THE EFFECT OF MOLECULAR SHAPE AND SYMMETRY ON DISCOTIC MESOGENS.

by

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ABSTRACT

In the field of material science, structure/property relationships can allow a more efficient design of materials exhibiting the desired properties. Self-assembled superstructures possess several advantages that can be exploited. The formation of complex architecture is dictated by the properties of the small sub-units. The formation of liquid crystalline phases requires molecular anisotropy, which is often achieved by using flat rigid rod or disc-shaped cores decorated with aliphatic chains. Other structural morphologies have also proven to allow the formation of these ordered fluid phases: plate, bent-core, bowl etc. Our research group is interested in disc-shaped molecules that have the ability to form liquid crystalline phases constituted of columns distributed in a two-dimensional lattice. The discs within a column are stacked on top of each other that could be used to conduct either energy or charges.

The research projects presented in this thesis were concerned in establishing the effect of molecular symmetry and shape on the mesogenic properties of compounds based on a dibenz[a,c]phenazine core decorated with alkoxy chains (four and six). Series of structural isomers have been synthesized and their mesogenic behaviour analyzed. Reducing the molecular symmetry of mesogens lowers the melting temperature and, to a smaller extent, the clearing temperature leading to broader liquid temperature ranges of
mesogenic behaviour. To study the effect of molecular shape, compounds with chains of different length and different motifs were prepared. This type of substitution leads to different mesogenic behaviour. Comparisons between structural isomers showed that this new substitution pattern lowered the clearing temperatures for these mesophases. The molecular shape of these compounds does have an effect on the mesophase and the results could allow more efficient engineering of systems used in various devices.

**Keywords:** liquid crystalline phases, self-assembly, columnar mesophases, structure/properties relationships.

Paulo Coelho, Warrior of the light
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Scheme 3.3: Synthesis of dialkyliodobenzene derivatives needed for the synthesis of Q(6,8). i) I₂, H₂O₂, H₂SO₄ (cat), H₂O (3.7 = 92 %); ii) BBr₃, CH₂Cl₂ (3.8 = 45 %); iii) C₆H₁₃Br, K₂CO₃, DMF (3.9a = 91 %); C₆H₁₇Br, K₂CO₃, DMF (3.9b = 79 %).

Scheme 3.4: Formation of 1,2-dialkoxy-4-iodobenzene. i) RBr, K₂CO₃, DMF (63-91 %); ii) I₂, HIO₃, AcOH, H₂SO₄. (55-71 %). R = C₆H₁₃, C₆H₁₇.

Scheme 3.5: Synthesis of unsymmetrical benzils. i) TMS-acetylene, (i-Pr)₂NH, Cul, PdCl₂(PPh₃)₂, THF (3.12a = 78 %); ii) K₂CO₃, MeOH, THF (3.13a = 79 %); iii) Cul, Pd(PPh₃)₄, (i-Pr)₂NH, THF (3.14 = 63 %); iv) I₂, DMSO (3.15 = 77 %).

Scheme 3.6: Formation of the phenanthrene-9,10-diones from the benzil precursors. R₁ = R₂ and R₁ ≠ R₂. i) VOF₃, BF₃-Et₂O, CH₂Cl₂. Yields: Q(6,6) = 75 %; Q(8,8) = 96 %; Q(6,8) = 73 %; Q(8,10) = 81 %.

Scheme 3.7: Synthesis of the diamine derivatives. i) RBr, K₂CO₃, DMF (3.10a = 91 %; 3.10b = 63 %; 3.10c synthesized by Johan Foster); ii) HNO₃, H₂SO₄ (3.17a = 78 %; 3.17b = 70 %; 3.17c = 64 %); iii) SnCl₂, HCl, EthOH (~80 %).
Scheme 3.8: Synthesis of the unsymmetrical diamine derivatives. i) C\textsubscript{10}H\textsubscript{2}Br, K\textsubscript{2}CO\textsubscript{3}, NBu\textsubscript{4}Br, butanone (3.19 = 29 %); ii) C\textsubscript{6}H\textsubscript{13}Br, K\textsubscript{2}CO\textsubscript{3}, NBu\textsubscript{4}Br, butanone (3.20 = 90 %); iii) HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4} (3.21 = 66 %); iv) SnCl\textsubscript{2}, HCl, EtOH (3.22 = 80 %).

Scheme 3.9: Formation of hexaalkoxydibenzo[a,c]phenazine derivatives. i) NaOAc, EtOH (35-77%).

Scheme 4.1: Synthesis of 2-decyloxy-1-hexyloxy-4-iodobenzene (4.5a) and 1-decyloxy-2-hexyloxy-4-iodobenzene (4.5b). i) C\textsubscript{6}H\textsubscript{13}Br, NBu\textsubscript{4}Br, K\textsubscript{2}CO\textsubscript{3}, butanone (4.1a = 52 %; 4.1b = 29 %); ii) acetic anhydride, pyridine (4.2a = 94 %; 4.2b = 96 %); iii) ICl, CH\textsubscript{2}Cl\textsubscript{2} (4.3a = 90 %; 4.3b = 97 %); iv) LiOH-H\textsubscript{2}O, THF, MeOH, H\textsubscript{2}O (4.4a = 96 %; 4.4b = 81 %); v) C\textsubscript{10}H\textsubscript{2}1Br, NBu\textsubscript{4}Br, K\textsubscript{2}CO\textsubscript{3}, butanone (4.5a = 80 %; 4.5b = 72 %).

Scheme 4.2: Formation of the free acetylene from the 1,2-dialkoxy-4-iodobenzene derivatives 4.5a and 4.5b. i) TMS-acetylene, Cui, PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, (i-PrhNH, THF (4.6a = 88 %; 4.6b = 98 %); ii) K\textsubscript{2}CO\textsubscript{3}, THF, MeOH (4.7a = 74 %; 4.7b = 89 %).

Scheme 4.3: Synthesis of QWide and Qlong. i) Cui, Pd(PPh\textsubscript{3})\textsubscript{4}, (i-PrhNH, THF (4.8a = 46 %; 4.8b = 82 %); ii) I\textsubscript{2}, DMSO (4.9a = 91 %; 4.9b = 92 %); iii) VOF\textsubscript{3}, BF\textsubscript{3}-Et\textsubscript{2}O, CH\textsubscript{2}Cl\textsubscript{2} (Q\textsubscript{wide} = 69 %; Q\textsubscript{long} = 72 %).

Scheme 4.4: Synthesis of Qmix. i) Cui, Pd(PPh\textsubscript{3})\textsubscript{4}, (i-PrhNH, THF (4.12); ii) I\textsubscript{2}, DMSO (4.13); iii) VOF\textsubscript{3}, BF\textsubscript{3}-Et\textsubscript{2}O, CH\textsubscript{2}Cl\textsubscript{2} (Qmix).

Scheme 4.5: i) Cui, Pd(PPh\textsubscript{3})\textsubscript{4}, (i-PrhNH, THF (4.12); ii) I\textsubscript{2}, DMSO (4.13); iii) VOF\textsubscript{3}, BF\textsubscript{3}-Et\textsubscript{2}O, CH\textsubscript{2}Cl\textsubscript{2} (Q(6,10)).

Scheme 4.6: Formation of mesogens by coupling the quinones with A(CN) and A(Ph). i) 2,3-Diaminomaleonitrile, AcOH (Q\textsubscript{wide}A(CN) = 30 %; Q\textsubscript{long}A(CN) = 38 %; QmixA(CN) = 29 %); ii) Phenylenediamine, AcOH (Q\textsubscript{wide}A(Ph) = 83 %, Q\textsubscript{long}A(Ph) = 63 %, QmixA(Ph) = 83 %, Q(8,8)A(Ph) = 95 %, Q(6,10)A(Ph) = 90 %).

Scheme 4.7: Formation of mesogens by coupling the quinones with A(4), A(6), A(8), A(10) and A(6,10). i) NaOAc, EtOH (Q\textsubscript{wide}A(6) = 55 %; Q\textsubscript{long}A(6) = 78 %; QmixA(6) = 37 %; Q\textsubscript{wide}A(8) = 57 %; Q\textsubscript{long}A(8) = 32 %; QmixA(8) = 57 %; Q\textsubscript{wide}A(10) = 42 %; Q\textsubscript{long}A(10) = 36 %; QmixA(A(10) = 48 %, Q\textsubscript{wide}A(6,10) = 30 %; Q\textsubscript{long}A(6,10) = 56 %; Q(10,10)A(4) = 43 %).

Scheme 6.1: Synthesis of 1,2-dialkoxy-4-iodobenzene derivatives. i) I\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, H\textsubscript{2}SO\textsubscript{4} (cat), H\textsubscript{2}O (3.7); ii) BBr\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2} (3.8); iii) C\textsubscript{6}H\textsubscript{13}Br, K\textsubscript{2}CO\textsubscript{3}, DMF (3.9a); C\textsubscript{6}H\textsubscript{17}Br, K\textsubscript{2}CO\textsubscript{3}, DMF (3.9b).

Scheme 6.2: Formation of 1,2-dihexyloxy-4-iodobenzene. i) C\textsubscript{6}H\textsubscript{13}Br, K\textsubscript{2}CO\textsubscript{3}, DMF (3.10a); ii) I\textsubscript{2}, HIO\textsubscript{3}, AcOH, H\textsubscript{2}SO\textsubscript{4} (3.11a).

Scheme 6.3: i) TMS-acetylene, (i-Pr\textsubscript{2})\textsubscript{2}NH, Cui, PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, THF (3.12a); ii) K\textsubscript{2}CO\textsubscript{3}, MeOH, THF (3.13a); iii) Cui, Pd(PPh\textsubscript{3})\textsubscript{4}, (i-Pr\textsubscript{2})\textsubscript{2}NH, THF (3.14); iv) I\textsubscript{2}, DMSO (3.15).

Scheme 6.4: i) VOF\textsubscript{3}, BF\textsubscript{3}-Et\textsubscript{2}O, CH\textsubscript{2}Cl\textsubscript{2}. 

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Scheme 6.5: Synthesis of symmetrical diamine derivatives. 

i) RBr, K$_2$CO$_3$, DMF (3.10a, 3.10b, 3.10c); ii) HNO$_3$ (3.17a, 3.17b, 3.17c); iii) SnCl$_2$, HCl, EtOH (3.18a, 3.18b, 3.18c).

Scheme 6.6: Synthesis of unsymmetrical diamine derivative A(6,10): 

i) C$_{10}$H$_{21}$Br, NBu$_4$Br, K$_2$CO$_3$, butanone (3.19); ii) C$_6$H$_{13}$Br, NBu$_4$Br, K$_2$CO$_3$, butanone (3.20); iii) HNO$_3$ (3.21); SnCl$_2$, HCl, EtOH (3.22).

Scheme 6.7: Synthesis of 2-decyloxy-1-hexyloxy-4-iodobenzene (4.5a) and 1-decyloxy-2-hexyloxy-4-iodobenzene (4.5b). 

i) C$_6$H$_{13}$Br, NBu$_4$Br, K$_2$CO$_3$, butanone (4.1a; 4.1b); ii) acetic anhydride, pyridine (4.2a; 4.2b); iii) ICl, CH$_2$Cl$_2$ (4.3a; 4.3b); iv) LiOH-H$_2$O, THF, MeOH, H$_2$O (4.4a; 4.4b); v) C$_{10}$H$_{21}$Br, NBu$_4$Br, K$_2$CO$_3$, butanone (4.5a; 4.5b).

Scheme 6.8: Formation of the free acetylene from the 1,2-dialkoxy-4-iodobenzene derivatives 4.5a and 4.5b. 

i) TMS-acetylene, CuI, PdCl$_2$(PPh$_3$)$_2$, (i-Pr)$_2$NH, THF (4.6a; 4.6b); ii) K$_2$CO$_3$, THF, MeOH (4.7a; 4.7b).

Scheme 6.9: Synthesis of Q$_{\text{wide}}$ and Q$_{\text{long}}$. 

i) CuI, Pd(PPh$_3$)$_4$, (i-Pr)$_2$NH, THF (4.8a = 46%; 4.8b = 82%); ii) I$_2$, DMSO (4.9a = 91%; 4.9b = 92%); iii) VOF$_3$, BF$_3$-Et$_2$O, CH$_2$Cl$_2$ (Q$_{\text{wide}}$ = 69%; Q$_{\text{long}}$ = 72%).

Scheme 6.10: Synthesis of Q$_{\text{mix}}$. 

i) CuI, Pd(PPh$_3$)$_4$, (i-Pr)$_2$NH, THF (4.8c); ii) I$_2$, DMSO (4.9c); iii) VOF$_3$, BF$_3$-Et$_2$O, CH$_2$Cl$_2$ (Q$_{\text{mix}}$).

Scheme 6.11: Synthesis of Q(6,10): 

i) CuI, Pd(PPh$_3$)$_4$, (i-Pr)$_2$NH, THF (4.12); ii) I$_2$, DMSO (4.13); iii) VOF$_3$, BF$_3$-Et$_2$O, DCM (Q(6,10)).

Compounds 4.10 and 4.11 were synthesized by Johan Foster.

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# Glossary (Abbreviations and Symbols)

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CHAPTER 1: INTRODUCTION

Preface:

This thesis reports some of the work executed with disc-shaped molecules based on the dibenzo[a,c]phenazine core. The main goal is to elucidate the structure/property relationships of organic materials such as liquid crystals. Once decorated with alkoxy chains, these molecules have the ability to form liquid crystalline phases in which molecules stack on top of each other to form columns. This type of architecture leads to materials having interesting properties such as anisotropic transport of charge or energy along the columns, which could be exploited in devices such as field effect transistors (FETs) and solar cells. Gaining an understanding of how the molecular structure influences the self-assembly process should allow the design of better devices using these types of functional materials. The information gained from these studies also has implications for other types of materials possessing complex two- or three-dimensional architectures arising from the self-assembly of simple molecular sub-units.
1.1 The Discovery of Ordered Materials

The last century has been marked by incredible progress in the field of materials science with polymers and silicon-based technologies that became integral to our daily lives. A large amount of research is devoted to improving the way materials are made, understanding and using their various properties.

1.1.1 Types of Materials

Research in the field of functional materials has led to an impressive amount of knowledge on how the composition and the molecular arrangement can affect the properties of a given materials. Establishing structure/property relationships would allow designed materials to possess properties that could be customized by a detailed and accurate knowledge of the interplay between the molecular features and macroscopic attributes.\textsuperscript{1,2}

1.1.2 Self-Assembled Materials

Self-assembly is the commonly observed tendency of molecules, or other building blocks, to spontaneously arrange into more complex two- or three-dimensional structures. It is responsible for many biological phenomena such as the formation of the double helix.
of DNA\textsuperscript{3,4} and the lipid membranes of cells\textsuperscript{5}. Although these examples are related to biology, self-assembly can also play important roles in more strictly chemical contexts. The term "supramolecular" is associated with any complex system that forms by the self-organization of molecular building blocks. In some cases, the obtained structure will possess voids, cavities or even channels that are available to catalyze reactions, store or deliver chemicals such as hydrogen and drugs.\textsuperscript{6,7}

While molecules are characterized by strong covalent bonds between atoms, the molecules or sub-units in supramolecular systems are bound by reversible non-covalent interactions.\textsuperscript{8} These sub-units can be organic, inorganic or a combination of both. The forces responsible for the self-assembly are weak but additive; they allow formation of structures stable over a broad range of temperatures or for a long period of time. Hydrogen bonding\textsuperscript{9}, van der Waals interactions\textsuperscript{10,11}, $\pi-\pi$\textsuperscript{12} and metal-ligand interactions\textsuperscript{13} are amongst the most commonly exploited in self-assembly.\textsuperscript{12,14,15} Since the interactions between the molecules are weak, the supramolecular assemblies can dissociate back to the sub-units with the appropriate stimuli (heat, pH, light, change in oxidation state, etc.). It also means that supramolecular systems can partially dissociate to repair errors occurring during the self-organization in order to obtain a more stable architecture.

Supramolecular materials can be obtained from the self-organization of molecules possessing functional groups that are able to recognize each other and create complex three-dimensional structures. This approach is called "bottom-up" because the sub-units
possess information that is transcribed from the molecule into the supramolecular assembly. The self-assembly of the sub-units leads to a material with a well-defined structure.\textsuperscript{16} The structure and composition of the sub-unit are directly related to the way the molecules will organize when creating the supramolecular material.

This area of research is relatively new but a large number of scientists have made contributions. Johannes Diderik van der Waals discovered in 1873 the presence of weak interactions between molecules.\textsuperscript{17} Later, the possibility of hydrogen bonding was confirmed by Moore and Winmill and later, by Latimer and Rodebush.\textsuperscript{18,19} The advances on the other types of weak interactions have allowed the field of supramolecular chemistry to grow at a rapid rate.\textsuperscript{6}

Gaining a better understanding of how the nature of the molecules affects the self-assembly process could allow for a more efficient design of materials. For example, the knowledge of how the structure of molecules affect the structure of the crystal formed would enable scientists to directly obtain crystals with desired features (e.g. pores or channels). Self-assembly also allows the formation of structures that could not be obtained otherwise. There are numerous systems where molecules self-organize and create ordered systems with desirable properties such as storage or transport of hydrogen and reactivity towards certain classes of molecules. Two specific examples of such systems are described below: molecular tectonics and micellar systems.
Molecular tectonics relies on the self-assembly of molecules decorated with recognition groups that direct the assembly of the building blocks, called tectons, into highly porous crystal structures shown in Figure 1.1. These channels can be used to store hydrogen or catalyze chemical reactions. Molecules typically pack in a compact fashion in order to maximize the stabilizing interactions between the molecules. The interactions between the recognition groups are strong enough to allow the molecules to form a stable open network of molecules. This strategy can be applied to a large number of molecules that are able to form stable crystals, but few systems are able to accommodate a large number of molecules in the channels. Also, the solvent molecules within the channels are usually necessary to the stability of the crystal, which collapses upon removal and/or exchange of these molecular guests, thus restricting the practical exploitation of these systems.

Figure 1.1: Schematic representation of molecular tectonics.
Amphiphilic molecules, which possess both hydrophilic and hydrophobic parts, can form micellar systems at appropriate concentrations (see Figure 1.2). When the pH of the solution is changed, or upon application of another stimulus, the micelles may break apart. The micelles can contain drugs that can be selectively liberated in the desired part of the body. For example, cancer cells have a different pH than healthy cells. The drugs can therefore be selectively liberated at the cancer cells in order to effectively treat the disease. Winnik and co-workers have demonstrated that dextran-based polymeric micelles can effectively transport insoluble drugs such as Cyclosporin A, a drug used to prevent organ rejection after an organ transplant.

![Figure 1.2: Formation of a micelle from amphiphile molecules.](image)

Our research group is interested in disc-shaped compounds that are able to form liquid crystalline phases. These phases arise when molecules arrange themselves via self-assembly into an ordered but fluid phase, hence the term liquid crystal. We are interested in understanding how the molecular structure affects the properties of the self-assembled phases. The following section contains an overview of liquid crystalline phases and their
properties. We will also discuss the techniques used to characterize the liquid crystalline phases.

1.2 The liquid crystalline phases

1.2.1 Historical Background

The discovery of liquid crystalline phases is traditionally attributed to the botanist Friedrich Reinitzer at the German University of Prague in the Institute of Plant Physiology in 1888. Reinitzer was extracting cholesterol derivatives from carrots to establish their molecular structures. One compound that he extracted was cholesteryl benzoate. Upon heating, the isolated compound did not melt like other compounds: it melted to a cloudy viscous liquid at around 146 °C, which then underwent a transition to a clear fluid liquid at 179 °C. The observed phenomenon was reversible and dramatic colour changes were observed at the transitions temperatures. He exchanged letters with Dr Otto Lehmann, who was a crystallographer at the Polytechnical School of Aachen, subsequently used X-Ray diffraction, along with polarized optical microscopy, to establish that the cloudy phases were in fact ordered liquids, now called liquid crystals. From those early discoveries, the field of liquid crystal research has expanded considerably.
1.2.2 Definitions

As the name suggests, liquid crystalline phases are phases of matter that possess properties of both crystals and liquids. Molecules in a crystal lattice are arranged in a highly ordered manner: they possess directional and positional order in the three dimensions. On the other hand, molecules in an isotropic liquid have no order and possess large rotational and translational motions, leading to a very fluid phase. The molecules in liquid crystalline phases have some directional and/or positional order like crystals, yet also possess some of the rotational and translational mobility observed in isotropic liquids. The molecules that form liquid crystalline phases are named mesogens. Following the same root, liquid crystalline phases are called mesophases, from the Greek "middle", because they are intermediate between liquid and solid. The term liquid crystal (LC) refers to a material that is in a liquid crystalline phase.

There are two main types of liquid crystals: thermotropic and lyotropic. Thermotropic phases (depicted in Figure 1.3) are observed upon variation of temperature, hence the prefix *thermo*. A crystalline solid, upon an increase of temperature, can melt to form one or more liquid crystalline phases that are observed over a specific temperature range. With further heating, the liquid crystalline phase "clears" to form an isotropic liquid that lacks long range order. These transitions are called melting ($T_m$: crystal to LC) and clearing temperatures ($T_c$: LC to isotropic liquid), respectively. A second class of liquid crystals are lyotropic LCs, which are observed with amphiphilic molecules in
solution. The formation of these phases depends mainly on the concentration of the molecules (hence the prefix lyo-, for dispersion or dissolution). The temperature of the solution can also have an influence on the formation of lyotropic phase. A specific class of lyotropic liquid crystals, called Chromonics, are observed from aqueous solutions of compounds containing aromatic rings. They exhibit behaviour that is intermediate between the lyotropic and the thermotropic liquid crystals. This thesis focuses on thermotropic liquid crystals.

![Temperature](image)

**Figure 1.3:** Schematic representation of the different phases of matter observed with compounds forming thermotropic liquid crystalline phases.

A characteristic feature of molecules that form liquid crystalline phases is shape anisotropy: one or two of the molecular dimensions is generally greater than the other(s). In the early days of liquid crystals, mesogens were either rod-shaped (calamitic) or disc-shaped (discotic) as shown in Figure 1.4. They were composed of a rigid core decorated with flexible chains. Figure 1.5 shows the molecular structure of some calamitic and discotic compounds known to form liquid crystalline phases.
Figure 1.4: Schematic representation of different types of mesogens: calamitic (rod-shaped) and discotic (disc-shaped).

