane was added and the mixture filtered and concentrated under vacuum. The crude product was purified by column chromatography on neutral alumina using dichloromethane:hexanes(1:1) mixture to give 2,3-bis((11-(1H-imidazol-1-yl)undecyl)thio)maleonitrile **6b** (962 mg, 55%) as a thick yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.1-2.20 (m, 28H), 2.22 (t, J =7.02 Hz, 4H), 3.27-3.49 (m, 4H), 3.27-3.49 (m, 4H), 4.16- 4.53 (m, 4H), 7.51-7.56 (m, 4H), 7.69- 7.74 (m, 2H)

^{13}C NMR (300 MHz, $CDCl_3$, δ): 26.45, 28.95, 29.17, 29.28, 29.38, 30.15, 30.99, 32.88, 35.03, 47.03, 62.28, 112.14, 118.84, 122.34, 129.12, 137.04.

MS [HR-MALDI] (m/z): Theoretical: 538.3616; Found: 583.3612.

5.6.6 Synthesis of TAPs



Mg powder (24.6 mg, 1 mmol) and 5 mg of iodine crystals were refluxed overnight in 50 mL of dry propan-1-ol under nitrogen until all Mg is reacted to Mg (II) propanolate. Maleodinitrile **6a** (2.754 g, 4 mmol) or **6b** (2.338 g, 4 mmol) was added and the suspension was heated at reflux for another 24 hrs. The resulting greenish-blue suspension was cooled to room temperature, filtered and the filter residue was washed with methanol. All alcohol extracts were combined, evaporated, and the residual Mg containing crude TAP was stirred in a mixture of 50 mL acetic acid and 10 mL methanol at 80 ^{o}C for 8 hrs to generate the metal-free TAP. Progress and completion of the demetallation was monitored by UV-VIS

spectroscopy. About 100 mL of water was added to the now purple solution and the product was extracted with H_2CCl_2 (3 x 100 mL), the combined organic layers were dried over anhydrous $MgSO_4$ and finally concentrated in vacuum. A partial purification was achieved by precipitation of the crude product from acetone solution by slow addition of a 2:1 mixture of methanol and water to obtain deep purple solid crude metal-free TAPs.

14aH (1.28g, 55%) UV/VIS (λ max in nm) MeOH, (ε / dm^3 mol^{-1} cm^{-1}): 355 (43000), 560 (20000), 640 (26010), 710 (31200).

14bH (1.65g, 60%) UV/VIS (λ max in nm) MeOH, (ε / dm^3 mol^{-1} cm^{-1}): 342 (44 000), 515 (19 500), 655 (26 560), 714 (33 210);

Crude ^{1}H NMR signals at 60 °C (300 MHz, D_2O, δ): 1.16 (br), 1.55 (br), 3.20 (s), 3.73(br), 7.31 (br), 8.30 (s).

Metal-free TAP **14aH** (1.378 g, 0.5mmol) or **14bH** (1.165 g, 0.5 mmol) was stirred in a solution of anhydrous copper(II) chloride (108 mg, 0.8 mmol) in 50 mL methanol at reflux for 5 hrs. Progress and completion of metallation was monitored by UV-VIS spectroscopy. Aqueous 5% ammonium chloride (100 mL) was added and the TAP was extracted with H_2CCl_2 (3 x 100 mL). The combined organic layers were extracted with water (2 x 100 mL), dried over anhydrous $MgSO_4$, and concentrated to obtain crude product as a deep blue solid.

14aCu Undecyl octa imidazolium tetraazaporphyrinato-copper (958 g, 80%), MS [HRMALDI] (m/z): Theoretical: 2393.3527 $[M+H]^+$; Found: 2393.3533.