Figure 1.5: Examples of molecular structures of calamitic (a-c) and discotic (d-f) mesogens.
A large amount of research has been executed in the field of liquid crystals and it has been demonstrated that other morphologies allow the formation of liquid crystalline phases as shown in Figure 1.6. Their molecular structures vary from bent (banana-shaped, Figure 1.6a)\textsuperscript{36,37}, to tetrahedral\textsuperscript{38} (Figure 1.6b) and octahedral\textsuperscript{39,40} (Figure 1.6c) cores. Bowl (Figure 1.7a)\textsuperscript{41}, hockey-stick (Figure 1.7b)\textsuperscript{42}, dumbbell (Figure 1.7c)\textsuperscript{43} and ring-shaped (Figure 1.7d)\textsuperscript{44} mesogens have also been shown to exhibit interesting mesogenic properties.

The following sections will describe in details the most common liquid crystalline phases observed. The phases observed with disc-shaped molecules will be depicted in more details since this thesis focus on this type of mesogen. Each of the phases shown is characterized by various degrees and type of ordering: short or long range, positional or directional. The molecular structure will have an important effect on the mesophases observed. The volume occupied by the various mesogenic parts (chains vs. core), along with the difference in polarity and flexibility of these different parts, will affect the structure of the liquid crystalline phases. As a general rule, the more ordered LC phases are observed at lower temperature.
Figure 1.6: Non-conventional mesogens. a) Bent core (banana-shaped); b) Tetrahedral core; c) Octahedral core.

Figure 1.7: Non-conventional mesogens. a) Bowl-shaped; b) Hockey-stick shaped; c) Dumbbell-shaped; d) Ring-shaped.
The molecular anisotropy of the mesogens favours the alignment of the molecules along one specific direction, sometimes called the director \((n)\) and depicted as an arrow showing the average orientation of the molecules within a specific mesophase (see Figures 1.8 and 1.10). The order parameter \((S)\) is a measure of how the molecules are, in average, aligned with respect of the director. It is calculated using Equation 1.1 shown below:

\[
S = \frac{1}{2} (3 \cos^2 \theta - 1) \tag{Equation 1.1}
\]

\(\theta\) represents the angle between the molecules and the director of the mesophase. A liquid crystalline phase with a high order parameter would indicate that the molecules are well aligned with the director and that \(\theta\) is small.\(^{45,46}\)

1.2.3 Phases observed with calamitic (rod-shaped) mesogens

The least ordered liquid crystalline phase is called a nematic phase and can be formed by either rod or disc-shaped molecules. In this phase, molecules possess only orientational order: they are aligned in one general direction (director) as shown in Figure 1.8. These molecules lack positional ordering: they do not pack in any kind of periodical array.
Another common phase observed with calamitic mesogens is called the smectic phase. This phase is characterized by a greater degree of order when compared to the nematic. The molecules pack into layers with formation of micro-domains containing either the flat rigid cores or the flexible aliphatic chains. More details on this phenomenon will be presented in section 1.2.5. Figure 1.9 shows the layered structure of the smectic phases SmA and SmC. In the SmA phase, the molecules are oriented perpendicular to the layers. If the molecules are tilted with respect to the layers, the phase is referred to as Smectic C (SmC) phase. This type of phase differs from a crystalline solid because of the mobility of the molecules within a layer or even between layers. Other LC phases have been observed with rod-shaped molecules (cubic, columnar etc.) but this is not the focus of this thesis.
These types of liquid crystalline phases have been used in a variety of applications such as liquid crystalline displays (LCDs). Unlike display devices based on cathode ray tubes (CRTs), LCDs are thinner and require less energy. They can be included in small devices that are battery operated. They appeared in the market in the 60's with wristwatches and pocket calculators. Nowadays, computer and TV screens based on LCDs are sold at a rate that has surpassed the original CRT screens. The price of these devices has decreased while the size of the monitors has increased with the image quality being conserved or even improved.\textsuperscript{47}
1.2.4 Discotic mesogens

Prior to the 1970’s, it was believed that only calamitic (rod-shaped) molecules could form liquid crystalline phases. However, in 1977, disc-shaped derivatives of benzenehexa-alkanoate were shown to exhibit liquid crystalline phases characterized by the formation of columns disposed in a hexagonal lattice. This discovery led to a large amount of research with disc-shaped molecules in order to assess their ability to form liquid crystalline phases.

Disc-shaped molecules can form LC phases with various morphologies. The less ordered phases, called Nematic Discotic (ND) and Nematic Columnar (NCol), are depicted in Figure 1.10. In the former phase, the molecules are parallel to each other and perpendicular to the director. In the latter phase, few molecules will form small columnar aggregates that are aligned with the director. If the aggregates are composed of a large amount of molecules, they form columns having the ability to pack into a variety of two-dimensional arrays. Figure 1.11 shows hexagonal (left) and rectangular (right) columnar liquid crystalline phases.
Figure 1.10: Nematic phases observed with disc-shaped molecules. a) Nematic discotic ($N_D$, the molecules are all more or less perpendicular to the director); b) Nematic Columnar ($N_{Col}$, the molecules form small aggregates more or less aligned with the director).

Disc-shaped molecules can also lead to LC phases possessing layer-like arrangement of the molecules (see Figure 1.12).\textsuperscript{55,56} The columns can form layers or columns separated by regions of aliphatic chains. This type of LC phase is called lamellar
columnar (Col$_l$).\cite{57,58} If the order of the columns is lost, layers of nematic phases can form a smectic phase (SmA$_D$).\cite{59,60} Depending on the strength of the interactions between the cores, the columns can be classified as either ordered or disordered as shown in Figure 1.13.

Figure 1.12: Layered LC phases observed with disc-shaped molecules. a) Lamellar columnar (Col$_l$); b) Smectic Discotic (SmA$_D$). The columns depicted are highly ordered but it should be noted that it is not always the case (see Figure 1.13).

Figure 1.13: Columns of disc-shaped molecules: ordered (left) and disordered (right).
In some cases, it is possible for the columns to branch and form complex interpenetrated networks of cylinders disposed into a cubic lattice.\(^{61}\) This highly ordered mesophase, denoted Cub\(_v\), can be regarded as an intermediate phase between the columnar and lamellar mesophases.\(^{62}\) These phases are not very common and their behaviour and properties are still not fully understood.\(^{63}\) These mesophases are difficult to study because they are very complex and co-exist with phases of other geometries such as smectic and columnar. In most cases, these phases occur at high temperatures, which decrease their stability, leading to more difficult recording of XRD data.\(^{56,64}\) The first cubic phases were originally observed with rod-shaped molecules but recent advances has shown that other molecular morphologies can also lead to the formation of these phases.\(^{59,63,65-67}\)

Unlike rod-shaped molecules, disc-shaped molecules cannot be used in devices where fast switching is a key feature (such as LCDs), because liquid crystalline phases of discotic mesogens tend to be very viscous. However, such materials do have numbers of properties that make them attractive candidates for applications where calamitic mesogens have not been traditionally exploited. These applications will be described in section 1.2.6.
1.2.5 Formation of liquid crystalline phases

Many factors can account for the formation of liquid crystalline phases. Firstly, the shape anisotropy is largely but not exclusively responsible for the formation of LC phases.\textsuperscript{68} The formation of micro-domains containing different portions of the mesogens has also an impact on the formation of the various mesophases. The molecular components (core vs. chains) are chemically and conformationally different.\textsuperscript{69,70} They will therefore tend to segregate and form micro-domains that do not mix well.\textsuperscript{71} The micro-domains contain either the flat rigid cores or the flexible aliphatic chains. Different types of inter-molecular interactions are observed in the various domains. The chains usually interact via van der Waals interactions while the cores are bonded by $\pi-\pi$ interactions. Figure 1.14 depicts the intermolecular interactions that would be observed between discotic mesogens forming a columnar LC phase. The balance between the different inter-molecular interactions will have an impact of the arrangement of the molecules within the LC phase and on the stability of the mesophase.
Figure 1.14: Schematic of the interactions observed between mesogens in a columnar hexagonal LC phase.

The phase segregation, occurring at a molecular level, leads to the formation of domains separated by interfaces. The shape of these interfaces dictates what type of mesophase is observed. Non-curved (linear) interfaces favour the formation of layered or lamellar mesophases (smectic and lamellar). Upon increase of the curvature of the interface, the mesophase will shift towards a columnar arrangement of the molecules. One of the components (core or chains) will create a cylindrical continuum of one component embedded into the second molecular component. Upon further increase of the curvature of the interface, the molecular aggregate will have a spherical shape with one component being surrounded by the second component.
To rationalize the formation of the various phases, the intermolecular interactions, the ratio between the various molecular components along with the interfaces curvature must be taken into account.\textsuperscript{75} If the intermolecular interactions are weak, the molecules are not held tightly and the shape anisotropy will favour the formation of a nematic phase where the molecules can move freely (see Figures 1.8 and 1.10).\textsuperscript{76,77} The presence of short chains around the core prevents the segregation (chains vs. cores) that could lead to the formation of micro-domains. Bulky groups appended to the cores can also prevent them from interacting with each other and forming aggregates where they stack into layers or columns. Upon the increase in the chain length, the ratio chains/core increases along with the intermolecular interactions. This favours the segregation of the component into micro-domains favouring the formation of layered or columnar mesophases.

Even today, there is a large amount of research conducted in the field of liquid crystals in order to get a better understanding of how the molecular structure of the mesogens can influence the morphology of the mesophases. Understanding the structure/property relationships may allow the formation of mesophases with the desired properties. Various groups have studied various systems and structure properties and presented how various structure modifications affect the mesophases. For the purpose of this thesis, only few examples will be described in the following section and it should be kept in mind that this is only a small portion of the work that has been executed in the field.
Porphyrin derivatives have been widely studied in the context of liquid crystals because of their potentially useful electronic, chemical and thermal properties. The first porphyrin derivatives (Figure 1.15a) decorated with eight flexible chains exhibited mesophases possessing columnar ordering. Upon addition of a phenyl spacer between the core and the chains, which are also in smaller number (Figure 1.15b), the mesophase observed is discotic lamellar.

Based on these results, Ohta and co-workers prepared various porphyrin derivatives in order to probe the effect observed on the mesogenic behaviour when the molecular structures were modified. They changed the number of bulky groups, the number and length of the chains appended to the core and the influence of phenyl spacers between the cores and the chains. Figure 1.16 shows the four types of porphyrin used, along with their associated mesophases. The different substitution patterns observed on the porphyrins derivatives have an impact on the shape of the molecules.

Figure 1.15: Porphyrin derivatives forming liquid crystalline phases. a) Columnar; b) Lamellar.
Derivatives with big bulky groups and large number of chains have a more disc-like molecular shape that facilitates the formation of hexagonal columnar phases (Figure 1.16a). Reducing the number of chains and/or bulky groups reduces the ability of the molecules to pack and the hexagonal packing in the LC phase is replaced by a rectangular columnar mesophase (Figure 1.16b). The ratio chains/core is reduced and the micro-segregation interfaces are favouring this new morphology. Further reduction of the number of chains and appended groups reduces further the chain/core volume ratio, which will favour lamellar arrangement of the columns (Figure 1.16c). The fourth derivative possesses a molecular shape that is more rod-like and the formation of layered mesophase is favoured as shown in Figure 1.16d.
Other research groups have demonstrated that it is possible to tailor the morphology of the mesophases via specific molecular modifications. While longer chains favour columnar packing, shorter chains favour lamellar packing.\textsuperscript{83-85} Levelut and Clerc have shown that the morphology of cubic mesophase can change upon modification of the chains appended to the rigid aromatic core.\textsuperscript{86} Molecules that normally form smectic
phases (SmA and SmC) can also from highly ordered cubic phases if the chains appended
to the core are long enough, allowing segregation of the different molecular
components.\textsuperscript{62} Wang and co-workers have shown that the use of aliphatic chains where
some of the hydrogens are replaced by fluorine atoms.\textsuperscript{87}

A similar effect is observed when the size of the core is increased: the columnar
mesophase is replaced by a lamellar arrangement of the molecules.\textsuperscript{88} Bulky appended
groups decreases the stability of the molecular aggregates and nematic mesophases are
preferred. Electron-withdrawing groups attached to the rigid cores favour the formation
of aggregates by increasing the strength of the inter-molecular interactions, favoring to
columnar packing. Cammidge and co-workers have demonstrated that the nature of the
atom between the core and the aliphatic chains has an impact on the morphology of the
LC phase. The mesogenic behaviour of triphenylene derivatives is lost when the oxygen
is replaced by a methylene group (-CH\textsubscript{2}-).\textsuperscript{89} The presence of electron-withdrawing atoms
seems to be essential to the formation of the mesophase. The polarization of the core,
induced by these atoms (O, S etc.), increases the intermolecular interactions and promotes
the formation of a liquid crystalline phase. The use of sulphur atoms to bridge the core to
the aliphatic chain led to the formation of stable helical columnar phases. The mesogenic
behaviour is affected by the number and relative positions of the thioether chains.\textsuperscript{90}
1.2.6 Practical uses of discotic mesogens

One of the drawbacks of early LCDs was their limited viewing angle that resulted from the birefringent mesophases. To address this problem, a thin layer of discotic mesogens in a nematic phase is placed in front of the LCDs. This optical compensation layer helped eliminate problem of the small viewing angle that restricted the potential of early liquid crystal displays. Because discotic nematic phases are exceedingly uncommon, it is still an important challenge to find ways to favour the formation of nematic phases rather than columnar phases.

The most common phases observed with disc-shaped molecules are characterized by the formation of columns that have been used in devices where charge transport is required: organic light emitting devices (OLEDs), field-effect transistors (FETs) and photovoltaics (PVs). They have also been incorporated in polymers that exhibit conductivity or luminescence. The conductivity of the columns comes from the fact that the aromatic cores stack on top of each other, allowing for charge to travel in the direction parallel to the columns. Each column can be seen as acting analogously to a molecular wire. The alkoxy chains surrounding the cores will act as an insulating layer and favour charge or energy transport in the direction parallel to the column axis as shown in Figure 1.17. The conductivity in the other directions has been found to be several orders of magnitude smaller.
Several research groups have investigated ways to improve the conductivity observed with columnar phases by increasing the degree of order within the columns. Van de Craats and co-workers have shown that increasing the size of the aromatic core was an efficient method to increase the conductivity along the columns by up to two orders of magnitude (see Figure 1.18). Larger overlap between two discs increases the degree of order within the columns and favours an uninterrupted pathway for the charges. They have also shown that when the alkyl chains are attached directly to the core, the conductivity was greater than if there is an oxygen spacer between the disc and the chain. The bigger oxygen atoms create steric hindrance that reduces the ability of the discs to stack into an ordered column. Bigger groups, such as phenyl rings, seem to have little influence on the stability of the columnar phases.

Figure 1.17: Application of columnar liquid crystals. a) View from the side: the charges or the energy can be transported through the column as depicted by the arrow (the chains have been omitted for clarity); b) View from the top: the flexible chains act as a protective layer, allowing charges or energy transport in only one direction. Aromatic cores are depicted in red and alkyl chains in black.
Collard and co-workers have also investigated the use of branched chains to decorate the aromatic core. They showed that branching close to the disc was destabilizing for the columnar phase while branching at the chain end had little to no influence. Installing chains branched in the middle had the effect of lowering the crystal to liquid crystal transition while the second transition was not affected (see Figure 1.19). Branching therefore represents a good strategy for obtaining a broader liquid crystalline phase. Mülken and co-workers prepared hexa-peri-hexabenzocoronene derivatives with branched chains and obtained liquid crystalline phases at room temperature and that possessed conductivities that made them potentially useful in optoelectronic information storage.
Substitution at that position lowers $T_m$ only, hence broadening the LC range.

Steric hinderance reduce the ability of discs to pack into columns

Little to no influence on the melting temperature

Figure 1.19: Effect of chain branching at different positions on the liquid crystalline phases.

To be useful in devices, columnar phases must satisfy criteria other than their ability to transport charges\textsuperscript{103,104} or energy.\textsuperscript{105,106} The ordered LC phases must be observed over a wide range of temperatures (e.g. \(-50\, ^{\circ}\text{C}\) to \(100\, ^{\circ}\text{C}\)) that allow the device to be functional at ambient temperature, even with large temperature fluctuations. Although the mesophase ordering might ideally be achieved by having an LC that is thermodynamically stable across their entire range, it might also be realized by supercooled glassy phases that indefinitely maintain LC ordering at lower temperatures.\textsuperscript{107,108}

In order to favour the formation of liquid crystalline phases possessing high conductivities, the formation of charge-transfer complexes has been evaluated.\textsuperscript{109-111} These systems have the advantage that once the two neutral species have exchanged
charges, they become strongly attracted to each other and this directs the self-assembly in a more reliable fashion.\textsuperscript{112} Their behaviour in the liquid crystalline phases is still under investigation in order to be incorporated into devices.\textsuperscript{113}

The upper temperature limit of the columnar phase must also be controlled. Because liquid crystalline phases are often very viscous, they are generally processed from their more fluid isotropic state. The clearing temperature must therefore be low enough to allow easy processing, but high enough to allow devices to perform properly if the ambient temperature fluctuates.\textsuperscript{96} The devices can also be prepared by spin-coating from a solution of the mesogens onto a conducting substrate. It is therefore essential that the compounds have a good solubility in volatile solvents in order to obtain films of good quality.\textsuperscript{100,101} Two applications of columnar liquid crystals, OLEDs and Xerography, will be presented below.\textsuperscript{91}

Organic Light-Emitting Devices (OLEDs) are devices that produce light upon application of an electric field. As a general rule, OLEDs are made of a photoactive layer sandwiched between two layers that are able to transport electrons and holes, respectively. The conducting layers are in contact with an anode and a cathode which, upon application of an electric field, will introduce holes or electrons in the conducting layers. The charges will be attracted to each other and migrate toward the central layer where they combine and produce light.\textsuperscript{114} Kitzerow and Bock have shown that perylene derivatives can be used as the electron-transporting layer while hexaalkoxytriphenylenelene
derivative are efficient hole-transporting materials (see Figure 1.20). Xie and co-workers have demonstrated that metallomesogens have the ability to form columnar liquid crystalline phases that possess conductivities up to two orders of magnitude higher than triphenylene derivatives.

![Compounds used in OLEDs by Kitzerow and Brock. Perylene (left) is the electron-transporting layer while triphenylene (middle) is used as hole-transporting layer. The di-copper complex (right) examined by Xie and co-workers have an exceptionally high carrier mobility in the LC phase.](image)

Figure 1.20: Compounds used in OLEDs by Kitzerow and Brock. Perylene (left) is the electron-transporting layer while triphenylene (middle) is used as hole-transporting layer. The di-copper complex (right) examined by Xie and co-workers have an exceptionally high carrier mobility in the LC phase.

Xerographic processes require the use of photoconductive materials in order to reproduce an image or text on another sheet of paper. The original copy is placed between a light source and a sheet of photoconductive material covering a rotating cylinder. The light passes through the paper and induces a charge modification on the photoconductive plate behind the original, only where there is no image or text. The toner (dry ink) covers the photoconductive plate and reproduces the original image or text. The toner will be transferred to another piece of paper and heating will fix the toner in place. The photoconductive plate must be made of a material that loses its charge upon light
exposure to allow the charges to remain where the image must be reproduced. The materials used for the photoconductive plate must have a high light sensitivity for the process to be quick and to require a small amount of energy to create the electrostatic charge separation.\textsuperscript{117}

Tschierske and co-workers have demonstrated that perylene bisimides have a good absorption in solution and in the solid state. They also form columnar phases that are stable over large ranges of temperature (up to 373 °C), which could be used in optoelectronic devices such as photocopiers (Figure 1.21, left).\textsuperscript{118} Eichhorn and co-workers have shown that phthalocyanines have a strong absorption and the substitution pattern shown in Figure 1.21 (right) increases the stability of the columnar phase over a broad range of temperatures. The material was also shown to be more easily aligned via shearing, hence facilitating the formation of devices.\textsuperscript{107}

![Figure 1.21: Typical compounds used in xerographic processes. Perylene bisimides (left) and phthalocyanines (right). M = Cu, Zn or “2H”.](image)

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1.2.7 Typical disc-shaped mesogens

As already noted, the first columnar phases were observed with hexaalkanoate derivatives of benzene. Many other classes of discotic mesogens have subsequently been discovered and several examples are shown in Figure 1.22. There are still a number of questions that have yet to be answered, even with the large amount of research executed on disc-shaped mesogens. Nematic phases obtained with discogens are less common and various researchers are using some of the strategies depicted in section 1.2.5 to favour the formation of these mesophases.

Figure 1.22: Examples of disc-shaped molecules forming liquid crystalline phases. a) hexaalkanoate benzene; b) triphenylene; c) hexaalkoxytricycloquinazoline.
1.3 Characterization of liquid crystalline phases

Liquid crystalline phases are characterized by three major techniques: polarized optical microscopy (POM), differential scanning calorimetry (DSC) and variable temperature X-ray diffraction (VT-XRD). POM gives information about the type of phase formed (e.g. nematic, smectic, columnar, etc.), DSC accurately measures the temperatures of phase transitions along with their enthalpies ($\Delta H$). VT-XRD is used to corroborate the microscopy assignment and provide lattice parameters such as the distance between layers or columns or the distances between molecules within a column. The combination of these techniques allows an unambiguous assignment of the type of liquid crystalline phase is formed. These techniques will be described in detail in the sections below.

1.3.1 Polarized Optical Microscopy

Polarized optical microscopy (POM) is one of the tools used to determine the presence, or absence, of order in a material and establish if the compound forms a liquid crystalline phase. Ordered materials may have refractive indices that are direction dependant, meaning that the material is birefringent. To perform this analysis, a sample is placed between two polarizers that are at angles of 90 degrees ("crossed") as shown in Figure 1.23. Non-polarized light enters the first polarizer to become linearly polarized.
and then passes through the sample before reaching the second polarizer. If the sample is
non-birefringent, the polarization of light will not be altered and no image will be
observed since no light will pass through the second polarizer. When the sample is
birefringent, the polarization of the light is altered and a portion of the light can pass
through the second polarizer.

![Diagram of light propagation through polarizers](image)

**Figure 1.23: Schematic representation of polarized optical microscope.**

The polarizing microscope is equipped with a heating stage that controls the
sample’s temperature. The solid is deposited on a microscope slide, heated to the
isotropic phase and a cover slip is placed on the liquid. The sample is slowly cooled down
from the isotropic liquid to allow formation of textures that are specific to the micro-
structure and defects occurring during the assembly of the molecules. The isotropic liquid
phase usually forms an image that is black, from the lack of order. Upon cooling, ordered
phases are formed and colored domains with specific textures start to form. The various
domains possess characteristic textures that allow preliminary identification of the type of
LC phase.
Each mesophase will grow in a specific manner, associated with specific defects, allowing a visual identification of the type of phase observed. The thickness of the sample, along with its alignment will affect the color of the textures observed. In some cases, the alignment of the molecules in some domains leads to an ordered domain that does not bend the light. These regions are called pseudo-isotropic because of the lack of texture, but represent regions where the molecules or the aggregates are perfectly perpendicular to the surface of the microscope slide. SmA and Col phases have a tendency to form such domains as shown in Figure 1.24 (a,c,d and f).

It is of interest to be able to direct the alignment of the mesophase on various surfaces. Layered phases of calamitic mesogens can be aligned using surface coating with polymers such as polyimides. Exposure to a electric or magnetic field can also be used to favour a uniform alignment of the molecules. Disc-shaped molecules do not respond to electric fields (molecular dipole too small) so other methods must be used to align the columns perpendicularly (homeotropic alignment) or parallelly (homogenous alignment). Columnar phases have a tendency to align perpendicular to the surface and create black domains in the POM texture. The colored domains can be re-aligned by heating the sample for a long period of time (i.e. 12-24 hours). This method is called annealing and would lead to a POM micrograph with no colored domains. It is also possible to align the columns parallel to the surface by mechanical shearing. Moving the cover-slide in one direction can favour the alignment of the columns parallel to the shear.
The compounds studied in our research group mainly form hexagonal columnar phases. These phases often give rise to textures that grow in a dendritic fashion (multi-branching tree-like growth) with features possessing six-fold symmetry. However, when the compounds are very pure, these textures tend to grow very rapidly and are extremely difficult to photograph. Reducing the rate of cooling can facilitate the capture these features. Examples of the images obtained are shown in Figure 1.24. Some compounds are more viscous and therefore form thicker layers of liquid crystalline material when sandwiched between the microscope and the cover-slip. The viscosity was not measured, but mainly observed during the preparation of the samples for the XRD data collection. These compounds gave rise to textures that were orange-colored. The other compounds formed textures with white and green shades of colours as shown in the figure below.

Figure 1.24: Representative micrographs captured with a polarized optical microscope with compounds forming hexagonal columnar phases. a) $Q_{\text{wide}}A(6,10)$, 131 °C, taken at 200X; b) $Q(8,8)A(8)$, 125 °C, no cover-slip, taken at 80X; c) $Q(8,8)A(8)$, 146 °C, taken at 200X; d) $Q(8,8)A(8)$, 135 °C, taken at 80X; e) $Q_{\text{wide}}A(CN)$, 240 °C, taken at 80X; f) $Q_{\text{wide}}A(CN)$, 243 °C, taken at 80X. The black regions correspond to domains where the columns are perpendicular to the microscope slide.
1.3.2 **Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry (DSC), is a thermal characterization technique that is used to measure phase transitions. It provides information about the temperatures at which transitions are observed as well as the enthalpy associated with these transitions. These values can be used to evaluate the relative stability of the different phases (crystal, LC and isotropic liquid). In the apparatus of a power-compensated DSC, two sample holders are imbedded in a heating platform (see Figure 1.25). Each sample holder is connected to an individual furnace that is connected to a temperature controller whose function is to maintain both sample holders at the same temperature. Therefore, if the analysed sample holder requires more or less heat in order to be at the same temperature as the reference holder, the circuit will adjust the input and record the difference in energy. The difference in input between the two holders is reported in units of energy such as J/g or J/mole and corresponds to the energy associated with the transition being observed.\textsuperscript{132}
The graph obtained from this experiment provides information such as the temperature of transitions, their enthalpies and whether they are endothermic or exothermic. In the case of an endothermic transition, the transformation requires more energy and the graph will show a positive peak ($\Delta H > 0 \text{ J/g}$). In the case of an exothermic transition, energy will be released from the sample and the peak observed will have a negative amplitude ($\Delta H < 0 \text{ J/g}$). The area under the peak corresponds to the enthalpy ($\Delta H$) of the transition.
Figure 1.26 shows a DSC endotherm obtained during the characterization of a liquid crystalline phase with our apparatus. The analyte is heated or cooled at a constant rate, 5 °C/minute, and the experiment is repeated to establish the reversibility of the phase behaviour. When the formation of liquid crystalline phases is reversible, the same transition temperatures (± 1 °C) enthalpies are observed for both heating and cooling curves. The sharpness of the peaks is also an indication of purity. When observed peaks were broad (more than 5 °C), samples were re-purified and reanalyzed by DSC.

Figure 1.26: Typical spectrum obtained with a liquid crystalline phase upon heating and cooling at 5 °C/minute. The structure of the molecule used to obtain this graph is shown below the curves.
1.3.3 Variable-Temperature X-Ray diffraction (VT-XRD)

Using X-ray diffraction, it is possible to obtain information concerning the arrangement of the molecules of a crystal. X-rays are produced when a beam of accelerated electrons (30 kV) hits a metallic target such as copper. The electron beam ionizes lower valence electrons (in the 1s orbital) of the metal. This creates a hole that is immediately filled by a higher valence electron (from other orbitals such as 2p, 3s), which releases energy in the form of X-ray radiation that is redirected towards the analyzed sample. The radiation interacts with the solid and produces a diffraction pattern that provides information concerning the position of the molecules in the lattice of the crystal. The repetition units in the solid will scatter the beams at specific angles. These angles can be indexed to periodic spacing between the molecules in the ordered material. These repeating distances are called d-spacing and can be calculated using Bragg’s law (Equation 1.2):

\[ n\lambda = 2dsin\theta \]  
Equation 1.2

Copper is usually used to produce X-rays and the wavelength of the radiation produced is \( \lambda = 1.54 \ \text{Å} \) while the value of \( n \) must be an integer, usually 1. A detector plate collects the reflected beams and produces a graph of the intensity of the reflected beams as a function of the angle at which they are reflected (2θ). Figure 1.27 shows a
typical X-ray diffractogram obtained with a hexaalkoxydibenzo[a,c]phenazine derivative. Using Equation 1.2, the d-spacing values are calculated from the reflection angles on the spectrum (see Appendix 2 for more details on the calculations and indexing of the peaks). In the case of the liquid crystalline phases, VT-XRD provides information about the 2D lattice of the columns (hexagonal or rectangular).

The values obtained from the 100 and 110 reflections are used to calculate the distance between two columns. The alkyl halo corresponds to the periodic arrangement between the alkyl chains in the liquid crystalline phase (~4.5 Å). The highest angle peak observed is associated with the distance between two adjacent discs in a column (~3.5 Å), which is also indicative of the degree of order in the liquid crystalline phase. As a general rule, if that peak is present, the phase is considered ordered. Figure 1.28 shows the planes observed with hexagonal and rectangular arrays of columns in liquid crystalline phases.
Figure 1.27: Typical diffractogram obtained with LC phase. The lattice parameters extracted from the diffractogram confirm the hexagonal packing of the discs in the liquid crystalline phase. This spectrum was recorded at 110 °C.

Figure 1.28: Planes observed within hexagonal 2D lattice (left) and rectangular 2D lattice (right).
1.4 Our area of research

Our research group's interest is to understand how the structure of molecules affects their liquid crystalline properties. In an early study from our laboratory, the effect of a small change in the core structure on the mesophase behaviour was investigated. To address this question, the benzotriphenylene Ib was prepared by a previous graduate student (Kevin Lau) and its properties compared to those of the known triphenylene 1a (see Figure 1.29). The liquid crystalline behaviour of the two mesogens differs significantly: the melting temperature of Ib is lower and its clearing temperature is higher, leading to a broader LC range. However, it was not clear if these differences arise from the larger aromatic core of the benzotriphenylene derivative, the methyl groups or the lower symmetry of the molecule. The nomenclature used to present transition temperature is shown in Figure 1.29. As an example, 1a is crystalline (Cr) up to 58 °C, then it is liquid crystalline (Col) up to 69 °C where it becomes an isotropic liquid (I). “Col” refers to the type of liquid crystalline phase observed, columnar in this case.
In order to establish the origin of these differences, an extensive series of compounds with different core sizes and symmetries would have to be synthesized. Unfortunately, the synthesis of benzotriphenylene derivatives is lengthy, which would make it difficult to obtain enough derivatives to probe the effect of core size, shape and symmetry on mesogenic behaviour. To that end, a different type of mesogen was envisioned to establish the structure/properties relationship with disc-shaped molecules derived from the triphenylene core.

An alternative approach is to employ modular synthesis in order to obtain a series of compounds. By condensation of a quinone and a diamine, we were able to obtain a large number of different types of compounds, as shown in Figure 1.30. The compounds depicted were used to probe a variety of structural features: the effect of the nature and the position of substituents, the presence and position of heteroatoms in the aromatic core and the size of the aromatic core.\textsuperscript{135-138}
Figure 1.30: Typical mesogens obtained by condensation of a phenanthrene-9,10-dione with various diamines in our research group.

This thesis will focus on work done with mesogens obtained when the quinone is condensed with a 1,2-dialkoxy-4,5-diaminobenzene as shown in Figure 1.31. The reaction affords hexaalkoxydibenzo[a,c]phenazine derivatives that form, as a general rule, columnar hexagonal liquid crystalline phases. The effect of molecular symmetry and molecular shape on physical properties of these molecules have been investigated.
Figure 1.31: Formation of a dibenz[a,c]phenazine derivative from the condensation of a diamine and a diketone precursors.

These compounds possess several advantages over the triphenylene derivatives studied in the past. Their melting temperatures are usually lower than their triphenylene counterparts, and they possess liquid crystallinity over a broader range of temperatures. The modular synthesis used to obtain these compounds allows the formation of a large number of compounds from a limited number of quinones and diamines. In contrast, triphenylene analogues often must be prepared via syntheses that require a larger number of steps to prepare additional members of a series.

In our quest to gather information about structure/properties relationships, the work presented in this thesis will focus on how the symmetry and the shape of mesogens affects the liquid crystalline phases observed. Chapter 3 will present a systematic study of the effect of molecular symmetry on mesogenic behaviour of hexaalkoxydibenzophenazine derivatives. Those results suggested that the molecular shape was also an important factor. Series of compounds derived from the same aromatic core were prepared and the effect of the molecular shape on the transition temperatures
was examined. Chapter 2 is an overview of the synthetic strategies used to obtain the quinones used in the symmetry and shape studies. Molecular features such as symmetry and shape were investigated in chapter 3 and 4, respectively. A short conclusion is presented in chapter 5 and the details on the experiments are compiled in chapter 6. A side project on triphenylene derivative is presented in the appendix 1. Appendix 2 shows in more details the calculations executed with the data obtained with the XRD experiments. Appendix 3 contains the NMR assignment of 2-acetyl-1-decyloxy-4-iodobenzene via various experiments.

1.5 Thermodynamic consideration on mesogenic behaviour

Chapters 3 and 4 will examine how structural features can affect the mesogenic behaviour of derivatives based on the dibenzo[a,c]phenazine core decorated with four to six alkoxy chains. Chapter 3 will focus on the molecular symmetry while Chapter 4 will describe a model based on the molecular shape of the mesogens. For these analyses, some thermodynamic concepts must be revisited in order to link molecular symmetry and shape to entropic and enthalpic changes occurring during phase transformation. The important concepts will be explained in detail in their respective chapters (3 and 4) in order to complement the analysis of the results obtained.
CHAPTER 2: SYNTHESIS OF PHENANTHRENE-9,10-DIONES AS BUILDING BLOCK FOR DISCOTIC MESOGENS

2.1 Introduction

In the field of liquid crystals, phenanthrene-9,10-diones decorated with alkyl or alkoxy chains are often coupled with diamines to form mesogenic compounds. They can be used in systems where modular synthesis is desirable to obtain a large number of compounds from a limited number of starting materials. They are most commonly formed by oxidative cyclization of the corresponding benzil derivatives; this is the approach that is used in our group as shown in Scheme 2.1.

Scheme 2.1: Formation of a phenanthrene-9,10-dione from a benzil. Conditions: $i$) VO$_3$, BF$_3$-Et$_3$O, CH$_2$Cl$_2$ (60-85 %).
Various strategies to form tetraalkoxyquinones have been reported in the literature. The substitution pattern of the quinones (Figure 2.1) will influence the type of synthesis used. The simple quinones (A) have been obtained by benzoin condensation or Friedel-crafts acylation. Unsymmetrical quinones (B) have been obtained by oxidation of diphenylacetylene precursors. Quinones C have been obtained by a two-step alkylation process of tetrahydroxybenzil, which is obtained by benzoin condensation. The yields (stepwise alkylation) are however very low. This chapter presents our attempts to synthesize the benzil precursors to the quinones C and D. These quinones will enable us to study the effect of the molecular shape on liquid crystalline properties. More details on the synthesis of quinones A and B will be presented in this chapter.

![Figure 2.1: Quinones with various substitution patterns.](image)

Figure 2.1: Quinones with various substitution patterns.
2.2 Strategies investigated to form benzil derivatives

A variety of synthesis approaches have been reported by different groups to prepare tetraalkoxy benzils. Some of these will be described in this chapter.

2.2.1 Kumada coupling

Ohta and co-workers investigated a number of synthetic routes to obtain benzil derivatives bearing long alkyl chains.\textsuperscript{139,140} Benzil derivatives can be obtained from the oxidation of a stilbene precursor with various reagents such as selenium oxide (Se$_2$O).\textsuperscript{139-141} To obtain stilbene precursors, Ohta and co-workers attempted to perform a Kumada coupling between vinyl chloride and the corresponding Grignard reagents in presence of a nickel catalyst.\textsuperscript{142,143} These reagents can be obtained from the corresponding bromo- or iodobenzene derivatives decorated with either alkyl or alkoxy chains. Scheme 2.2 shows the synthesis described previously. The Grignard reagents were successfully prepared but the Kumada couplings did not afford the desired precursors. However, it should be noted that tetraalkoxystilbene derivatives have been produced in the past using other synthetic strategies.\textsuperscript{144-146}
Scheme 2.2: Kumada coupling attempted to obtain dialkyl or dialkoxy benzil. 

\[ \text{R}_1\text{MgX} \rightarrow \text{Cl} \rightarrow \text{R}_1\text{R}_2 \rightarrow \text{R}_1\text{R}_2 \rightarrow \text{R}_1\text{R}_2 \rightarrow \text{R}_1\text{R}_2 \]

1) \( \text{NiCl}_2(\text{dppe}) \); 2) \( \text{SeO}_2, 90\% \text{AcOH, H}_2\text{SO}_4 \).

2.2.2 Acyloin coupling

The acyloin condensation (Scheme 2.3) was evaluated by Ohta as a means to afford the desired tetraalkyl- or tetraalkoxy- benzils. Treatment of 3,4-dialkylated ethyl benzoates with sodium (Na) in xylene produced the corresponding benzoins. However, this approach was unsuccessful when the starting materials are 3,4-dialkoxybenzoates. Very recently, the acyloin condensation was successfully employed to form benzils from 3,5-dialkoxybenzoate derivatives.\(^{147}\)

Scheme 2.3: Acyloin condensation forming the benzoin which can be oxidized to the benzil derivative. 

1) Na, Xylene; 2) SeO\(_2\), 90 % AcOH, H\(_2\)SO\(_4\).
2.3 Benzoin Condensation

2.3.1 Historical overview of the Benzoin Condensation

The first tetraalkoxy benzil was synthesized over a century ago by Fritsch who prepared veratril (3,3',4,4'-tetramethoxybenzil) by treating veratraldehyde (3,4-dimethoxybenzaldehyde) with potassium cyanide (KCN) in an alcoholic solvent to form the benzoin veratroin. The product was oxidized by copper oxide (CuO) in presence of ammonia to afford veratril. Pearl also converted ethers of vanillin such as 4-benzyloxy-3-methoxybenzaldehyde in order to prepare the corresponding benzil derivatives. Kubiczek repeated in 1946 the reactions developed by Fritsch but using CuSO₄ instead of CuO. Veratril can be hydrolysed in HBr and acetic acid to afford 3,3',4,4'-tetrahydroxybenzil as shown in Scheme 2.4. It was also shown that piperonaldehyde can undergo benzoin condensation. The resulting benzil must be cleaved with PCl₅. The examples of successful benzoin condensation are limited to these substrates: no reaction occurs when 3,4-dialkyl or 3,4-dialkoxybenzaldehydes are used as starting materials.
Scheme 2.4: Formation of tetrahydroxybenzil from veratraldehyde. i) KCN, EtOH, H₂O; ii) CuSO₄, pyridine, H₂O; iii) HBr, AcOH.

Therefore, the alkoxylated benzil derivatives must be obtained by alkylation of tetraalkoxybenzil. Ohta and co-workers have shown that it is possible to selectively alkylate the tetrahydroxybenzil at the para position of the ketone in order to obtain a different substitution pattern on the benzil as shown in Scheme 2.5. The yields reported are however low (< 45 %), suggesting formation of side-products and difficult isolation of the desired product. For these reasons, that synthesis was not pursued in the present work.
Scheme 2.5: Partial or full alkylation of tetrahydroxybenzil. I) $R_1\text{Br}$ (4 eq.), $K_2\text{CO}_3$, N,N-dimethylacetamide; II) $R_1\text{Br}$ (2 eq.), $K_2\text{CO}_3$, N,N-dimethylacetamide; III) $R_2\text{Br}$ (2 eq.), $K_2\text{CO}_3$, N,N-dimethylacetamide.

Wenz was the first to use the benzoin condensation in the context of liquid crystalline materials.\textsuperscript{155} The standard conditions are as follow: treatment of dimethoxybenzaldehyde with KCN in a EtOH/H$_2$O mixture affords veratrin which is then oxidized with CuSO$_4$ in pyridine and H$_2$O. Those two steps afford the benzil in low yields (25 to 40 %) but the reaction can be carried-out on a multi-gram scale. Benzils decorated with four identical alkoxy chains used to be obtained using that methodology.
2.3.2 Using the Benzoin Condensation to form Quinones C and D

To start the synthetic investigations, the use of a benzoin condensation to obtain quinones with the substitution pattern C (see Figure 2.1) was examined. To that end, the use of various protecting groups that would allow selective deprotection of only one of the positions on the benzene ring, followed by alkylation was investigated (see Scheme 2.6). As a model for this approach, we used benzaldehyde decorated with short chains since 3,4-dimethoxybenzaldehyde undergoes benzoin condensation.

Scheme 2.6: Formation of quinone C from the appropriate benzil formed by protected benzaldehyde derivatives. i) KCN, EtOH, H₂O; ii) CuSO₄, pyridine, H₂O; iii) Deprotection of PG₁; iv) Alkylation with R₁; v) Deprotection of PG₂; vi) Alkylation with R₂.
Vanillin, 4-hydroxy-3-methoxybenzaldehyde, can be converted to ethers and treated appropriately to form corresponding benzils. Selective deprotection and alkylation would allow obtaining benzil derivatives with the substitution pattern necessary to form quinone C (Figure 2.1). If this system allows the formation of the benzil and successful deprotection, a similar approach could be used to obtain the desired benzil derivatives from benzaldehyde bearing appropriate protecting groups.\textsuperscript{156,157} Scheme 2.7 shows the formation of the vanillin protected with a benzyl (Bn) ether in 86 % yield. Scheme 2.8 shows the protection of vanillin with a methylenemethoxy (MOM) group in 78 % yield.

Scheme 2.7: Synthesis of protected Vanillin and attempted Benzoin condensation. i) BnCl, K$_2$CO$_3$, EtOH (86 %); ii) KCN, H$_2$O, EtOH (0 %).

Scheme 2.8: Synthesis of protected Vanillin and attempted Benzoin condensation. i) MOMCl, NaH, THF (78 %); ii) KCN, H$_2$O, EtOH (0 %).

These benzaldehyde derivatives were then treated with KCN in water and ethanol in an attempt to form the corresponding benzoins. The benzil protected vanillin was shown to undergo benzoin condensation by Pearl and co-workers.\textsuperscript{149-151} However, even
when using the conditions they reported, we were not able to isolate the desired product. Increasing the reaction time, increasing or lowering the concentrations of benzaldehyde or KCN, or performing the reaction under nitrogen atmosphere did not allow the formation of the desired product. The starting material was isolated almost quantitatively in every case. The same results were obtained with the MOM protected vanillin. We therefore decided to investigate alternate catalysts, instead of KCN, in order to promote the formation of the benzoin intermediate.

2.4 Imidazolium-based catalysed benzoin condensation

2.4.1 N-Heterocyclic carbenes and their uses in organic synthesis

The use of potassium cyanide as a catalyst in the benzoin condensation has limitations in terms of efficiency and is acutely toxic. It has therefore been of interest to find other compounds that would be able to catalyze the benzoin condensation. Imidazolium-based carbenes are the most used and studied class of N-heterocyclic carbene (NHC).\textsuperscript{158,159} They are able to promote a variety of C-C bond forming reactions by acting as strong nucleophiles. Reactions catalyzed by these systems include benzoin condensation, acylation, transesterification and 1,2-additions.\textsuperscript{160} These systems can also promote the formation of crossed-benzoins under similar conditions.\textsuperscript{161-165} Miyashita and co-workers have reported the synthesis of veratroin using deprotonated
dimethylbenzimidazolium iodide salts as catalysts to promote the formation of benzoins.\textsuperscript{165}

2.4.2 Synthesis of Benzimidazolium Salts to Catalyze Benzoin Condensation

The synthesis of the precatalyst was achieved via two different synthetic routes (Scheme 2.9).\textsuperscript{166-169} The first method requires treating benzimidazole with methyl iodine (Mel) in presence of a base (KOH) in acetone at room temperature to yield methylimidazolium which is treated again with Mel and heated at reflux to afford the desired salt (steps \textit{i} and \textit{ii}). Alternatively, treatment of benzimidazole (\textit{iii}) with methyl sulfate (Me\textsubscript{2}SO\textsubscript{4}) in presence of sodium bicarbonate (NaHCO\textsubscript{3}) in water affords the precatalyst in a single step. The one step process affords the desired product in 35 % yield while the two-step process has an overall yield of 50 %. The two-step process was employed because of its higher yields.