14bCu Octyl octa methyl imidazolium tetraazaporphyrinato-copper bromide (1.197 g, 85%)

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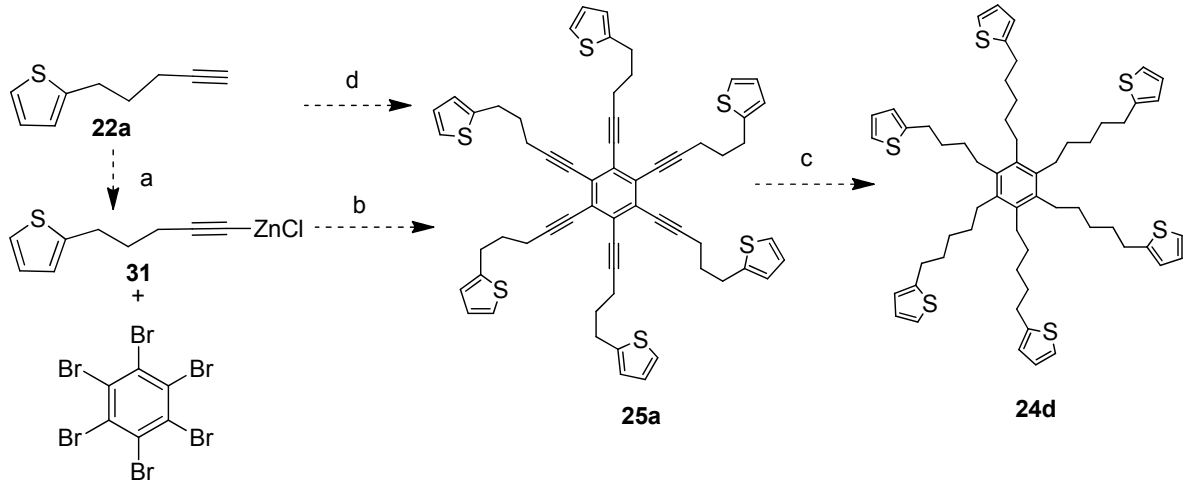
6 Chapter 6: Conclusions and Future Work

In this thesis several novel discotic molecules were prepared. A viable synthetic pathway to heptamer ester **18a** and heptamer amide **18b** has been developed but purification was successful only for the heptamer ester. Heptamer amide was more difficult to purify because of its H-bonding amide groups and decomposition products of triphenylene **25**. Most promising for further purification is the use of GPC stationary phases with smaller exclusion volumes while chromatographic separations on silica are limited by the strong aggregation of **18b**. Furthermore, the structures of **18a** and **18b** must be confirmed by MS and EA measurements before their mesomorphism is studied by polarized optical microscopy, thermal analysis, X-ray diffraction, and variable temperature UV-Vis and IR spectroscopy. (Chapter 2)

In chapter 3, two main synthetic route for the preparation of hexa(thiophenylalkyl)benzenes **24** were developed. First one is [2+2+2] cyclotrimerization of di(thiophenylalkyl)acetylenes **8** and second one is the hexa Sonogoshira coupling of **22** to hexabromo benzene. Initial difficulties with the synthesis of the precursor di(thiophenylalkyl)acetylenes **8** have been overcome but the yields of some of the steps must certainly be improved if larger scale preparations are necessary.

Many other catalysts (e. g. CpCo-η^4-cyclooctadiene complex) could be tested for the [2+2+2] cyclotrimerization but it is unclear to us what modifications to the catalyst system may be most promising. In contrast, not all reported cross-coupling conditions for the hexa Sonogashira reaction with hexabromobenzene have yet been tested by us because of time constrains. For example the catalyst system 4 mol% $PdCl_2(CH_3CN)_2$ and 8 mol% X-Phos has been successfully employed in hexa Sonogoshira coupling reactions. Another reported synthetic route to hexa-alkynyl substituted benzenes uses the zinc chloride salts of acetylenes and their $Pd(PPh_3)_4$ catalyzed cross-coupling to hexabromobenzene

generates the hexa-substituted product in a reasonable yield of 60%. An example synthetic pathway for the preparation of **24d** is given in Scheme 6.1.



Scheme 6.1: Proposed synthesis of 24d Reaction conditions: a. nBuLi, $ZnCl_2$; b. $Pd(PPh_3)_4$, Et_3N, CuI, THF, refl. c. H_2, 10% Pd/C, EtOAc, rt. ; d. 4 mol % $PdCl_2(CH_3CN)_2$, 8 mol % X-Phos, 3 mol CuI , $(iPr)_2$ HN, dioxane, 80°C.