Scheme 2.9: Synthesis of dimethylbenzimidazolium iodine as catalyst for the benzoin condensation. \textit{i}) KOH, Mel, acetone, room temperature (90 %); \textit{ii}) Mel, reflux (90 %); \textit{iii}) NaHCO\textsubscript{3}, Me\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O, room temperature (35 %).
With the pre-catalyst in hand, we attempted to repeat the experiments reported for the conversion of veratraldehyde to veratroin. The carbene catalyst was obtained \textit{in situ} by treating the precatalyst with DBU as the base in dioxane in presence of veratraldehyde (3,4-dimethoxybenzaldehyde). Using these conditions, we were only able to isolate the starting material. Different sets of conditions (solvent, base and concentrations) were examined in order to observe the formation of the desired benzil. When the solvent used was methanol and the base was sodium methoxide, the benzil (not the benzoin) was directly formed in yields between 40-45 %. About 50 % of the starting material was also recovered. Similar results were obtained if the solvent was thoroughly dried and/or degassed. The yield of the benzil however decreased to about 30 % with about 65 % of the starting material isolated.

The same experiments were performed with the protected Vanillin derivatives (-Bn and -MOM) since KCN did not afford the formation of the corresponding benzoin. These derivatives were treated at first with DBU in dioxane to reproduce literature precedents.\textsuperscript{165} Only the starting materials were isolated again. Different solvents (methanol, ethanol), bases (NaH, NaOEt), reaction times and temperatures were examined but the starting materials were recovered in every case.
2.5 Friedel-Crafts Acylation

2.5.1 Historical Background

The Friedel-Crafts acylation has been used to afford benzil derivatives directly from the corresponding 1,2-dialkoxybenzene by treating it with oxalyl chloride.\textsuperscript{170} This reaction was first reported in the early 1900's by Staudinger, who obtained the benzil as a side-product during the formation of acid chloride derivatives.\textsuperscript{171-173} More recently, Mohr and co-workers employed this approach on mono or disubstituted benzene derivatives functionalized with either alkyl or alkoxy groups to form the benzil in reasonable yields on up to 30 grams of starting material.\textsuperscript{174} The work presented by Mohr \textit{et al.} used carbon disulphide (CS\textsubscript{2}) as the reaction solvent and yields of 2-45 \% were reported, which depended on the type and length of chains appended to the benzene ring. Benzene derivatives bearing alkoxy chains produced the benzil in higher yields than alkyl substituted compounds, presumably because of the increased activation of the ring by the alkoxy groups. Ong and co-workers also used this strategy to obtain derivatives with alkoxy chains with \( n = 4, 6, 8, 10 \) and 12.\textsuperscript{175} Previous students in the Williams group had tried to use this synthesis in order to obtain benzils, but their efforts were not successful.

In the course of the present work, the Friedel-Crafts acylation was examined in order to determine if it could be used to obtain symmetrical benzils. This approach would
be faster than using the benzoin condensation and avoid the use of potassium cyanide. Didecyloxybenzene was prepared and treated with neat oxalyl chloride and aluminium chloride (AlCl₃) in freshly distilled carbon disulphide (CS₂). The corresponding benzil was obtained in 54 % yield after purification by column chromatography and recrystallization. The reaction did not work with the same degree of success if the solvent was not freshly distilled, or with older bottles of oxalyl chloride. We therefore decided to switch to a solution of oxalyl chloride in dichloromethane (CH₂Cl₂) and to use dry dichloromethane as the reaction solvent. We were able to store these for longer periods of time and obtain the desired product under these conditions.

2.5.2 Selectivity of the Friedel-Crafts Acylation

To obtain quinone C (Figure 2.1), the corresponding benzil needs to be formed under conditions that control the position at which the oxalyl chloride attaches to the ring. A 1,2-dialkoxybenzene derivative with two different alkoxy substituents (R₁ ≠ R₂) that is allowed to react with oxalyl chloride would produce a mixture of products as shown in Scheme 2.10. These two products would likely be difficult to separate. Due to steric hindrance, the acylation is not expected to occur at the carbon ortho of the bulky alkoxy chains.
Scheme 2.10: Non-selective Friedel-Crafts acylation leading to a mixture (1:1) of products.

It has been shown that electrophilic aromatic substitution (EAS) of 2-alkoxyphenyl acetates occurs selectively at the position para to the alkoxy chain as shown in Scheme 2.11.\textsuperscript{176,177} For example, Boden and co-workers used this strategy to obtain selectively alkylated biphenyl precursors of triphenylene discotic polymers. From these results, we anticipated that treating a 2-alkoxyphenyl acetate with oxalyl chloride in presence of a Lewis acid would afford the corresponding benzil shown in Scheme 2.12.

Scheme 2.11: Selective EAS on 2-alkoxyphenylacetate.

Scheme 2.12: Expected Friedel-Crafts acylation forming the benzil from 2-alkoxyphenylacetate. \textit{i}) oxalyl chloride, AlCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}. 
We prepared 2-alkoxyphenyl acetates (R = CH₃, C₆H₁₃) in order to establish if their reactivity toward EAS could be used to form benzils by Friedel-Crafts acylation. Guaiacol (2-methoxyphenol) was treated with acetic anhydride in presence of pyridine and afforded 2-methoxyphenyl acetate (see Scheme 2.13). The protected guaiacol was treated with oxalyl chloride in presence of AlCl₃ in dry CH₂Cl₂. Under these conditions, the desired product was not obtained and the starting material was isolated. Increasing the reaction times and temperatures only afforded the starting material, along with appreciable quantities of guaiacol resulting from the cleavage of the acetate groups.

Mohr and co-workers reported that the acylation of 1,2-dimethoxybenzene under Friedel-Crafts conditions afforded very small amounts of the desired benzil (< 2 %); whereas derivatives with longer chains afforded the desired product in higher yields: 23 % for 1,2-didecyloxybenzene and 42 % for 1,2-dihexyloxybenzene. We therefore decided to synthesize 2-hexyloxyphenyl acetate in order to determine whether replacing the methoxy group by a longer chain would likewise promote the formation of the desired benzil. Pyrocatechol (1,2-dihydroxybenzene) was alkylated with one equivalent of 1-bromohexane in presence of potassium carbonate (K₂CO₃) and tetrabutylammonium bromide (NBu₄Br) in butanone.

2-Hexyloxyphenol was treated with acetic anhydride and pyridine to form 2-hexyloxyphenylacetate (see Scheme 2.14). The product was treated with oxalyl chloride and AlCl₃ using the same conditions that afforded the symmetrical benzils. Modifications
of the reaction conditions such as time, temperature, ratios and concentrations (phenyl acetate, AlCl₃) were examined but the desired product was never obtained. The starting material was isolated quantitatively in most trials and extensive cleavage of the acetate was observed when the solvent was refluxed.

Scheme 2.13: Acetylation of Guaiacol and attempted Friedel-Crafts Acylation. i) Acetic anhydride, pyridine (78 %); ii) Oxalyl chloride, AlCl₃, DCM (no reaction).

Scheme 2.14: Attempted synthesis of 1,2-bis(3-acetate-4-hexyloxy)benzil. i) C₆H₁₃Br, K₂CO₃, NBu₄Br, butanone (52 %); ii) Acetic anhydride, pyridine (94 %); iii) Oxalyl chloride, AlCl₃, DCM (no reaction).
2.6 Oxidation of Diphenylacetylene precursor

2.6.1 Historical background

It is possible to obtain benzil derivatives by oxidizing diphenylacetylene derivatives in dimethylsulfoxide (DMSO).\textsuperscript{178} Reagents such as stoichiometric iodine or catalytic \( \text{PdCl}_2 \) have both been successfully employed to promote this oxidation.\textsuperscript{179-181} Both methods allow the formation of benzil derivatives, but the less expensive iodine has been preferred. This approach has been used in our lab in order to obtain unsymmetrical quinones B (see Figure 3.1) via the route shown in Scheme 2.15.\textsuperscript{182}

Scheme 2.15: Synthesis of benzil B. \( i \) \( \text{R}_3\text{Br, K}_2\text{CO}_3, \text{NBu}_4\text{Br, butanone; } ii \) \( \text{HIO}_3, \text{I}_2, \text{H}_2\text{SO}_4, \text{AcOH; } iii \) \( \text{TMS-C}_2\text{H, CuI, PdCl}_2(\text{PPh}_3)_2, (i\text{-Pr})_2\text{NH, THF; } iv \) \( \text{K}_2\text{CO}_3, \text{MeOH, THF; } v \) \( \text{CuI, Pd(PPh}_3)_4, (i\text{-Pr})_2\text{NH; } vi \) \( \text{I}_2, \text{DMSO.} \)
This synthesis is longer than the other strategies presented above and requires the use of two different palladium catalysts to obtain the desired benzil. However, it should allow access to benzils that are precursors to quinones B, C and D as shown in Scheme 2.16. Quinones C and D have not yet been reported in the literature and this route is the only one discussed that would allow us to obtain the quinone D with four different substituents.

Scheme 2.16: Synthesis of benzils C and D. i) TMS-C₂H, CuI, PdCl₂(PPh₃)₂, (i-Pr)₂NH, THF; ii) K₂CO₃, MeOH, THF; iii) CuI, Pd(PPh₃)₄, (i-Pr)₂NH; iv) I₂, DMSO.

2.6.2 Formation of benzils C and D

The synthesis shown in the previous section was used to prepare the benzil precursors to quinones C and D. Iodination of 2-alkoxyphenylacetates occurs selectively at the position para to the alkoxy group. This acetate group was then removed and the
product alkylated to afford the corresponding 1,2-dialkoxy-4-iodobenzene as shown in Scheme 2.17. This strategy has been used by Boden and co-workers to obtain 2-hexyloxy-4-idoanisole as precursors to triphenylene derivatives with unsymmetrical substitution patterns. Boden and co-workers did not report experiments to confirm that the iodine was attached para to the alkoxy chain. A sample of pure 2-decyloxyphenyl acetate was therefore examined by heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) NMR, which confirmed that the EAS occurs para to the alkoxy chain. Appendix 2 contains the spectra along with a detailed interpretation.

Scheme 2.17: Regioselective synthesis of 1,2-dialkoxy-4-iodobenzenes. $i)$ R$_2$Br, K$_2$CO$_3$, NBu$_4$Br, butanone; $ii)$ Acetic anhydride, pyridine; $iii)$ ICl, DCM; $iv)$ LiOH-H$_2$O, MeOH, THF, H$_2$O; $v)$ R$_2$Br, K$_2$CO$_3$, NBu$_4$Br, butanone.
The 1,2-dialkoxy-4-iodobenzene derivatives decorated with hexyloxy and decyloxy chains were prepared and used to obtain quinones C and D. The synthesis of quinone D, which has never been reported, is shown in Scheme 2.18 and will be discussed in more detail in Chapter 4.

Scheme 2.18: Synthesis of unsymmetrical quinone with substitution pattern D with 1,2-dialkoxy-4-iodobenzene derivatives.  

1. TMS-Acetylene, PdCl₂(PPh₃)₂, CuI, (i-Pr)₂NH, THF;  
2. K₂CO₃, MeOH, THF;  
3. Pd(PPh₃)₄, CuI, (i-Pr)₂NH, THF;  
4. I₂, DMSO;  
5. BF₃-Et₂O, VOF₃, CH₂Cl₂.

2.7 Conclusion and Future Work

Benzil derivatives have been known for a very long time and there are numerous ways to synthesize them. The presence and position of long alkyl or alkoxy chains can
affect the reactivity or the solubility of the benzaldehyde derivatives. As discussed in this chapter, we investigated synthesis routes that would allow the formation of benzils bearing substitution patterns that are not reported in the literature. The use of a diphenylacetylene precursor is the only efficient way examined to obtain the new benzil precursors of quinones C and D. The acetylene and benzils presented in this section did not form liquid crystalline phases as examined by polarized optical microscopy.

Other approaches to these quinones could be envisioned. The most promising method was developed by Babudri and co-workers, who have shown that treating oxalyl chloride with Grignard reagents in presence of CuBr and LiBr produces α-diones as shown in Scheme 2.19.\textsuperscript{183} They tested this methodology on a variety of substrates: aryl and aliphatic halides show formation of benzils in good yields (75-98 \%). It would be interesting to see if it is a viable synthesis to obtain the desired benzils.

Scheme 2.19: Formation of benzil from Grignard reagents. \textit{i}) Mg, THF; \textit{ii}) CuBr-2LiBr, THF.

3.1 Introduction and Historical Background

Melting point determination has been, since the early days of organic chemistry, an important method for determining both the identity and purity of compounds. A large number of factors are responsible for the melting point of a molecule, including intermolecular interactions such as hydrogen bonding, dipole-dipole, van der Waals or $\pi$-$\pi$ interactions. However, other factors such as shape and symmetry have a non-negligable influence on the melting point of a compound. Numerous research groups have tried to establish, using theoretical and empirical models, the melting point of various organic compounds. A scientific model that reliably predicts the melting point by analyzing the molecular structure remains an elusive and important goal. The models usually give good results when series of similar compounds are investigated, but when the difference is too pronounced, they fail to accurately predict the melting point of regular solids, i.e. compounds that melt directly from a solid to an isotropic liquid. The compounds studied form liquid crystalline phases and therefore have two transitions: crystal to liquid crystal.
and liquid crystal to isotropic liquid. Systems of this type have yet to be incorporated into structure/property relationships studies.

Regular solids have been investigated with respect to their melting point and how their shape and symmetry affects the melting point. It has been shown that by lowering the molecular symmetry of regular solids, it is possible to lower the melting point.\textsuperscript{178} This strategy has also been employed to lower the melting temperature of compounds forming liquid crystalline phases.\textsuperscript{154,184} However, to the best of our knowledge, no systematic studies of the effect of molecular symmetry on the mesogenic behaviour of structural isomers has been carried out. Therefore, we decided to investigate the effect of molecular shape on physical properties of mesogenic compounds forming series of isomers.

In a previous study carried out in our group, the effect of molecular symmetry on the transition temperatures of compounds forming liquid crystalline phases was investigated. Isomers of tetraalkoxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile were synthesized and their melting temperature ($T_m$, crystal to liquid crystal) and clearing temperature ($T_c$, liquid crystal to isotropic liquid) were compared.\textsuperscript{178} These compounds were obtained from the condensation of diaminomaleonitrile with the appropriate tetraalkoxyphenanthrene-9,10-diones in acetic acid (CH$_3$COOH) as shown in Scheme 3.1. The synthesis of symmetrical and non-symmetrical phenanthrene-9,10-dione 3.1a and 3.1b will be described further in this chapter.
Scheme 3.1: Synthesis of tetraalkoxydibenzoquinoxaline derivatives 3.2a and 3.2b. \( i \) AcOH reflux. Yields: 55 \% (4.2a), 57 \% (4.2b).

\[
\begin{align*}
3.1a & \quad R_1 = R_2 = C_6H_{17} \\
3.1b & \quad R_1 = C_6H_{13}, \quad R_2 = C_{10}H_{21} \\
3.2a & \quad R_1 = R_2 = C_6H_{17} \\
3.2b & \quad R_1 = C_6H_{13}, \quad R_2 = C_{10}H_{21}
\end{align*}
\]

Compounds 3.2a and 3.2b form a pair of isomers with one being of higher symmetry than the other: four eight-carbon chains for 3.2a compared to two chains with six carbons on one side and two with ten carbons on the other side for 3.2b. The transition temperatures of the less symmetrical isomer are lower than for the more symmetrical one. The melting temperature \( (T_m) \) was lowered from 87.5 to 37.8 °C and the clearing temperature \( (T_c) \) was lowered from 252.1 to 215.6 °C. The range over which the liquid crystalline phases were observed was increased from 166.4 to 177.8 degrees. These results suggest that breaking the symmetry of discotic mesogens can lower their transition temperatures \( (T_m > T_c) \) and broaden the liquid crystal range.
The results inspired a more detailed investigation of the effect of symmetry on transition temperatures of organic compounds forming liquid crystalline phases. Numerous research groups have tried to draw conclusions as how molecular symmetry can affect physical properties such as the melting point, the boiling point and the solubility of “normal” organic compounds. Thomas Carnelley published in 1882 two papers in which he compared about 15 000 different compounds with respect to symmetry and their melting points. From this, he established the following rule: “...of two or more isomeric compounds, those whose atoms are the more symmetrically and the more compactly arranged melt higher than those in which the atomic arrangement is asymmetrical or in the form of long chains.”

Brown and Brown named this observation Carnelley’s rule in 2000. These authors attempted to explain why molecules like methane, with no molecular dipole, exhibit such a high melting point when compared to other alkanes. They examined the thermodynamic implications of molecular symmetry (enthalpy and entropy changes)
upon phase transitions such as melting. These concepts will be discussed in greater length later in this chapter. Various strategies have been explored in order to estimate the entropy of melting and the melting point of organic molecules.\textsuperscript{188} It is not straightforward to execute such an estimation because of all the intermolecular interactions and other factors such as shape that can have an effect on the melting point.

For series of isomers that melt directly to isotropic liquids, the symmetry has a strong influence on the melting point, while the boiling point is unaffected by this molecular feature.\textsuperscript{189} The melting of a solid is characterized by an increase in rotational and conformational degrees of freedom. The gain in translational freedom is limited at melting because the molecules are still in contact with their neighbours. The transition from liquid to gas is, however, characterized by a large gain in translational movement and expansion due to loss of intermolecular interactions.\textsuperscript{190}

The stability of the solid phase depends on the symmetry of the molecules since they are constrained in a crystal lattice. The molecules in the liquid phase have gained degrees of freedom that allow them to rotate or change conformation. The stability of the liquid phase depends on intermolecular interactions, which are less sensitive to the symmetry of the molecules. Series of anthracene derivatives show a strong variation of the melting point with the relative position of the substituents while their boiling points remains almost unchanged.\textsuperscript{191} It is therefore reasonable to expect that the molecular symmetry will have a greater effect on the melting temperature than on the clearing

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temperature of a mesogen. The melting of a compound from solid to liquid crystal is characterized by a greater gain in disorder than the liquid crystal to isotropic liquid transition. Therefore, the first transition is expected to be more sensitive to molecular factors such as symmetry.

The melting point of a compound is the specific temperature where $G$, the Gibbs free energy of a given phase at a given pressure is the same for both the liquid and the solid phase (Equation 3.1). At that temperature, both phases are in equilibrium and the difference in free energy is equal to zero (Equation 3.2). Figure 4.1 shows a graph of the free energy as a function of the temperature for a solid and a liquid phase.

$$G_{(\text{solid})} = G_{(\text{liquid})} \quad \text{Equation 3.1}$$

$$\Delta G_{\text{melting}} = 0 \quad \text{Equation 3.2}$$
Equation 3.2 can be rewritten in terms of enthalpy (H) and entropy (S) leading to Equation 3.3. At the transition temperature, the difference in enthalpy is equal to the change of entropy multiplied by the transition temperature (Equation 3.4).

\[ \Delta G_m = \Delta H_m - T_m \Delta S_m = 0 \]  \hspace{2cm} \text{Equation 3.3} \\
\[ \Delta H_m = T_m \Delta S_m \]  \hspace{2cm} \text{Equation 3.4} \\
\[ T_m = \Delta H_m / \Delta S_m \]  \hspace{2cm} \text{Equation 3.5}
Equation 3.5 implies that in order to lower the melting point of a crystalline solid, one must decrease $\Delta H_m$, increase $\Delta S_m$ or even both. In the context of Carnelley’s rule, both entropy and enthalpy may have an influence on the transition temperature. The analysis can be executed using two different methods. When considering a pair of Carnelley’s isomers (two isomers with different degrees of symmetry), we can fix the enthalpy change or the entropy change.

Firstly, if we assume that our two isomers ($I_1$ and $I_2$) have the same entropy and that the melting point of $I_1$ is higher than the melting point of $I_2$, therefore the enthalpy is responsible for the different transition temperatures ($\Delta S_{I_1} = \Delta S_{I_2}$ and $T_1 > T_2$). This implies that a symmetrical molecule would have a greater ability to pack in the solid state than an unsymmetrical molecule since the enthalpy is a measure of the forces between molecules. A symmetrical molecule would have a crystal lattice where the intermolecular interactions are stronger than for a less symmetrical molecule and it would require more energy to induce a phase transition from solid to liquid and the change in enthalpy would be greater ($\Delta H_{I_1} > \Delta H_{I_2}$), leading to a greater $T_{I_1}$.

On the other hand, we can make the argument that the enthalpies of both isomers are the same and that the transition temperatures are different because the change in entropy upon melting is different for these two isomers. From Equation 3.5, if $T_1 > T_2$ and $\Delta H_{I_1} = \Delta H_{I_2}$, we know that $\Delta S_{I_1} < \Delta S_{I_2}$. This means that the change in entropy upon
melting is smaller for molecules possessing higher degrees of symmetry. There is therefore a direct relationship between the entropy and the symmetry of a molecule.

The symmetry number $\sigma$ corresponds to the number of equivalent positions that can be adopted by a molecule within a crystal lattice. These degenerated positions can be obtained via rigid rotation of a molecule around a symmetry axis. Compounds 3.2a and 3.2b have symmetry numbers of 2 and 1 respectively as shown below.

![Compounds 3.2a and 3.2b with their respective symmetry numbers.](image)

The relationship between the symmetry number and the entropy of a compound can be found using the Boltzmann entropy equation:

$$S = k \ln(W)$$  

**Equation 3.6**
k is the Boltzmann constant (1.38066 \times 10^{-23} \text{ JK}^{-1}) and W corresponds to the number of microstates accessible within a specific system. In other words, it relates to the number of distinguishable ways a molecule can be found in a crystal lattice. The entropy of a crystal lattice will be affected by the amount of disorder (defects in the spatial arrangement and presence of impurities) and thermal motion (vibrations). As the temperature decreases, the thermal motions decrease as well, leading to a crystal lattice with an entropy of zero at 0 Kelvin. This is, however, only true for an ideal crystal lattice. The presence of impurities or defects in the crystal lattice creates a certain amount of entropy that remains even if the system is cooled down to 0 kelvin. This entropy is labelled residual entropy $S_{\text{res}}$, which can be related to the symmetry number using the Boltzmann entropy Equation 3.6 ($S = k \ln W$).

Examining a system where N molecules can adopt one of the two equivalent orientations, leading to a total of $2^N$ possible orientations. The entropy becomes:

$$S = k \ln(2^N) = Nk \ln(2)$$

Assuming that there is one mole of molecules, the entropy becomes

$$S = nR \ln(2); \ R \ln(2) = 5.8 \text{ JK}^{-1}\text{mol}^{-1}$$
For any given system, where there are \( s \) possible orientations, the entropy becomes Equation 3.8:\textsuperscript{194}

\[ S_{\text{res}} = R \ln \sigma \]  \hspace{1cm} \text{Equation 3.7}

where \( S_{\text{res}} \) refers to the residual entropy of a compound, \( \sigma \) is the molecular symmetrical number and \( R \) is the gas constant. The amount of residual entropy at 0 K depends on the symmetry number (\( \sigma \)) of the molecules. Going back to the isomers \( I_1 \) and \( I_2 \), it is possible to calculate their relative residual entropies using \( \sigma_1 = 2 \) and \( \sigma_2 = 1 \). The more symmetrical isomer will have a greater residual entropy. It has also been shown that boiling temperatures are almost insensitive to the molecular symmetry, allowing us to make the assumption that isotropic liquids have similar entropies. The situation is depicted in Figure 3.3: the more symmetrical isomer has a smaller change in entropy because of its greater residual entropy, which leads to a higher melting point.
Figure 3.3: Representation of the change in entropy upon melting for two isomers with different degrees of symmetry.

To the best of our knowledge, no systematic study on the effect of symmetry on liquid crystalline phase transition temperatures has been reported. It was therefore decided to test the applicability of Carnelley’s rule to liquid crystals. More specifically, we wanted to establish if lowering the molecular symmetry of discotic mesogens would lower both transition temperatures ($T_m$ and $T_c$) and broaden the liquid crystalline phase range. It was essential to find a suitable mesogenic core that would enable us to perform the task of analyzing the effect of symmetry on the physical properties of their liquid crystalline phases. Our group has been synthesizing derivatives of dibenzo[a,c]phenazine and that core was chosen for this study. These compounds are obtained from a modular synthesis in which the condensation of a diamine with a diketone forms the dibenzo[a,c]phenazine derivative as shown in Figure 3.4.
Figure 3.4: Synthesis of dibenzo[a,c]phenazine derivatives from diamine and a diketone derivatives.

From a limited number of diamine and diketone derivatives, it was possible to obtain a large number of structural isomers. Molecules possessing the same total number of carbons around the aromatic core were compared. Two isomers with different symmetry number ($\sigma$) are denoted Carnelley’s isomers. The symmetry number corresponds to the number of equivalent positions a molecule can occupy in a ideal crystal lattice. Symmetrical molecules will have a greater symmetry number than an unsymmetrical ones. A molecule with a $C_2$ rotation axis (180 degrees rotation) will possess a symmetry number of 2 ($\sigma = 2$). Molecules that do not possess any rotation axis will have a symmetry number of 1 ($\sigma = 1$). The transition temperatures of the compounds in this study will be evaluated with respect of the symmetry number of the molecules. The difference between the transition temperatures (melting and clearing), as well as the difference in the liquid crystalline range of the two isomers will be calculated as follows:
\[ \Delta T_m = T_{m(unsymmetrical)} - T_{m(symmetrical)} \]  

Equation 3.8

\[ \Delta T_c = T_{c(unsymmetrical)} - T_{c(symmetrical)} \]  

Equation 3.9

\[ \Delta \text{Range} = \text{Range (unsymmetrical)} - \text{Range (symmetrical)} \]  

Equation 3.10

Therefore, if Carnelley’s rule does apply to liquid crystalline transitions, \( \Delta T_m \) and \( \Delta T_c \) will have a negative value. Following the same idea, if the liquid crystalline range is broader, \( \Delta \text{Range} \) will be positive. We synthesized 19 hexaalkoxydibenzo[a,c]phenazine derivatives and obtained 16 pairs of Carnelley’s isomers from which we obtained \( \Delta T_m \), \( \Delta T_c \) and \( \Delta \text{Range} \). The values are reported in Section 3.3 (Table 3.7) and analyzed in detail.

3.2 Synthesis

For the purpose of this project, 19 compounds have been synthesized and their liquid crystalline properties examined. Johan E. Foster synthesized and characterized seven of these compounds.\(^{195}\) The remaining 12 compounds were synthesized and characterized in order to extend the analysis and obtain complete series of isomers. This study was limited to mesogens having alkoxy chains containing six, eight or ten carbons.
The phenanthrene-9,10-dione (Q(6,6), Q(8,8), Q(10,10) and Q(6,8)) derivatives were obtained from their corresponding benzil precursors for which the synthesis was presented in detail in Chapter 3. The symmetrical benzils 3.6a and 3.6b were obtained in four steps from 3,4-dimethoxybenzaldehyde via a benzoin condensation with average overall yields of 30% as shown in Scheme 3.2. This method was employed in the past, before the Friedel-Crafts acylation was shown to be a useful method to obtain the benzil precursor as demonstrated in Chapter 2.

Scheme 3.2: Synthesis of the symmetrical benzils. i) KOH, KCN, EtOH, H₂O (3.3 = 55%); ii) CuSO₄, pyridine, H₂O (3.4 = 48%); iii) HBr/AcOH (3.5 = 57%); iv) RBr, K₂CO₃, butanone, NBu₄Br (3.6a = 52%: 3.6b = 53%).

The unsymmetrical benzils were obtained by consecutive Sonagashira coupling reactions on the appropriate 3,4-dialkoxy-1-iodobenzene. The quinone Q(8,10) was synthesized from the benzil B(8,10) 3.16 synthesized by Johan Foster. The quinone Q(6,10) was not needed for this study. The quinone Q(6,8) 3.15 was synthesized from
1,2-dihexyloxy-4-iodobenzene 3.9a and 1,2-dioctyloxy-4-iodobenzene 3.9b through the formation of the diphenylacetylene precursor as shown in Chapter 2. Two different approaches were explored to obtain the 1,2-dialkoxy-4-iodobenzene derivatives. The first method (Scheme 3.3) required treating veratrole (1,2-dimethoxybenzene) with iodine in presence of hydrogen peroxide, water and sulphuric acid as a catalyst. The product (3.7) was cleaved with BBr₃ to obtain the free dihydroxybenzene derivative 3.8. Alkylation afforded the 1,2-dihexyloxy-4-iodobenzene (3.9a) and the 1,2-dioctyloxy-4-iodobenzene derivatives (3.9b).

Scheme 3.3: Synthesis of dialkoxyiodobenzene derivatives needed for the synthesis of Q(6,8). i) I₂, H₂O₂, H₂SO₄ (cat), H₂O (3.7 = 92 %); ii) BBr₃, CH₂Cl₂ (3.8 = 45 %); iii) C₆H₁₃Br, K₂CO₃, DMF (3.9a = 91 %); C₈H₁₇Br, K₂CO₃, DMF (3.9b = 79 %).

In the second approach, the 1,2-dialkoxybenzene derivatives (3.10a and 3.10b) were treated with iodine in presence of iodic acid (I₂/HIO₃) in a mixture of acetic acid and sulphuric acid and afforded compounds 3.11a and 3.11b (Scheme 3.4). The final product was easier to obtain via the first route shown in Scheme 3.3 (3.9a and 3.9b).
Scheme 3.4: Formation of 1,2-dialkoxy-4-iodobenzene. i) RBr, K$_2$CO$_3$, DMF (63-91%); ii) I$_2$, HIO$_3$, AcOH, H$_2$SO$_4$ (55-71%). R = C$_6$H$_{13}$, C$_8$H$_{17}$.

\[ \text{3.10a: } R = \text{C}_6\text{H}_{13} \]
\[ \text{3.10b: } R = \text{C}_8\text{H}_{17} \]
\[ \text{3.11a: } R = \text{C}_6\text{H}_{13} \]
\[ \text{3.11b: } R = \text{C}_8\text{H}_{17} \]

The benzil derivatives leading to the unsymmetrical quinones were obtained from diphenylacetylene precursors, which were obtained from 1,2-dialkoxy-4-iodobenzene derivatives. As shown in Scheme 3.5, 3.9a was reacted with trimethylacetylene under the Sonagashira conditions (CuI, PdCl$_2$(PPh$_3$)$_2$, (i-Pr)$_2$NH and tetrahydrofuran) to produce the protected acetylene 3.12a. The TMS group was then removed with potassium carbonate (K$_2$CO$_3$) in a mixture of methanol and THF to afford 3.13a. The second Sonagashira coupling between 3.13a and 3.9b was carried out with Pd(PPh$_3$)$_4$ instead of PdCl$_2$(PPh$_3$)$_2$ to avoid the acetylene homocoupling. The resulting diphenylacetylene 3.14 was oxidized to the corresponding benzil 3.15 with iodine in dimethylsulfoxide (DMSO).

The phenanthrene-9,10-diones were obtained from the benzil derivatives (3.6a, 3.6b, 3.15 and 3.17) when treated with vanadium oxyfluoride (VOF$_3$) in the presence of a lewis acid BF$_3$•Et$_2$O in dichloromethane (CH$_2$Cl$_2$) as shown in Scheme 3.6. The quinones were labelled to indicate which chains were appended: Q(X,X) or Q(X,Y) where X and Y correspond to the number of carbons on the aliphatic chains. As
examples, Q(8,8) possess four octyloxy chains while Q(6,8) possess two hexyloxy chains on one side and two octyloxy chains on the other.

Scheme 3.5: Synthesis of unsymmetrical benzils. i) TMS-acetylene, (i-Pr)$_2$NH, CuI, PdCl$_2$(PPh$_3$)$_2$, THF (3.12a = 78 %); ii) K$_2$CO$_3$, MeOH, THF (3.13a = 79 %); iii) CuI, Pd(PPh$_3$)$_4$, (i-Pr)$_2$NH, THF (3.14 = 63 %); iv) I$_2$, DMSO (3.15 = 77 %).

Scheme 3.6: Formation of the phenanthrene-9,10-diones from the benzil precursors. R$_1$ = R$_2$ and R$_1$ ≠ R$_2$ i) VOF$_3$, BF$_3$•Et$_2$O, CH$_2$Cl$_2$. Yields: Q(6,6) = 75 %; Q(8,8) = 96 %; Q(6,8) = 73 %; Q(8,10) = 81 %.
The symmetrical and unsymmetrical diamine derivatives were obtained from catechol as shown in Scheme 3.7 and Scheme 3.8 respectively. The symmetrical diamines were obtained by alkylation of catechol (3.10a, 3.10b, 3.10c) followed by nitration with nitric acid (HNO₃, 3.17a, 3.17b, 3.17c) and reduction with stannous chloride (SnCl₂) in the presence of hydrochloric acid (HCl) in ethanol (100%) (3.18a, 3.18b, 3.18c) afforded the hydrochloric salts as shown in Scheme 3.7. Due to the instability of the diamino derivatives, they were synthesized and used immediately to form dibenzo[a,c]phenazine derivatives. The unsymmetrical diamines were prepared by sequential monoalkylation of catechol (3.19 and 3.20), followed by nitration (3.21) and reduction (3.22) as described above (see Scheme 3.8). The symmetrical diamines were labelled A(Z) while the unsymmetrical one was labelled A(Z,Z'). Here again, Z corresponds to the number of carbons on the aliphatic chains appended to the benzene ring. A(8) correspond to the diamine with two octyloxy chains and A(6,10) is the unsymmetrical diamine with one hexyloxy chain and one decyloxy chain.
Scheme 3.7: Synthesis of the diamine derivatives. 

1. RBr, K$_2$CO$_3$, DMF (3.10a = 91%; 3.10b = 63%; 3.10c synthesized by Johan Foster);
2. HNO$_3$, H$_2$SO$_4$ (3.17a = 78%; 3.17b = 70%; 3.17c = 64%); 
3. SnCl$_2$, HCl, EtOH (~80%).

Scheme 3.8: Synthesis of the unsymmetrical diamine derivatives. 

1. C$_{10}$H$_{21}$Br, K$_2$CO$_3$, NBu$_4$Br, butanone (3.19 = 29%); 
2. C$_{6}$H$_{13}$Br, K$_2$CO$_3$, NBu$_4$Br, butanone (3.20 = 90%); 
3. HNO$_3$, H$_2$SO$_4$ (3.21 = 66%); 
4. SnCl$_2$, HCl, EtOH (3.22 = 80%).

The last step consisted of coupling the different diamine salts with the quinones to obtain the hexaalkoxydibenzo[a,c]phenazines derivatives as shown in Scheme 3.9. The reactions were carried out in anhydrous ethanol in the presence of a large excess of sodium acetate. The final compounds were obtained as bright yellow solids in yields varying between 35 and 77%.
In this chapter, six phenanthrene-9,10-diones and four 4,5-dialkoxy-1,2-diaminobenzene derivatives were synthesized and coupled to afford 19 dibenzo[a,c]phenazine derivatives. In order to facilitate the discussion, the compounds were named according to the number of carbons on the appended chains of the quinones and the diamines used (see Figure 3.4). The dibenzo[a,c]phenazine derivatives are named Q(X,Y)A(Z) or Q(X,Y)A(Z,Z') according to the type of aliphatic chains appended to the quinone and the diamine used to form the final product. As examples, Q(8,8)A(8) possess six octyloxy chains around the aromatic core and Q(8,8)A(6,10) possess four octyloxy chains at the bottom (from the quinone) and two different chains at the top (hexyloxy and decyloxy). Table 3.1 shows the 19 symmetrical and unsymmetrical compounds obtained.
Figure 3.5: Phenathrene-9,10-dione and diamine derivatives used for this project.

Table 3.1: Compounds synthesized for the symmetry study.

<table>
<thead>
<tr>
<th>Symmetrical isomers</th>
<th>Less Symmetrical isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(6,6)A(8)</td>
<td>Q(6,8)A(6)</td>
</tr>
<tr>
<td>Q(6,6)A(10)</td>
<td>Q(6,6)A(6,10)</td>
</tr>
<tr>
<td>Q(8,8)A(6)</td>
<td>Q(6,8)A(8)</td>
</tr>
<tr>
<td>Q(6,6)A(10)</td>
<td>Q(6,10)A(6)</td>
</tr>
<tr>
<td>Q(8,8)A(8)</td>
<td>Q(6,8)A(10)</td>
</tr>
<tr>
<td>Q(8,6)A(10)</td>
<td>Q(8,10)A(6)</td>
</tr>
<tr>
<td>Q(8,8)A(10)</td>
<td>Q(8,10)A(8)</td>
</tr>
<tr>
<td>Q(8,10)A(6)</td>
<td>Q(8,10)A(10)</td>
</tr>
<tr>
<td>Q(10,10)A(8)</td>
<td>Q(8,10)A(10)</td>
</tr>
<tr>
<td>Q(10,10)A(6)</td>
<td>Q(10,10)A(6,10)</td>
</tr>
</tbody>
</table>
3.3 Results

The phase behaviour of the compounds was determined using the techniques described in the introduction (section 1.3): POM, DSC and VT-XRD. Tables 3.2, 3.3 and 3.4 show the results from the DSC experiments. Each compound produces an endotherm with two peaks corresponding to the melting and clearing temperatures and the results of the first run were similar to the ones obtained during the second run.

Polarized optical microscopy showed that all compounds form liquid crystalline phases (see Figure 3.3). The dendritic texture indicated that columnar hexagonal phases are formed by all the compounds. The assignment of the liquid crystalline phases was confirmed by the VT-XRD data collected and summarized in Tables 3.5 and 3.6. As explained in section 1.3, the presence of a hexagonal columnar phase could be confirmed by the observation of a strong peak corresponding to the 100 plane and a much weaker peak corresponding to the 110 plane. In a true columnar hexagonal phase, the ratio of 2θ of 110/100 must be 1.73. This peak is sometimes not observed at all but the phase is still assigned as hexagonal based on the POM experiment. For the compound Q(6,6)A(10), the XRD data showed the presence of a columnar rectangular phase with two strong peaks corresponding to the 200 and 110 planes.
Figure 3.6: Representative micrographs of compounds part of the symmetry study. The textures were observed upon slow cooling from the isotropic phase. a) Q(8,8)A(6), 200X, 139.1 °C; b) Q(6,6)A(8), 200X, 141 °C; c) Q(8,8)A(8), 80X, 135 °C; d) Q(8,8)A(8), 80X, 125 °C, no cover-slip.

Table 3.2: Transition temperatures for compounds Q(6,6)A(8) to Q(6,10)A(6). Cr = Crystal, Col_h = hexagonal columnar, Col_r = rectangular columnar, I = Isotropic liquid, T_t = Transition temperature and ΔH = enthalpy of transition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>T_t°C (ΔH/J g⁻¹)</th>
<th>Phase</th>
<th>T_t°C (ΔH/J g⁻¹)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(6,6)A(8)</td>
<td>Cr</td>
<td>80.7 (56.2)</td>
<td>Col_h</td>
<td>138.3 (4.6)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.3 (-48.5)</td>
<td></td>
<td>135.8 (-4.8)</td>
<td></td>
</tr>
<tr>
<td>Q(6,8)A(6)</td>
<td>Cr</td>
<td>39.3 (22.0)</td>
<td>Col_h</td>
<td>152.7 (4.3)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.1 (-33.6)</td>
<td></td>
<td>149.7 (-5.5)</td>
<td></td>
</tr>
<tr>
<td>Q(6,6)A(6,10)</td>
<td>Cr</td>
<td>48.6 (38.3)</td>
<td>Col_h</td>
<td>122.7 (3.2)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.4 (-33.4)</td>
<td></td>
<td>118.6 (-2.5)</td>
<td></td>
</tr>
<tr>
<td>Q(8,8)A(6)</td>
<td>Cr</td>
<td>75.9 (74.0)</td>
<td>Col_r</td>
<td>146.1 (3.4)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.4 (-71.1)</td>
<td></td>
<td>142.7 (-5.2)</td>
<td></td>
</tr>
<tr>
<td>Q(6,8)A(8)</td>
<td>Cr</td>
<td>39.3 (22.0)</td>
<td>Col_h</td>
<td>152.7 (4.3)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.1 (-33.6)</td>
<td></td>
<td>149.7 (-5.2)</td>
<td></td>
</tr>
<tr>
<td>Q(6,6)A(10)</td>
<td>Cr</td>
<td>77.6 (51.0)</td>
<td>Col_r</td>
<td>107.5 (2.3)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.9 (-24.9)</td>
<td></td>
<td>104.3 (-1.7)</td>
<td></td>
</tr>
<tr>
<td>Q(6,10)A(6)</td>
<td>Cr</td>
<td>43.2 (42.3)</td>
<td>Col_h</td>
<td>129.5 (3.5)</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.2 (-4.0)</td>
<td></td>
<td>126.6 (-3.3)</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3: Transition temperatures for compounds Q(8,8)A(8) to Q(8,8)A(6,10). Cr = Crystal, Col\textsubscript{h} = hexagonal columnar, I = Isotropic liquid, T\textsubscript{f} = Transition temperature and \(\Delta H\) = enthalpy of transition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>(T_f/^\circ C (\Delta H/J g^{-1}))</th>
<th>Phase</th>
<th>(T_f/^\circ C (\Delta H/J g^{-1}))</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(8,8)A(8)</td>
<td>Cr</td>
<td>61.9 (38.7) Col\textsubscript{h} 64.0 (1.0)</td>
<td>Col\textsubscript{h} 30.8 (-40.9)</td>
<td>141.3 (4.0)</td>
<td>Col\textsubscript{h} 138.6 (-43.9)</td>
</tr>
<tr>
<td>Q(6,8)A(10)</td>
<td>Cr</td>
<td>39.9 (35.2)</td>
<td>Col\textsubscript{h} 15.2 (-3.3)</td>
<td>119.7 (3.3)</td>
<td>Col\textsubscript{h} 117.1 (-33.3)</td>
</tr>
<tr>
<td>Q(6,10)A(8)</td>
<td>Cr</td>
<td>43.4 (35.7) Col\textsubscript{h} 15.8 (-3.7)</td>
<td>128.3 (0.5)</td>
<td>Col\textsubscript{h} 126.0 (-3.9)</td>
<td>1</td>
</tr>
<tr>
<td>Q(8,10)A(6)</td>
<td>Cr</td>
<td>73.0 (60.6) Col\textsubscript{h} 15.5 (-36.5)</td>
<td>137.0 (2.2)</td>
<td>Col\textsubscript{h} 133.4 (-2.7)</td>
<td>1</td>
</tr>
<tr>
<td>Q(8,8)A(6,10)</td>
<td>Cr</td>
<td>47.5 (42.3) Col\textsubscript{h} 6.8 (-26.2)</td>
<td>137.3 (4.2)</td>
<td>Col\textsubscript{h} 131.1 (-3.6)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.4: Transition temperatures for compounds Q(8,8)A(10) to Q(10,10)A(6,10). Cr = Crystal, Col\textsubscript{h} = hexagonal columnar, I = Isotropic liquid, T\textsubscript{f} = Transition temperature and \(\Delta H\) = enthalpy of transition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>(T_f/^\circ C (\Delta H/J g^{-1}))</th>
<th>Phase</th>
<th>(T_f/^\circ C (\Delta H/J g^{-1}))</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(8,8)A(10)</td>
<td>Cr</td>
<td>69.6 (67.8)</td>
<td>Col\textsubscript{h} 15.5 (-50.7)</td>
<td>122.5 (0.9)</td>
<td>Col\textsubscript{h} 117.7 (-1.3)</td>
</tr>
<tr>
<td>Q(8,10)A(6)</td>
<td>Cr</td>
<td>62.7 (52.0) Col\textsubscript{h} 15.7 (-41.4)</td>
<td>134.3 (1.7)</td>
<td>Col\textsubscript{h} 130.7 (-2.0)</td>
<td>1</td>
</tr>
<tr>
<td>Q(10,10)A(6)</td>
<td>Cr</td>
<td>73.3 (72.1) Col\textsubscript{h} 27.9 (-58.4)</td>
<td>130.6 (3.4)</td>
<td>Col\textsubscript{h} 126.3 (-3.4)</td>
<td>1</td>
</tr>
<tr>
<td>Q(6,10)A(10)</td>
<td>Cr</td>
<td>40.9 (37.5) Col\textsubscript{h} 16.3 (-28.1)</td>
<td>108.4 (1.61)</td>
<td>Col\textsubscript{h} 104.6 (-1.9)</td>
<td>1</td>
</tr>
<tr>
<td>Q(10,10)A(8)</td>
<td>Cr</td>
<td>80.2 (70.0) Col\textsubscript{h} 35.1 (-56.1)</td>
<td>133.1 (4.7)</td>
<td>Col\textsubscript{h} 131.0 (-4.1)</td>
<td>1</td>
</tr>
<tr>
<td>Q(8,10)A(10)</td>
<td>Cr</td>
<td>41.3 (36.7) Col\textsubscript{h} 17.4 (-37.6)</td>
<td>126.5 (4.24)</td>
<td>Col\textsubscript{h} 124.1 (-3.5)</td>
<td>1</td>
</tr>
<tr>
<td>Q(10,10)A(6,10)</td>
<td>Cr</td>
<td>46.6 (26.0) Col\textsubscript{h} 16.0 (-5.6)</td>
<td>125.1 (3.2)</td>
<td>Col\textsubscript{h} 122.3 (-2.7)</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 3.5: Lattice parameter obtained from XRD for Q(6,6)A(8) to Q(8,10)A(6).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature (°C)</th>
<th>d-spacing (Å)</th>
<th>Miller indices (hkl)</th>
<th>Phase, lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(6,6)A(8)</td>
<td>125</td>
<td>20.1</td>
<td>100</td>
<td>Colₜₜ, a = 23.2 Å</td>
</tr>
<tr>
<td>Q(6,6)A(8)</td>
<td>100</td>
<td>4.3</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 22.6 Å</td>
</tr>
<tr>
<td>Q(6,8)A(6)</td>
<td>130</td>
<td>4.4</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 24.1 Å</td>
</tr>
<tr>
<td>Q(6,8)A(8)</td>
<td>70</td>
<td>4.5</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 23.8 Å</td>
</tr>
<tr>
<td>Q(6,6)A(10)</td>
<td>85</td>
<td>12.9</td>
<td>400</td>
<td>Colₜₜ, a = 51.2 Å, b = 20.9 Å</td>
</tr>
<tr>
<td>Q(6,10)A(6)</td>
<td>65</td>
<td>12.7</td>
<td>110</td>
<td>Colₜₜ, a = 23.9 Å</td>
</tr>
<tr>
<td>Q(8,8)A(8)</td>
<td>120</td>
<td>4.4</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 24.6 Å</td>
</tr>
<tr>
<td>Q(6,10)A(8)</td>
<td>115</td>
<td>4.3</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 23.5 Å</td>
</tr>
<tr>
<td>Q(6,8)A(10)</td>
<td>70</td>
<td>4.5</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 24.4 Å</td>
</tr>
<tr>
<td>Q(8,10)A(6)</td>
<td>115</td>
<td>4.7</td>
<td>Alkyl halo</td>
<td>Colₜₜ, a = 23.6 Å</td>
</tr>
</tbody>
</table>
Table 3.6: Lattice parameters obtained from XRD for compounds Q(8,8)A(10) to Q(10,10)A(6,10).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature (°C)</th>
<th>d-spacing (Å)</th>
<th>Miller indices (hkl)</th>
<th>Phase, lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(8,8)A(10)</td>
<td>110</td>
<td>22.5</td>
<td>100</td>
<td>Colh, a = 25.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.7</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(8,10)A(8)</td>
<td>110</td>
<td>22.2</td>
<td>100</td>
<td>Colh, a = 25.6 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.8</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(10,10)A(6)</td>
<td>80</td>
<td>22.5</td>
<td>100</td>
<td>Colh, a = 25.9 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(6,10)A(10)</td>
<td>60</td>
<td>21.8</td>
<td>100</td>
<td>Colh, a = 25.2 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(10,10)A(8)</td>
<td>100</td>
<td>22.6</td>
<td>100</td>
<td>Colh, a = 26.1 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.1</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(8,10)A(10)</td>
<td>100</td>
<td>22.2</td>
<td>100</td>
<td>Colh, a = 25.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(6,6)A(6,10)</td>
<td>100</td>
<td>18.9</td>
<td>100</td>
<td>Colh, a = 21.8 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.4</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(8,8)A(6,10)</td>
<td>100</td>
<td>21.5</td>
<td>100</td>
<td>Colh, a = 24.9 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π-π</td>
<td></td>
</tr>
<tr>
<td>Q(10,10)A(6,10)</td>
<td>115</td>
<td>21.4</td>
<td>100</td>
<td>Colh, a = 24.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π-π</td>
<td></td>
</tr>
</tbody>
</table>