Described in chapter 4 are the synthesis and properties of two new sets of TAPs that contain either eight alkyl azide or eight alkynyl groups. Their thermal stability was at least 80 °C lower than for analogous alkenyl substituted TAPs and decreases with decreasing spacer length. Only few of the TAPs with shorter alkyl spacers display columnar mesophases but, surprisingly, include the metal-free derivative **17aH**. Mixtures of azide and alkyne TAPs can be cross-linked *via* CuAAC in Langmuir films and as thin films to generate insoluble polymers. It was also shown that a 1:1 mixture of a discotic TAPs **16aCu** and **17aCu** can be cross-linked by thermally activated azide-alkyne cycloaddition in their columnar mesophases and without significantly affecting the hexagonal columnar mesophase. However, more systematic studies are required to probe the full scopes of thermally activated and CuAAC catalyzedcross-linking of these materials in thin films and mesophases.

In chapter 5, successful cyclization to TAPs for both maleodinitrile derivatives **6a** or **6b** containing methylimidazolium (cationic) or imidazolium (neutral) terminal groups was performed. The formation of the TAP ring was clearly established by its characteristic UV-VIS spectra but purification and

characterization of these TAPs has not been completed. Chromatographic purification was complicated by the low solubility of both **14a** and **14b** in common solvents and solution NMR spectra have not been conclusive because of substantial signal broadening due to strong aggregation at room temperature and at elevated temperature (60°C). Both purification and characterization will have to be successfully completed before materials properties can be reasonably investigated.

Appendix

Chemicals

All reagents and solvents were purchased from Sigma-Aldrich and Fluka Chemical Companies and used as purchased unless otherwise stated. Drying agents ($MgSO_4$ as well as 3 Å and 4 Å molecular sieves) were purchased from VWR. 1-Propanol and methanol were dried over 4 Å and 3 Å molecular sieves, resepctively. Tetrahydrofuran and diethyl ether were obtained from a solvent purification system (Innovative Technology Inc. MA, USA, Pure-Solv 400). Silica gel 60 (35-70mesh ASTM, from EM Science, Germany) was used for column chromatography and Silica Gel 60 aluminum backed sheets (EM Science, Germany) for thin layer chromatography.

Instrumentation

^{1}H-NMR & ^{13}C-NMR spectra were obtained on Bruker NMR spectrometers (DRX 500 MHz,DPX 300 MHz and DPX 300 MHz with auto-tune). The residual proton signal of deuterated chloroform ($CDCl_3$) functioned as a reference signal. Multiplicities of the peaks are given as s = singlet, d = doublet, t = triplet, and m = multiplet. Coupling constants are given in Hz and only calculated for 1st-order systems. Data are presented in the following order (multiplicity, coupling constant, integration). Fourier Transform Infrared spectra (FT-IR) were obtained on a Bruker Vector 22. Relative peak intensities in IR are abbreviated as vs = very strong, s = strong, m= medium, w = weak, br = broad. Liquid samples were performed as films on potassium bromide plates and solid samples were run as potassium bromide pellets. Mass spectrometry measurements were performed by Kirk Green at the Regional Center for Mass Spectrometry (McMaster University) and Jiaxi Wang at the Mass Spectrometry and Proteomics Unit (Queen's University). UV/VIS absorption spectra were run on a Varian Cary 50 Conc UV-Visible Spectrophotometer.

Polarized light microscopy was performed on an Olympus TPM51 polarized light microscope that is equipped with a Linkam variable temperature stage HCS410 and digital photographic imaging system (DITO1). Calorimetric studies were conducted on a Mettler Toledo DSC 822^e and thermal gravimetric analysis was performed on a Mettler Toledo TGA SDTA 851e. Helium (99.99%) was used to purge the system at a flow rate of 60 mL/min. Samples were held at 30 °C for 30 min before heated to 550 °C at a rate of 5 °C/min. All samples were run in aluminium crucibles. XRD measurements were run on a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector and GADDS software package. The tube is operated at 40 kV and 40 mA and CuKα1 radiation (λ=1.54187 Å) with an initial beam diameter of 0.5 mm is used. A modified Instec hot & cold stage HCS 402 operated *via* controllers STC 200 and LN2-P (for below ambient temperatures) was used for variable temperature XRD measurements.

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