For each pair of isomers, $\Delta T_m$, $\Delta T_c$ and the range were calculated according to Equations 3.7 to 3.9 and are shown in Table 3.7. For a more visual representation of the results, histograms showing the incidence of the values obtained for $\Delta T_m$, $\Delta T_c$ or $\Delta$Range were plotted (Figure 3.6, 3.7 and 3.8). A negative value for $\Delta T_m$ or $\Delta T_c$ indicates that by breaking the symmetry, the transition temperature was lowered. A positive value of
ΔRange means that breaking the symmetry broadened the liquid crystalline range. The histograms were constructed with bin sizes of 5 °C, with the median bin centred at 0 °C.

Table 3.7: Differences in transition temperatures and LC range for the 16 pairs of compounds.

<table>
<thead>
<tr>
<th>Less-Symmetrical isomer</th>
<th>Symmetrical isomer</th>
<th>ΔT_m (°C)</th>
<th>ΔT_c (°C)</th>
<th>ΔRange (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(6,8)A(6)</td>
<td>Q(6,6)A(8)</td>
<td>-41.4</td>
<td>14.4</td>
<td>+57</td>
</tr>
<tr>
<td>Q(6,6)A(6,10)</td>
<td>Q(6,6)A(8)</td>
<td>-32.0</td>
<td>-15.7</td>
<td>+17</td>
</tr>
<tr>
<td>Q(6,10)A(6)</td>
<td>Q(6,6)A(10)</td>
<td>-34.4</td>
<td>22.0</td>
<td>+56</td>
</tr>
<tr>
<td>Q(6,8)A(8)</td>
<td>Q(6,6)A(10)</td>
<td>-23.6</td>
<td>30.5</td>
<td>+53</td>
</tr>
<tr>
<td>Q(6,10)A(6)</td>
<td>Q(8,8)A(6)</td>
<td>-32.7</td>
<td>-16.6</td>
<td>+17</td>
</tr>
<tr>
<td>Q(6,8)A(8)</td>
<td>Q(8,8)A(6)</td>
<td>-21.8</td>
<td>-8.1</td>
<td>+14</td>
</tr>
<tr>
<td>Q(6,10)A(8)</td>
<td>Q(8,8)A(8)</td>
<td>-18.5</td>
<td>-13.0</td>
<td>+1</td>
</tr>
<tr>
<td>Q(6,8)A(10)</td>
<td>Q(8,8)A(8)</td>
<td>-22.0</td>
<td>-21.5</td>
<td>+1</td>
</tr>
<tr>
<td>Q(8,10)A(6)</td>
<td>Q(8,8)A(8)</td>
<td>+11.1</td>
<td>-4.2</td>
<td>-22</td>
</tr>
<tr>
<td>Q(8,8)A(6,10)</td>
<td>Q(8,8)A(8)</td>
<td>-14.4</td>
<td>-4.0</td>
<td>+11</td>
</tr>
<tr>
<td>Q(8,10)A(8)</td>
<td>Q(8,8)A(10)</td>
<td>-6.9</td>
<td>+11.8</td>
<td>+18</td>
</tr>
<tr>
<td>Q(6,10)A(6)</td>
<td>Q(8,8)A(10)</td>
<td>-28.8</td>
<td>-14.1</td>
<td>+14</td>
</tr>
<tr>
<td>Q(8,10)A(8)</td>
<td>Q(10,10)A(6)</td>
<td>-10.6</td>
<td>+3.7</td>
<td>+13</td>
</tr>
<tr>
<td>Q(10,6)A(10)</td>
<td>Q(10,10)A(6)</td>
<td>-32.4</td>
<td>-22.3</td>
<td>+9</td>
</tr>
<tr>
<td>Q(8,10)A(10)</td>
<td>Q(10,10)A(8)</td>
<td>-38.9</td>
<td>-6.7</td>
<td>+33</td>
</tr>
<tr>
<td>Q(10,10)A(6,10)</td>
<td>Q(10,10)A(8)</td>
<td>-33.6</td>
<td>-8.0</td>
<td>+25</td>
</tr>
</tbody>
</table>
Figure 3.7: Histogram showing the incidence of the variation of $T_m$. Each bin is 5 °C and the median is centered at 0 °C.

Figure 3.8: Histogram showing the incidence of the variation of $T_c$. Each bin is 5 °C and the median is centered at 0 °C.
Figure 3.9: Histogram showing the incidence of the variation of liquid crystalline range. Each bin is 5 °C and the median is centered at 0 °C.

The histogram obtained from the comparisons for the melting temperatures shows that out of the 16 comparisons, 15 have positive values, indicating that breaking the molecular symmetry of the discotic mesogens lowers the melting point. Only one comparison shows an increase of the melting temperature with a decrease of the molecular symmetry. Q(8,10)A(6) is a less-symmetrical isomer of Q(8,8)A(8) and has a $T_m$ that was increased from 61.9 °C to 73.0 °C. This exception will be discussed in section 3.4.
The histogram for $\Delta T_c$ has 11 pairs for which $T_c$ is lower for isomers possessing lower symmetry number ($\sigma$). The five comparisons for which the value of $T_c$ has increased upon decreasing the molecular symmetry are listed below:

- Q(6,8)A(6) vs. Q(6,6)A(8)
- Q(6,10)A(6) vs. Q(6,6)A(10)
- Q(6,8)A(8) vs. Q(6,6)A(10)
- Q(8,10)A(10) vs. Q(8,8)A(10)
- Q(8,10)A(10) vs. Q(10,10)A(6)

It can be concluded that $T_c$ is less influenced by the molecular symmetry since not all the comparisons showed a decrease of clearing temperature when the molecular symmetry was lowered. Also, $T_m$ was lowered by a greater magnitude than $T_c$, leading to a broader range for most of the pairs of isomers ($\Delta T_m > \Delta T_c$). This can be confirmed by examining the histogram for the variation of the range, which shows that the phase range was increased in 18 out of 19 comparisons. The only exception is Q(8,10)A(6) versus Q(8,8)A(8), where $T_m$ was increased and $T_c$ was lowered.
3.4 Discussion

3.4.1 Analysis of the histograms

To establish whether these results are statistically significant, statistical analysis was carried out. Student T-test was employed because of its simplicity and efficiency with small sized data sets. The confidence intervals (C. I.) were calculated at 95 and 99 % confidence levels for a sample size of 16 using Equation 3.11 corresponds to the average temperature difference (absolute value of $\Delta T_m$, $\Delta T_c$ or $\Delta$Range), $n$ is the number of values used (also called degree of freedom), $s$ is the standard deviation and $t(\alpha/2, n-1)$ is found in statistical tables according to the degree of confidence and the degree of freedom. More details on the calculations can be found in the experimental section.

$$ C.I. = \bar{x} \pm \frac{t(\alpha/2, n-1) \cdot s}{\sqrt{n}} $$

Equation 3.11

The calculations were executed with $T_m$, $T_c$ and the LC range and the results are summarized in Table 3.8. The confidence intervals for $\Delta T_m$ are negative and do not include zero, indicating that they are statistically significant: decreasing the molecular symmetry is a good tool to lower the melting temperature of mesogens. The average for $|\Delta T_c|$ is much smaller than $|\Delta T_m|$ but remains negative. The confidence intervals for
\( T_c \) are also negative but they intersect with zero. This indicates that the depression of the clearing temperature from the symmetry is not significant from a statistical point of view. However, the melting temperature was lowered to a greater extent than the clearing temperature. The logical consequence is an increase of the liquid crystalline range. The calculations show that the range was increased (\( \Delta \text{Range} > 0 \)) and the confidence intervals do not include zero. As mentioned before, regular solids behave in the same way: lowering symmetry lowers systematically their melting point.

<table>
<thead>
<tr>
<th>Table 3.8: Statistical analysis of the values plotted in the histograms for ( \Delta T_m, \Delta T_c ) and ( \Delta \text{Range} ) range</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta T_m ) (( ^\circ \text{C} ))</td>
</tr>
<tr>
<td>Average</td>
</tr>
<tr>
<td>Standard Deviation</td>
</tr>
<tr>
<td>Confidence Interval (95 % )</td>
</tr>
<tr>
<td>Confidence Interval (99 % )</td>
</tr>
</tbody>
</table>

3.4.2 Exception to Carnelley’s rule

For one pair of isomers (Q(8,8)A(8) vs. Q(8,10)A(6)), breaking the molecular symmetry led to an increase of \( T_m \). In this particular case, the molecular shape of the molecule seems to have a more important effect than its symmetry. The mesogenic cores
have a general elliptical shape and installing shorter chains along the long axis of the molecule (diamine side) gives the molecule a more circular shape, which may allow a more efficient packing of the molecules in the solid state in spite of the low symmetry. This may suggest that the effect of molecular shape on liquid crystalline properties could be an important structural feature to study.

Another possible explanation for this violation of Carnelley's rule is that the transition temperatures of Q(8,8)A(8) are abnormally low. As a general rule, increasing the length of the chains around the aromatic core leads to a decrease in the transition temperatures. Most of our compounds, along with the one published by Ong's and co-workers, do follow this rule. Figure 3.9 shows the progression of the transition temperatures for dibenzo[a,c]phanazine derivatives having six identical alkoxy chains. The progression is linear and Q(8,8)A(8) behaves as expected.
However, other series of compounds show that Q(8,8)A(8) has abnormally low melting temperature and high clearing temperature. Figure 3.10 shows the progression of the transition temperatures for different compounds with octyloxy chains on the top. The progression shows that Q(8,8)A(8) has a melting temperature much lower than the other compounds of that series. Figure 3.11 shows a similar progression with compounds obtained by the condensation of Q(8,8) with various diamines. Again, Q(8,8)A(8) has an unusually low melting temperature and a high clearing temperature, which could explain why Carnelley’s rule is not obeyed when Q(8,8)A(8) is compared to its less symmetrical isomer Q(8,10)A(6).
Figure 3.11: Transition temperatures of mesogens decorated with two octyloxy chains on the top.

Figure 3.12: Progression of the transition temperatures of compounds obtained from the condensation of Q(8,8) with various diamines.
3.5 Conclusion and Future Work

Using hexaalkoxydibenzo[a,c]phenazine derivatives, we were able to establish that Carnelley’s rule, which applies to solids, also applies to liquid crystalline transitions. By synthesizing series of structural isomers with different degrees of molecular symmetry, we were able to show that by breaking the molecular symmetry of discotic mesogens, the transition temperatures were lowered. The melting temperature is lowered by about 24 degrees, the clearing temperature by about 3 degrees and the liquid crystalline range was increased by 20 degrees. The melting temperature is more influenced by the molecular symmetry than the clearing temperature. This is not surprising since molecules in the liquid crystalline phase already possess some randomness and their molecular symmetry has a less important impact on the next transition from liquid crystal to isotropic liquid. The enthalpy associated with this transition also supports this ($\Delta H_{\text{melting}} > \Delta H_{\text{clearing}}$).

From all the pairs of structural isomers studied, only one case had a lower melting temperature for the compound possessing a greater symmetry. From this particular case, it was evident that the shape of the molecule can have an important influence on the physical properties of compounds forming liquid crystalline phases. We therefore decided to investigate it in more detail in chapter 4.
3.6 Experimental Section

Some of the molecules used in this chapter were synthesized by Johan E. Foster. Their characterization will not be included but can be found in the supplementary information section of the following paper: Voisin, E., Foster, J. E., Rakotomalala, M. and Williams, V. E. Chem. Mater. 2009, 21, 3251-3261.

Experimental procedures can be found in chapter 6, section 6.2.
CHAPTER 4: EFFECT OF MOLECULAR SHAPE ON LIQUID CRYSTALLINE PROPERTIES OF DISCOTIC MESOGENS

4.1 Introduction

In Chapter 3, we encountered isomers for which the molecular shape, rather than just the symmetry, had a significant effect on the transition temperatures. In particular, the less symmetrical isomer of Q(8,8)A(8), Q(8,10)A(6) exhibits a melting temperature that is higher than its symmetrical counterpart (Figure 4.1). We suggested that this phenomenon was due to the molecular shape of the compounds. Hexaalkoxydibenzo[a,c]phenazine derivatives have a somewhat elliptical core, which can be accentuated or reduced by varying the pendent alkoxy chains. This variation of the molecular anisotropy likely can affect the properties of the liquid crystalline phases since these phases are observed as a consequence of the molecular anisotropy. In the case of Q(8,10)A(6), the shorter chains are positioned along the long axis of the aromatic core, leading to a more circular molecule. This shape may allow the molecules to pack more efficiently in the solid state leading to a higher melting temperature.
In the example depicted in Figure 4.1, the shape of the molecule appears to be more important than its symmetry. It was also observed that molecular shape can have a significant effect on the morphology of the liquid crystalline phase observed. Most of the compounds reported in Chapter 4 form hexagonal columnar liquid crystalline phases. However, Q(6,6)A(10) forms a rectangular columnar phase. This molecule has the same symmetry as its isomer Q(8,8)A(6) but exhibits markedly different phase behaviour. Both compounds have similar melting temperatures, but their clearing temperatures differ by almost 40 °C. Q(6,6)A(10) is a very elongated molecule compared to Q(8,8)A(6), which may explain the difference in $T_c$: the liquid crystalline phase is less stable for the more elliptical isomer, leading to a lower $T_c$. The less circular shape of Q(6,6)A(10) also prevents it from forming a hexagonal array of columns in the liquid crystal state. The columnar rectangular phase is able to accommodate the more elongated shape of the molecules as shown in Figure 4.2. The mesogens within a columns will tilt to allow the formation of a stable liquid crystalline phase.
Understanding how the molecular structure of mesogens affects the morphology of the liquid crystalline phases would be useful. Studies in this field are underway and more data is needed to fully understand how the molecular structure affects the mesophase assembly. Mullen, Boden and Yatabe have demonstrated that molecules with larger aromatic core were more prone to form columnar liquid crystalline phases.\textsuperscript{117,137,200-202} Electron-withdrawing groups also increase the strength of $\pi-\pi$ interactions between adjacent discs while having a small effect on the molecular assembly.\textsuperscript{203,204} Elliptical-shaped mesogens have also been studying and found to form liquid crystalline phases with columnar morphologies.\textsuperscript{205,206} Further work is required in order to design mesogens exhibiting precisely the desired properties.
We therefore decided to investigate in more detail the effect of molecular shape on the physical properties of discotic mesogens. To this end, it is necessary to create a molecular system that could be selectively modified in order to tailor the effect of shape on mesogenic behaviour. Other structural features such as symmetry had to persist in order to limit their effect on the observed properties. Hexaalkoxydibenzo[a,c]phenazine derivatives are well suited for such a study since they are obtained using a modular synthesis that allows the formation of a large amount of final compounds from a limited number of quinone and diamines. Our approach consisted in creating quinones of different molecular shape by modifying the length and positions of the chains around the aromatic core.

The dibenzophenazine core is depicted in Figure 4.3a with the approximative dimensions calculated using carbon-carbon bonds of 1.40 Å.\textsuperscript{177} The aromatic core possess two main axes with different lengths: a long axis measuring about 8.51 Å and a short one measuring 6.99 Å. Once substituted with flexible aliphatic chains, the molecular shape will depend on the length and position of the various chains. Figure 4.3b show a generic molecule along with the space one would expect the various chains to occupy.
Long chains increase short axis: widened molecular shape

Long chains increase long axis: elongated molecular shape

Figure 4.3: Dibenzo[a,c]phenazine derivatives. a) Aromatic core with dimensions, b) Schematic representation of the space occupied by the various flexible chains.

For a series of isomers appended with the same chains at the top, one could expect that using aliphatic chains of different lengths may affect the molecular structure and therefore the mesogenic behaviour. If the chains labelled $R_1$ are longer than the $R_2$ chains, the long molecular axis might increase and elongate the overall molecular shape. On the other hand, if the $R_2$ chains are longer than the $R_1$, the short molecular axis will increase and reduce the ellipticity of the molecule, leading to a more circular molecular shape as depicted in Figure 4.4 below.
Figure 4.4: Mesogens derived from hexaalkoxydibenzo[a,c]phenazine core with various chain lengths leading to different molecular shapes.

To obtain these mesogens, it is necessary to first prepare phenanthrene-9,10-diones with the appropriate substitution patterns. Quinones with that substitution pattern have never, to the best of our knowledge, been prepared. We decided to investigate the synthetic routes that were used in the lab to obtain this new type of quinone (Figure 4.5).
Figure 4.5: Quinones with appropriate substitution to probe the effect of molecular shape on liquid crystalline properties. The space-filling models are shown for both quinones.

From all the different approaches presented in chapter 2, the use of a diphenylacetylene precursor is the most efficient route to obtain benzil derivatives with the substitution patterns depicted in Figure 4.5. The new quinones $Q_{\text{wide}}$, $Q_{\text{long}}$ and $Q_{\text{mix}}$ shown in Figure 4.6 were prepared and allowed to react with diamines in order to obtain discotic mesogens analogous to the ones presented in the previous chapter. $Q(6,10)$, $Q(8,8)$ and $Q(10,10)$, which had previously been prepared, were also used as precursors to prepare other mesogens that would enable us to fully investigate the importance of molecular shape. The symmetrical quinones were reacted with the six diamines shown in
Figure 4.7. The unsymmetrical quinones (Q_{mix} and Q(6,10)) were not condensed with the unsymmetrical diamine A(6,10) since the resulting mixture of products would be difficult to separate.

![Diagram of quinones and diamines](image)

\[ Q_{\text{wide}} : R_1 = R_3 = C_6H_{13}, R_2 = R_4 = C_{10}H_{21} \\
Q_{\text{long}} : R_1 = R_3 = C_{10}H_{21}, R_2 = R_4 = C_6H_{13} \\
Q_{\text{mix}} : R_1 = R_4 = C_6H_{13}, R_2 = R_3 = C_{10}H_{21} \]

Figure 4.6: Quinones with new substitution pattern obtained by the diphenylacetylene route mentioned in chapter 2.

![Images of A(CN), A(Ph), A(4), A(6), A(8), A(10), A(6,10)](image)

Figure 4.7: Structure of diamines condensed with quinones to obtain discotic mesogens.
4.2 Synthesis

The mesogens were obtained from condensation of quinones and diamines under the same conditions used for the compounds part of the study on chapter 4. The diamines were obtained using the same methods presented in chapter 3.\textsuperscript{207} The quinones $Q_{\text{wide}}$, $Q_{\text{long}}$ and $Q_{\text{mix}}$ were synthesized via diphenylacetylene precursors using the procedure presented in chapter 3. The first step required the formation of 1,2-dialkoxy-4-iodobenzene derivatives with two different alkoxy chains appended to the benzene ring. The synthesis was adapted from a literature procedure for the synthesis of 2-hexyloxy-5-iodoanisole that was used to form a triphenylene core.\textsuperscript{176} We started from 1,2-dihydroxybenzene, which was monoalkylated with either bromohexane 4.1a or bromodecane 4.1b in the presence of $\text{K}_2\text{CO}_3$, $\text{NBu}_4\text{Br}$ and butanone. This procedure was adapted from a literature method; the amount of base was reduced from 32 equivalents per hydroxyl group to 0.5 equivalent per hydroxyl group in order to reduce the amount of dialkylated product.\textsuperscript{208}

The oils obtained were treated with acetic anhydride and pyridine to form 2-hexyloxyphenyl acetate 4.2a or 2-decyloxyphenyl acetate 4.2b. Reaction with iodine monochloride (ICI) led to the formation of 2-hexyloxy-5-iodophenyl acetate 4.3a and 2-decyloxy-5-iodophenyl acetate 4.3b. Cleavage of the acetate group was achieved with $\text{LiOH-H}_2\text{O}$ in water, THF and methanol and afforded 1-hexyloxy-4-iodophenol 4.4a and 1-decyloxy-4-iodophenol 4.4b. A second alkylation was performed, using conditions
similar to the ones used in the first step. The synthesis of 1-decyloxy-2-hexyloxy-4-iodobenzene \(4.5a\) and 2-decyloxy-1-hexyloxy-4-iodobenzene \(4.5b\) is shown in Scheme 4.1.

![Diagram of Scheme 4.1: Synthesis of 2-decyloxy-1-hexyloxy-4-iodobenzene (4.5a) and 1-decyloxy-2-hexyloxy-4-iodobenzene (4.5b).](image)

Scheme 4.1: Synthesis of 2-decyloxy-1-hexyloxy-4-iodobenzene (4.5a) and 1-decyloxy-2-hexyloxy-4-iodobenzene (4.5b). \(i\) \(\text{C}_6\text{H}_{13}\text{Br}, \text{NBu}_4\text{Br}, \text{K}_2\text{CO}_3, \text{butanone (4.1a = 52 %; 4.1b = 29 %); ii) acetanhydride, pyridine (4.2a = 94 %; 4.2b = 96 %); iii) ICl, CH}_2\text{Cl}_2 (4.3a = 90 %; 4.3b = 97 %); iv) LiOH-H}_2\text{O, THF, MeOH, H}_2\text{O (4.4a = 96 %; 4.4b = 81 %); v) C}_{10}\text{H}_{21}\text{Br, NBu}_4\text{Br, K}_2\text{CO}_3, \text{butanone (4.5a = 80 %; 4.5b = 72 %).}

From the 1,2-dialkoxy-4-iodobenzene derivatives obtained, the three quinones shown in Figure 4.6 were synthesized following the procedure described in chapter 2, Section 2.6. The compounds \(4.5a\) and \(4.5b\) were transformed to the protected acetylene \((4.6a\) and \(4.6b)\) and then deprotected to afford compounds \(4.7a\) and \(4.7b\) as shown in Scheme 4.2. The acetylenes were coupled with the appropriate 1,2-dialkoxy-4-iodobenzene to afford the symmetrical diphenylacetylene precursors \(4.8a\) and \(4.8b\). These intermediates were oxidized to the benzils \(4.9a\) and \(4.9b\) prior to being cyclized to the
quinones $Q_{\text{wide}}$ and $Q_{\text{long}}$ that correspond to quinones with substitution pattern shown in Figure 4.5 (see Scheme 4.3).

Scheme 4.2: Formation of the free acetylene from the 1,2-dialkoxy-4-iodobenzene derivatives 4.5a and 4.5b. i) TMS-acetylene, CuI, PdCl$_2$(PPh$_3$)$_2$, (i-Pr)$_2$NH, THF (4.6a = 88 \%; 4.6b = 98 \%); ii) K$_2$CO$_3$, THF, MeOH (4.7a = 74 \%; 4.7b = 89 \%).

Scheme 4.3: Synthesis of $Q_{\text{wide}}$ and $Q_{\text{long}}$. i) CuI, Pd(PPh$_3$)$_2$, (i-Pr)$_2$NH, THF (4.8a = 46 \%; 4.8b = 82 \%); ii) I$_2$, DMSO (4.9a = 91 \%; 4.9b = 92 \%); iii) VOF$_3$, BF$_3$-Et$_2$O, CH$_2$Cl$_2$ ($Q_{\text{wide}}$ = 69 \%; $Q_{\text{long}}$ = 72 \%).
The quinone of lower symmetry, $Q_{\text{mix}}$, was prepared by using the free acetylene $4.7b$ and the 1,2-dialkoxy-4-iodobenzene $4.5a$ as shown in Scheme 4.4. The diphenylacetylene $4.8c$ was oxidized to the benzil $4.9c$ prior to cyclisation affording $Q_{\text{mix}}$. Another unsymmetrical quinone ($Q(6,10)$) was synthesized in order to complete the series of compounds examined. Its synthesis was achieved from 1,2-decyloxy-4-iodobenzene $4.11$ and 1,2-hexyloxy-4-ethynylbenzene $4.10$ synthesized by Johan Foster. The unsymmetrical diphenylacetylene $4.12$ was oxidized to the benzil $4.13$ using the same method presented for the other benzils. Cyclization afforded the quinone $Q(6,10)$ as shown in Scheme 4.5.

Scheme 4.4: Synthesis of $Q_{\text{mix}}$. i) CuI, Pd(PPh$_3)_4$, (i-Pr)$_2$NH, THF ($4.8c$); ii) I$_2$, DMSO ($4.9c$); iii) VOF$_3$, BF$_3$-Et$_2$O, CH$_2$Cl$_2$ ($Q_{\text{mix}}$).

$4.8c$: $R_1 = \text{C}_{10}H_{21}$, $R_2 = \text{C}_8H_{13}$, $R_3 = \text{C}_6H_{13}$, $R_4 = \text{C}_{16}H_{21}$

$4.9c$: $R_1 = \text{C}_{10}H_{21}$, $R_2 = \text{C}_8H_{13}$, $R_3 = \text{C}_6H_{13}$, $R_4 = \text{C}_{16}H_{21}$
Scheme 4.5: i) CuI, Pd(PPh₃)₄, (i-Pr)₂NH, THF (4.12); ii) I₂, DMSO (4.13); iii) VOF₃, BF₃·Et₂O, CH₂Cl₂ (Q(6,10)).

The three different quinones (Q_long, Q_wide and Q_mix) do not form liquid crystalline phases, but they were reacted with diamines to obtain compounds that would. The mesogens were named according to the quinones and diamines used in their synthesis. Figure 4.7 shows the structure and the name of the diamines used. If a compound was obtained by the condensation of Q_long and A(CN), it was named Q_long A(CN). Scheme 4.6 shows the compounds obtained by the condensation of the quinones with A(CN) and A(Ph). Scheme 4.7 shows the compounds obtained by the condensation of 1,2-dialkoxy-4,5-diaminobenzene derivatives. These compounds are similar to the ones presented in chapter 4 and some will be used for comparison. Figure 4.8 shows all the compounds synthesized for this chapter. Q(8,8)A(Ph) and Q(6,10)A(Ph) were added to the series for
a more complete picture of the effect of shape on the melting point of this type of compound. Q(10,10)A(4) was included because it was an isomer of some of the compounds obtained and possessed a much shorter elliptical shape with butyloxy chains on the amine part of the aromatic core.

\[
\begin{array}{cccccccc}
Q_{\text{wide}} & A(\text{CN}) & Q_{\text{wide}} & A(\text{Ph}) & Q_{\text{wide}} & A(6) & Q_{\text{wide}} & A(8) \\
Q_{\text{long}} & A(\text{CN}) & Q_{\text{long}} & A(\text{Ph}) & Q_{\text{long}} & A(6) & Q_{\text{long}} & A(8) \\
Q_{\text{mix}} & A(\text{CN}) & Q_{\text{mix}} & A(\text{Ph}) & Q_{\text{mix}} & A(6) & Q_{\text{mix}} & A(8) \\
Q(8,8) & A(\text{Ph}) & Q(10,10) & A(\text{Ph}) & \\
\end{array}
\]

Figure 4.8: Compounds synthesized for this chapter.
Scheme 4.6: Formation of mesogens by coupling the quinones with A(CN) and A(Ph). i) 2,3-Diaminomaleonitrile, AcOH (Q_{wide}A(CN) = 30 %; Q_{long}A(CN) = 38 %; Q_{mix}A(CN) = 29 %); ii) Phenylenediamine, AcOH (Q_{wide}A(Ph) = 83 %, Q_{long}A(Ph) = 63 %, Q_{mix}A(Ph) = 83 %, Q(8,8)A(Ph) = 95 %, Q(6,10)A(Ph) = 90 %).
Scheme 4.7: Formation of mesogens by coupling the quinones with A(4), A(6), A(8), A(10) and A(6,10).

1) NaOAc, EtOH (Q\text{wide}A(6) = 55\%; Q\text{long}A(6) = 78\%; Q\text{mix}A(6) = 37\%; Q\text{wide}A(8) = 57\%; Q\text{long}A(8) = 32\%; Q\text{mix}A(8) = 57\%; Q\text{wide}A(10) = 42\%; Q\text{long}A(10) = 36\%; Q\text{mix}A(10) = 48\%, Q\text{wide}A(6,10) = 30\%; Q\text{long}A(6,10) = 56\%; Q(10,10)A(4) = 43\%).

4.3 Characterization of compounds and their liquid crystalline phases

The compounds and their liquid crystalline phases were characterized using the methods described in Chapter 1 and 3. All compounds examined under POM form textures that indicate hexagonal columnar packing of the disc-shaped molecules. Typical textures observed are shown in Figure 4.9. The values obtained by DSC are listed in Tables 4.1 to 4.3. For most compounds, the first and second runs were reproducible and similar temperatures and enthalpies were recorded. The values were recorded on heating
and cooling at a rate of 5 °C/min. Finally, variable-temperature X-ray diffraction (XRD) was performed and confirmed the initial identification of the columnar phases. The strong peak corresponding to the 100 plane was observed in every diffractogram, along with the peak assigned to the 110 plane. The data collected is summarized in Tables 4.4 to 4.6.

![Figure 4.9: Typical textures obtained by POM with mesogens synthesized. a) Q_{wide}A(CN), 244 °C, 80X; b) Q_{wide}A(6,10), 128 °C, 80X; c) Q_{wide}A(8), 85 °C, 80X; d) Q_{long}A(CN), 254 °C, 200X; e) Q_{long}A(CN), 257 °C, 80X; f) Q_{long}A(8), 128 °C, 200X; g) Q_{long}A(6,10), 114 °C, 80X; h) Q_{mix}A(10), 108 °C, 80X; i) Q_{mix}A(CN), 264 °C, 80X.](image)
Table 4.1: Transition temperatures for compounds formed with A(Ph) and A(CN). Cr = Crystal, Col\_h = Hexagonal columnar, I = Isotropic liquid, T\_r = Transition temperature and \(\Delta H\) = enthalpy of transition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>(T_r^\circ)(\text{C} (\Delta H/\text{J g}^{-1}))</th>
<th>Phase</th>
<th>(T_r^\circ)(\text{C} (\Delta H/\text{J g}^{-1}))</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_wide A(CN)</td>
<td>Cr</td>
<td>80.0 (56.2)</td>
<td>Col_h</td>
<td>251.4 (5.3)</td>
<td>I</td>
</tr>
<tr>
<td>Q_long A(CN)</td>
<td>Cr</td>
<td>77.8 (56.8)</td>
<td>Col_h</td>
<td>251.1 (5.0)</td>
<td>I</td>
</tr>
<tr>
<td>Q_mix A(CN)</td>
<td>Cr</td>
<td>47.0 (30.0)</td>
<td>Col_h</td>
<td>250.0 (5.1)</td>
<td>I</td>
</tr>
<tr>
<td>Q_wide A(Ph)</td>
<td>Cr</td>
<td>136.3 (80.5)</td>
<td>I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q_long A(Ph)</td>
<td>Cr</td>
<td>136.4 (78.8)</td>
<td>I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q_mix A(Ph)</td>
<td>Cr</td>
<td>102.0 (22.6)</td>
<td>I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q(8,8) A(Ph)</td>
<td>Cr</td>
<td>150.1 (96.7)</td>
<td>I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q(6,10) A(Ph)</td>
<td>Cr</td>
<td>137.3 (85.9)</td>
<td>I</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Transition temperatures for compounds obtained with A(6) and A(10). Cr = Crystal, Col\_h = Hexagonal columnar, I = Isotropic liquid, T\_r = Transition temperature and \(\Delta H\) = enthalpy of transition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>(T_r^\circ)(\text{C} (\Delta H/\text{J g}^{-1}))</th>
<th>Phase</th>
<th>(T_r^\circ)(\text{C} (\Delta H/\text{J g}^{-1}))</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_wide A(6)</td>
<td>Cr</td>
<td>69.9 (61.9)</td>
<td>Col_h</td>
<td>137.2 (3.8)</td>
<td>I</td>
</tr>
<tr>
<td>Q_long A(6)</td>
<td>Cr</td>
<td>60.1 (28.8)</td>
<td>Col_h</td>
<td>130.6 (3.8)</td>
<td>I</td>
</tr>
<tr>
<td>Q_mix A(6)</td>
<td>Cr</td>
<td>40.7 (50.4)</td>
<td>Col_h</td>
<td>128.5 (4.0)</td>
<td>I</td>
</tr>
<tr>
<td>Q_wide A(10)</td>
<td>Cr</td>
<td>58.2 (31.5)</td>
<td>Col_h</td>
<td>121.0 (3.7)</td>
<td>I</td>
</tr>
<tr>
<td>Q_long A(10)</td>
<td>Cr</td>
<td>70.6 (66.7)</td>
<td>Col_h</td>
<td>105.1 (1.7)</td>
<td>I</td>
</tr>
<tr>
<td>Q_mix A(10)</td>
<td>Cr</td>
<td>74.4 (70.8)</td>
<td>Col_h</td>
<td>116.9 (1.9)</td>
<td>I</td>
</tr>
</tbody>
</table>
Table 4.3: Transition temperatures for compounds formed with A(4), A(8) and A(6,10). Cr = Crystal, 
Col_h = Hexagonal columnar, I = Isotropic liquid, T = Transition temperature and ΔH = enthalpy of 
transition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>T_i°C (ΔH/J g⁻¹)</th>
<th>Phase</th>
<th>T_i°C (ΔH/J g⁻¹)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_wide A(8)</td>
<td>Cr</td>
<td>70.8 (70.6)</td>
<td>Cr</td>
<td>133.6 (4.3)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.0 (-63.5)</td>
<td>Col_h</td>
<td>130.9 (-4.5)</td>
<td></td>
</tr>
<tr>
<td>Q_long A(8)</td>
<td>Cr</td>
<td>65.7 (64.8)</td>
<td>Col_h</td>
<td>122.4 (3.3)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.3 (-38.5)</td>
<td></td>
<td>119.5 (-2.7)</td>
<td></td>
</tr>
<tr>
<td>Q_mix A(8)</td>
<td>Cr</td>
<td>64.8 (32.5)</td>
<td>Col_h</td>
<td>123.0 (0.5)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.3 (-5.5)</td>
<td></td>
<td>117.3 (-2.3)</td>
<td></td>
</tr>
<tr>
<td>Q_wide A(6,10)</td>
<td>Cr</td>
<td>33.5 (2.4)</td>
<td>Col_h</td>
<td>125.6 (3.2)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.7 (-2.5)</td>
<td></td>
<td>122.6 (-3.3)</td>
<td></td>
</tr>
<tr>
<td>Q_long A(6,10)</td>
<td>Cr</td>
<td>41.5 (49.5)</td>
<td>Col_h</td>
<td>114.8 (3.1)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.0 (-3.2)</td>
<td></td>
<td>111.9 (-2.9)</td>
<td></td>
</tr>
<tr>
<td>Q(10,10)A(4)</td>
<td>Cr</td>
<td>76.6 (52.0)</td>
<td>Col_h</td>
<td>123.9 (3.3)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.4 (-39.7)</td>
<td></td>
<td>121.6 (-3.0)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Data obtained from the variable temperature XRD experiments for compounds obtained 
via condensation with A(CN) and A(6).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature (°C)</th>
<th>d-spacing (Å)</th>
<th>Miller indices (hkl)</th>
<th>Phase, lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_wide ACN</td>
<td>125</td>
<td>18.8</td>
<td>100</td>
<td>Coh, a = 21.8 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π–π</td>
<td></td>
</tr>
<tr>
<td>Q_long ACN</td>
<td>125</td>
<td>19.0</td>
<td>100</td>
<td>Coh, a = 21.9 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>π–π</td>
<td></td>
</tr>
<tr>
<td>Q_mix ACN</td>
<td>125</td>
<td>18.6</td>
<td>100</td>
<td>Coh, a = 21.5 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.8</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π–π</td>
<td></td>
</tr>
<tr>
<td>Q_wide A(6)</td>
<td>110</td>
<td>20.9</td>
<td>100</td>
<td>Coh, a = 24.2 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.1</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π–π</td>
<td></td>
</tr>
<tr>
<td>Q_long A(6)</td>
<td>110</td>
<td>20.7</td>
<td>100</td>
<td>Coh, a = 23.9 Å,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.9</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π–π</td>
<td></td>
</tr>
<tr>
<td>Q_mix A(6)</td>
<td>100</td>
<td>20.7</td>
<td>100</td>
<td>Coh, a = 23.9 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.9</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>π–π</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.5: Data obtained from the variable temperature XRD experiments for compounds obtained via condensation with A(8) and A(6,10).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature (°C)</th>
<th>d-spacing (Å)</th>
<th>Miller indices (hkl)</th>
<th>Phase, lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q\textsubscript{wide} A(8)</td>
<td>115</td>
<td>21.6</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 24.9 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.5</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{long} A(8)</td>
<td>100</td>
<td>21.2</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 24.5 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.3</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{mix} A(8)</td>
<td>105</td>
<td>21.4</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 24.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.3</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{wide} A(6,10)</td>
<td>100</td>
<td>21.4</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 24.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.3</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{long} A(6,10)</td>
<td>100</td>
<td>21.4</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 24.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.2</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: Data obtained from the variable temperature XRD experiments for compounds obtained via condensation with A(10) and Q(10,10)A(4).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature (°C)</th>
<th>d-spacing (Å)</th>
<th>Miller indices (hkl)</th>
<th>Phase, lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q\textsubscript{wide} A(10)</td>
<td>105</td>
<td>22.2</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 25.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.8</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{long} A(10)</td>
<td>90</td>
<td>21.9</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 25.3 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.7</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{mix} A(10)</td>
<td>100</td>
<td>22.2</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 25.7 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.9</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.6</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
<tr>
<td>Q(10,10)A(4)</td>
<td>110</td>
<td>21.2</td>
<td>100</td>
<td>Co\textsubscript{h}, a = 24.5 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.2</td>
<td>110</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>4.3</td>
<td>Alkyl halo</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>(\pi \text{-}\pi)</td>
<td></td>
</tr>
</tbody>
</table>
4.4 Results/Discussion

For the purpose of this study, twenty compounds were synthesized in order to
determine the effect of molecular shape on mesogenic properties. Compounds
synthesized for the symmetry study (chapter 3), along with others prepared by Johan
Foster, were included in the analysis. As part of the analysis, the transition temperatures,
liquid crystalline range and lattice constant obtained from XRD were considered. We
obtained five series of molecules where all compounds in a series are structural isomers.
Figure 4.10 shows the structure of the molecules in each series.

![Figure 4.10: Structures of compounds forming series 1 to 5. R₁, R₂, R₃, and R₄ = C₆H₁₃, C₈H₁₇, C₁₀H₂₁.](image)

Figures 4.10: Structures of compounds forming series 1 to 5. R₁, R₂, R₃, and R₄ = C₆H₁₃, C₈H₁₇, C₁₀H₂₁.
4.4.1 Series 1: Tetraalkoxydibenzo[a,c]phenazine derivatives

As model molecules, the quinones ($Q_{\text{wide}}$, $Q_{\text{long}}$, $Q_{\text{mix}}$) were condensed with 1,2-phenylene diamine as shown in Scheme 4.6. The quinones $Q(8,8)$ and $Q(6,10)$ were also condensed with this diamine to obtain a more comprehensive series of compounds. Although previously prepared analogues $Q(6,6)A(\text{Ph})$ and $Q(10,10)A(\text{Ph})$ were shown to be non-mesogenic, it was of interest to determine whether changes in shape and symmetry could lead to the formation of liquid crystalline phases. However, the five compounds synthesized did not exhibit mesogenic behaviour on heating or cooling: they crystallized directly from the isotropic liquids to crystalline solids without forming liquid crystalline phases.

![Compounds](image)

Figure 4.11: Compounds obtained by the condensation of the quinones with 1,2-phenylenediamine. Their melting points and enthalpies are indicated below the structure.
Figure 4.11 shows the compounds obtained, along with their melting temperatures measured by DSC. Compounds Q(8,8)A(Ph), Q_{\text{wide}}A(Ph) and Q_{\text{long}}A(Ph) have a symmetry number ($\sigma = 2$), which is higher than the remaining compounds Q_{\text{mix}}A(Ph) and Q(6,10)A(Ph) in this series ($\sigma = 1$). Within each row, the molecules have the same degree of symmetry but their melting points are different, indicating that the new substitution pattern has an effect on their phase behaviour.

The compound Q_{\text{wide}}A(Ph) has a lower melting temperature than Q(8,8)A(Ph). Q_{\text{long}}A(Ph) has also a lower melting temperature than Q(8,8)A(Ph). Q_{\text{wide}}A(Ph) and Q_{\text{long}}A(Ph) have identical melting temperatures. These comparisons suggest that compounds decorated by mixtures of aliphatic chains have less stable crystal phases. They melt at lower temperatures (136 °C vs. 150 °C) and the enthalpy of melting is also smaller than what is observed with Q(8,8)A(Ph) (81 and 79 J/g vs. 97 J/g). The last comparison shows that the position of the long decyloxy chains has no influence on the phase stabilities.

The analysis of the compounds in the second row only partially confirms that decreasing symmetry lowers the melting point. Compound Q_{\text{mix}}A(Ph) melts at 102 °C, which is much lower than the symmetrical isomers Q(8,8)A(Ph), Q_{\text{wide}}A(Ph) and Q_{\text{long}}A(Ph). However, Q(6,10)A(Ph) melts at a temperature similar to Q_{\text{wide}}A(Ph) and Q_{\text{long}}A(Ph): 136 °C. This observation, along with the large difference between the unsymmetrical isomers Q(6,10)A(Ph) and Q_{\text{mix}}A(Ph), suggests that the variation of
melting point cannot, in this case, be directly related to the symmetry. The difference between these two isomers is the distribution of the chains around the quinone. The high melting point of Q(6,10)A(Ph) may be caused by a greater ability of the molecules to pack in the solid phase. The enthalpy of melting of 85.9 J/g for Q(6,10)A(Ph) supports this. Also, Q_{mix}A(Ph) has a low enthalpy of melting of 22.6 J/g, suggesting a less stable solid. The distribution of the short chains in Q_{mix}A(Ph) may not allow the long chains to fill the voids in order to form a more stable solid. The bigger voids observed with Q(6,10)A(Ph) might be easier to fill with the long chains, leading to a more stable solid phase. This could explain why two compounds of same symmetry have melting temperatures that are so different.

The length of the side chains may also be partially responsible for the behaviour of the three new compounds. As a general rule, increasing the length of the chains appended to the core tends to reduce the transition temperatures. The previously reported compounds Q(10,10)A(Ph) and Q(6,6)A(Ph) have a melting points of 133 °C and 170 °C respectively.\textsuperscript{135,137} Q(10,10)A(Ph) has a melting temperature that is very close to those of the symmetrical isomers Q_{wide}A(Ph) and Q_{long}A(Ph). It is possible that the molecules pack to accommodate the longest chains to create a solid phase with a stability similar to Q(10,10)A(Ph).

For this first class of compounds, neither symmetry nor shape modifications led to induction of mesogenic behaviour. The stability of the crystalline solids is influenced by
the distribution of the longest chains around the aromatic core, as well as their symmetry. In these cases, the exact nature of these effects remains ambiguous and more work is required to fully understand what structural modifications are necessary to induce mesogenic behaviour.

4.4.2 Interdigitation in the liquid crystalline phases

As described in Chapter 1, a large number of groups have tried to gather information about structure/property relationship in order to engineer materials possessing specific characteristics. The field of discotic liquid crystals is characterized by two specific goals: room temperature mesophases and high conductivity along the columns. Various strategies have been employed to lower the melting and clearing transitions. Materials with high conductivity must also possess other properties such as room temperature mesogenic behaviour and high solubility for easy processing. 184,209

When there is a mixture of chains of different lengths, it is possible for the long chains to occupy the voids created by the short chains. This phenomenon is called interdigitation and has been investigated in several contexts. Preece and co-workers investigated the impact of interdigitation on the adhesion between two surfaces covered with self-assembled monolayers of n-dialkyl sulfides. 210 As the difference between the two chains increases, the adhesion between the two surfaces also increases. It has been
postulated that the long chains are able to fill the voids created by the short chains. The chains interact with each other via van der Waals interactions and form a more stable assembly.  

Allen and co-workers have proposed to use interdigitation in order to obtain more stable liquid crystalline phases. Since the observed conductivity of a LC phase depends on the stability of the columns, finding ways to stabilize the self-assembly of the disc-shaped molecules into columns was of interest. Stable liquid crystalline phases would exhibit high clearing temperature, low melting temperature and a broad liquid crystalline range. The discs within a column would be more ordered and the mobility of charges or energy would be greater. Triphenylene derivatives have been synthesized via numerous method that allowed the formation of a number of compounds with various degrees of symmetry and different substitution patterns.  

Using mesogens based on the triphenylene core, they synthesized series of structural isomers that could be used to establish the effect of interdigitation on the transitions temperatures and the ordering of the discs within the columns. To establish if compounds are able to interdigitate, the inter-columnar distances obtained from the XRD experiment must be examined. Within a series of mesogens where the number of carbons in the chains increases, the intercolumnar distances are expected to increase as well. If a mesogen is decorated with chains of different length, it is reasonable to expect the long chains to fill the voids created by the short chains. This will allow the formation of a
mesophase where the discs are close from each other, in spite of the presence of the long chains. Structural isomers are expected to have similar inter-columnar distances if one of them is able to interdigitate.

The interdigitation can have opposite effects on the stability of the liquid crystalline phases. When molecules belonging to different columns interdigitate, they get closer to each other from the intermolecular interactions. This will have a destabilizing effect on the mesophase because the discs will have a tendency to slip from one column to the other. On the other hand, interdigitation will lock discs in place, decreasing their ability to rotate within a column. Greater π-π interactions between discs will arise and lead to more ordered columns, allowing the charges to travel more efficiently. The formation of the mesophase will be affected by the delicate balance between these competing effects that contribute to the stability of the LC phase.

The mesogenic behaviour is strongly affected by the number and length of the aliphatic chains attached to the rigid core. Each system has a critical point where the maximum transition temperatures are obtained. Shorter chains reduce the stability of the mesophase from decreased intermolecular interactions. A minimum of aliphatic carbons are necessary to induce the formation of various mesophases (micro-domains and segregation, Chapter 1). Longer chains are characterized by a greater number of possible conformations that increase the disorder within the phase. Also, the chains have a
tendency to coil in order to fill the space between the rigid cores, leading to more circular molecular shapes.\textsuperscript{214}

The triphenylene derivatives they used to investigate interdigitation in the liquid crystalline phases are shown in Figure 4.12. They used a triphenylene decorated with six pentyloxy chains (C\textsubscript{5}C\textsubscript{5}) and its structural isomers decorated with two types of chains, butyloxy and hexyloxy (C\textsubscript{4}C\textsubscript{6}). The inter-columnar distances obtained for these two isomers are very similar: 19.8 Å for C\textsubscript{5}C\textsubscript{5} and 19.9 Å for C\textsubscript{4}C\textsubscript{6}, suggesting that there is interdigitation in the mesophase of C\textsubscript{4}C\textsubscript{6}. Other pairs of isomers possessing similar inter-columnar distances confirmed that interdigitation is observed when the aromatic cores are decorated with chains containing different numbers of carbon: C\textsubscript{4}C\textsubscript{4} and C\textsubscript{3}C\textsubscript{5}, C\textsubscript{7}C\textsubscript{7} and C\textsubscript{5}C\textsubscript{9}.

\begin{figure}[h]
\centering
\includegraphics{figure4_12.jpg}
\caption{Triphenylene derivatives used by Allen and co-workers to establish the phenomenon of interdigitation and its effect on inter-columnar distances and transition temperatures.}
\end{figure}

\textbf{C\textsubscript{5}C\textsubscript{5}: Cr 69 Col 122 I} \\
\textit{a = 19.8 Å} \\

\textbf{C\textsubscript{4}C\textsubscript{6}: Cr 58 Col 96 I} \\
\textit{a = 19.8 Å}
The transitions temperatures observed with these two isomers suggest however that the isomers decorated with two types of alkoxy chains (C_4C_6) are less stable than their uniformly substituted counter-part (C_5C_5). The transition temperatures are shown in Figure 4.12. The melting temperature of the C_4C_6 isomer is 10 °C lower and the clearing temperature is 26 °C. The enthalpies associated with the transitions are also lower for the isomer decorated with two types of aliphatic chains, suggesting that in spite of the interdigitation of the chains, the mesophase is less stable.

As part of their study, they also synthesized a asymmetrical isomer of C_5C_5 called C_4C_6-asym. Its transition temperatures and enthalpies are very similar to the first isomer of C_5C_5 presented, C_4C_6-sym. The transition temperatures (60 °C and 95 °C) of the less symmetrical isomer are virtually identical to the more symmetrical isomer (58 °C and 95 °C) in spite of its reduced molecular symmetry. The enthalpies of transition are also very similar, along with the inter-molecular distances (20.1 Å for C_4C_6-asym), suggesting the presence of inter-digitation between the long and short chains. In this particular case, the intermolecular interactions between the chains were able to stabilize the mesophase of C_4C_6-asym. The mesophase of the unsymmetrical isomer was therefore stabilized by interdigitation. Other series of isomer exhibit a similar behaviour: C_6C_6, C_5C_7-sym and C_5C_7-asym.

Mesogens decorated with mixtures of chains have similar inter-columnar distances than their structural isomers decorated with only one type of aliphatic chains.
This suggests that the voids created by the short chains can be filled by the long chains. The mesogens with different chains exhibit lower transition temperatures than their uniform (one type of chain) counter-part. The difference in the enthalpies for these transitions also confirms this observation. Isomers decorated with the same types of chains but possessing different degrees of symmetry can exhibit similar thermal properties (temperatures and enthalpies) in the presence of stabilizing interdigitation. This is not always the case and some of our series of compounds are not stabilized by interdigitation.

Ong and co-workers synthesized series of compounds also based on the dibenzo[a,c]phenazine core decorated with six aliphatic chains. They studied the effect of the length of the chains at the top of the mesogen on the liquid crystalline properties. Derivatives decorated with short chains (four carbons) exhibited high transition temperatures and broad range of liquid crystallinity. When the chains appended at the top were much longer (12 carbons), the transition temperatures were both lowered. The clearing temperature was however lowered to a greater extent; reducing the range of mesogenic behaviour. This also suggests that an elongated molecular shape is destabilizing for the liquid crystalline phase. The use of an unsymmetrical diamine (6 and 12 carbons) had some very surprising effect on the mesophase stability. The presence of chains of different length allows interdigitation to take place and affects the stability of the mesophase. The melting temperature was lowered from the decreased symmetry
while the clearing temperature was kept elevated from the ability of the mesogens to interdigitate.

The formation of liquid crystalline phases is affected by a variety of factors that are difficult to deconvolute (i.e. symmetry, shape, interdigitation). The effect of molecular shape on the mesogenic behaviour will be examined, along with the ability of our isomers to interdigitate and form stable liquid crystalline phases.  

4.4.3 Series 2: 2,3,6,7-Tetraalkoxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile derivatives

![Diagram of compounds](image)

Figure 4.13: Compounds obtained by the condensation of the quinones with diaminomaleonitrile. Transition temperatures ($T_m$ and $T_c$) and enthalpies are indicated below the structure.
2,3,6,7-Tetraalkoxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile derivatives were initially reported by Ohta and co-workers in 1995. Subsequently, our research group investigated several members of this series in order to probe the effect of molecular symmetry on their mesogenic properties (see Chapter 3). These compounds have very broad liquid crystalline phases, which are normally only observed with mesogens possessing much larger aromatic cores. Three new mesogens of this type were prepared via condensation of Qwide, Qlong and Qmix with 2,3-diaminomaleonitrile (see Figure 4.12 and Scheme 4.6). These also exhibit broad liquid crystalline phases with clearing temperature as high as 251 °C. The transition temperatures of the new compounds were compared with the compounds originally obtained from Q(8,8) and Q(6,10).

Figure 4.13 is divided in two rows with the molecules on the top possessing a higher symmetry number (σ = 2) than the compounds at the bottom (σ = 1). QwideA(CN) has a similar Tc (251 °C) and a lower Tm (80 °C) than Q(8,8)A(CN) (86 and 252 °C). QlongA(CN) also has a similar Tc (251 °C) and a lower Tm (77 °C) than Q(8,8)A(CN). The thermal properties of QwideA(CN) and QlongA(CN) are too similar to provide information on the effect of the substitution pattern on the mesogenic behaviour. The mesogenic properties of the new symmetrical isomers are very similar, preventing us from drawing conclusions concerning the effect of the molecular shape of the molecules on the mesophase morphology and thermal properties. As presented by Allen and co-
workers, compounds having four identical chains melt at higher temperatures than compounds decorated with chains of different length.\textsuperscript{212}

The inter-columnar distances obtained for this series suggest that there is presence of interdigitation in the mesophases of $Q_{\text{wide}}A(CN)$ and $Q_{\text{long}}A(CN)$. Their lattice constants are 21.8 and 21.9 Å respectively, which is similar to the inter-columnar distance obtained for $Q(8,8)A(CN)$, 21.5 Å. The values observed for the enthalpies of melting for the isomers interdigitating are greater than the ones observed for $Q(8,8)A(CN)$: 56.2 and 56.8 J/g vs. 38.2 J/g. The enthalpies observed upon melting are also bigger for the $Q_{\text{wide}}A(CN)$ and $Q_{\text{long}}A(CN)$ isomers: 5.3 and 5.0 J/g vs. 2.3 J/g. These values suggest that the interdigitated mesophases are more stable than $Q(8,8)A(CN)$.

In this particular series of symmetrical isomers, the mesogenic properties are virtually identical. The ability of these derivatives to stack in an anti-parallel fashion may lead to columns with similar chains distribution (similar transition temperatures and similar inter-columnar distances). The columns may possess similar packing abilities, leading to liquid crystalline phases with similar mesogenic behaviour in spite of the different chain distribution.
The second row of compounds in Figure 4.13 contains the unsymmetrical compounds $Q_{\text{mix}}A(\text{CN})$ and $Q(6,10)A(\text{CN})$. Their melting temperatures are 47 and 38 °C and clearing temperatures are 250 and 215 °C respectively. Various effects have to be examined in order to fully understand the mesogenic behaviour. As presented in the previous chapter, a decrease in molecular symmetry has a systematic lowering effect on the melting temperature. The melting temperature of $Q_{\text{mix}}A(\text{CN})$ is lower than all the symmetrical isomers presented in Figure 4.13. It is also lower than $Q(8,8)A(\text{CN})$, as expected from the presence of a mixture of chains.

The inter-columnar distance observed in the mesophase of $Q_{\text{mix}}A(\text{CN})$ is 21.5 Å, which is identical to $Q(8,8)A(\text{CN})$. From this, it is possible to assume that there is interdigitation between the short and long chains in the liquid crystalline phase. The enthalpy observed upon clearing is 5.1 J/g for the $Q_{\text{mix}}A(\text{CN})$ isomer. This value is greater than the value observed for $Q(8,8)A(\text{CN})$ (2.3 J/g). The clearing temperature of the unsymmetrical isomer is very similar to the clearing temperature of the symmetrical isomers shown in Figure 4.13. It is therefore possible to assume that for $Q_{\text{mix}}A(\text{CN})$, the interdigitation led to a mesophase with a high stability in spite of the low molecular symmetry.\textsuperscript{217,218} This stabilization was not observed with $Q(6,10)A(\text{CN})$, which has a lower clearing enthalpy in spite of the similar inter-columnar distance.
The data obtained from this series of isomer indicates that isomers decorated with mixtures of chains have lower melting temperatures than structural isomers decorated with only one type of aliphatic chain. The inter-columnar distances suggest that there is interdigitation within the liquid crystalline phases. The high clearing temperatures and enthalpies suggests that this lead to more stabilized mesophases. The less symmetrical isomer Q_{mixA(CN)} also shows an inter-columnar distance consistent with interdigitation. Its high clearing temperature and enthalpy confirms that interdigitation was able to stabilize the mesophase in spite of the low molecular symmetry. Q_{wideA(CN)} and Q_{longA(CN)} have mesogenic behaviour that are too similar to be directly influenced by the molecular shape of the mesogens.

4.4.4 Series 3, 4 and 5: 2,3,6,7,11,12-Hexaalkoxydibenzo[a,c]phenazine derivatives

Figure 4.14: General structures of compounds in series three, four and five.
The hexaalkoxydibenzo[a,c]phenazine derivatives were separated into three series according to the number of carbons in the chains on the top of the molecule. Their general structures are shown in Figure 4.14. Series 3 contains isomers obtained from the condensation of the quinones with A(6), series 4 with A(8) and A(6,10) and series 5 with A(10). Figure 4.15 shows the symmetrical isomers along with their transition temperatures and enthalpies. Figure 4.19 shows the unsymmetrical isomers with their transition temperatures and enthalpies.
4.4.4.1 Series of symmetrical isomers

Figure 4.15: Symmetrical isomers used to probe the effect of molecular shape on mesogenic properties.
To establish the effect of molecular shape on the mesogenic properties, comparisons will be made between various series of mesogens. In the first two comparisons, the mesogens (Q_{wide}A(X) and Q_{long}A(X)) will be compared to the isomer decorated with four chains containing eight carbons (Q(8,8)A(X)). The overall shape difference in these two comparisons is expected to be minimal since the isomers have similar distribution of the carbons in the aliphatic chains. Variations of the mesogenic behaviour are therefore caused by the modification in the distribution of the carbons around the quinone used to obtain the mesogens.

**Comparison 1**

![Comparison 1](image-url)

R = C_{6}H_{13}  
Cr 70 Col 137 I

R = C_{8}H_{17}  
Cr 71 Col 134 I

R = C_{10}H_{21}  
Cr 58 Col 121 I

Cr 76 Col 146 I

Cr 62 Col 141 I

Cr 70 Col 123 I

Figure 4.16: Comparison 1: mesogenic behaviour of isomers Q_{wide}A(X) vs. Q(8,8)A(X). X = 6, 8 and 10.
Comparison 2

\[ R = C_6H_{13} \quad \text{Cr 60 Col 131 I} \quad \text{Cr 76 Col 146 I} \]
\[ R = C_8H_{17} \quad \text{Cr 66 Col 122 I} \quad \text{Cr 62 Col 141 I} \]
\[ R = C_{10}H_{21} \quad \text{Cr 71 Col 105 I} \quad \text{Cr 70 Col 123 I} \]

Figure 4.17: Comparison 2: mesogenic behaviour of isomers \( Q_{\text{long}}A(X) \) vs. \( Q(8,8)A(X) \). \( X = 6, 8 \) and 10.

Figure 4.16 shows the comparisons between the compounds \( Q_{\text{wide}}A(X) \) and \( Q(8,8)A(X) \) where the diamines are decorated with two chains containing either six, eight or ten carbons (Comparison 1). Figure 4.17 shows the comparisons between the compounds \( Q_{\text{long}}A(X) \) and \( Q(8,8)A(X) \): Comparison 2. From comparisons 1 and 2, it is possible to establish some trends. As mentioned before, the molecular shape of the isomers is expected to be constant and variation in mesogenic properties arises from different sources. The six pairs of isomers from comparisons 1 and 2 show that the isomers decorated with only one type of chains around the quinone have higher clearing temperatures than their structural isomers decorated with mixtures of chains. This is in agreement with the data presented by Allen and co-workers. The variations observed with the melting temperatures do not follow any trend. The clearing temperature is
systematically lowered when chains of different lengths are used. The molecular shape remained the same and was therefore not responsible for the variation in the thermal properties of these mesogens.

The inter-columnar distances of the various isomers are all very similar. This indicates that interdigitation in the liquid crystalline phase is possible. However, the thermal behaviour suggests that the mesophases were not stabilized by this phenomenon. These compounds have a greater number of chains than the compounds form Series 2. The intermolecular interactions may have reached a critical point where they actually promote slippage of the discs instead of stabilizing the liquid crystalline phase.

**Comparison 3**

![Comparison 3](image)

<table>
<thead>
<tr>
<th>R</th>
<th>Cr</th>
<th>Col</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₃</td>
<td>70</td>
<td>137</td>
<td>I</td>
</tr>
<tr>
<td>C₈H₁₇</td>
<td>71</td>
<td>134</td>
<td>I</td>
</tr>
<tr>
<td>C₁₀H₂₁</td>
<td>58</td>
<td>121</td>
<td>I</td>
</tr>
</tbody>
</table>

Figure 4.18: Comparison 3: mesogenic behaviour of isomers Qₚₖₑₐ₄ (X) vs. Qₜₒₐ₉ₐ₄ (X). X = 6, 8 and 10.
Figure 4.18 shows the comparisons between the mesogenic properties of the Q\textit{wide}A(X) and Q\textit{long}A(X). The position of the long chains around the core is expected to have an impact on the molecular shape of the isomers and therefore on their mesogenic properties as depicted in Figure 4.3 and 4.4. Again, a systematic lowering effect is observed between the Q\textit{wide}A(X) and Q\textit{long}A(X) isomers. Higher clearing temperatures are observed for isomers obtained from the Q\textit{wide} quinone. In this case, the two types of isomers have the same chain distribution but different molecular shapes. The difference in the mesogenic behaviour can therefore be associated with different molecular shapes that arise from the position of the long decyloxy chains. When the long chains are on the sides (Q\textit{wide}), the liquid crystalline phase is more stable and clears at a higher temperature. The variation of the melting temperatures does not follow any specific trend and no conclusions can be drawn from the data obtained. Again the inter-columnar distances suggests the presence of interdigitation but no stabilization seems to arise from it.

The analysis of the trends observed with the mesogenic behaviour of the symmetrical isomers of series 3, 4 and 5 shows that a mixture of chains of different lengths has a lowering effect on the clearing temperature. Also, the presence of long aliphatic chains at a position that increases the elongation of the molecular shape destabilizes the mesophase, which clears at a lower temperature. The linear trend for the clearing temperature is as follow:

\[ T_c(\text{Q}(8,8)) > T_c(\text{Q}_{\text{wide}}) > T_c(\text{Q}_{\text{long}}) \]
The trends observed with the melting temperatures do not allow any conclusions to be drawn. The general rule states that the transition temperatures should decrease as the number of carbons in the aliphatic chains increases. This is not what is observed in this case and further modeling is required in order to rationalize the results obtained.

4.4.4.2 Series of unsymmetrical isomers.

Unsymmetrical isomers were synthesized and their mesogenic behaviour examined. The unsymmetrical isomers were either obtained from unsymmetrical diamines (A(6,10), Comparison 4) or unsymmetrical quinones (Q_{mix}, Comparison 5).
Figure 4.19: Unsymmetrical isomers: \( Q(8,8)A(6,10) \), \( Q_{\text{wide}}A(6,10) \), \( Q_{\text{long}}A(6,10) \), \( Q(6,10)A(X) \) and \( Q_{\text{mix}}A(X) \), \( X = 6, 8 \) and 10.

Figure 4.20 below shows the isomers obtained from the condensation of various quinones with the unsymmetrical diamine \( A(6,10) \). These isomers are less symmetrical than the isomers obtained with the symmetrical amine \( A(8) \) and all show lower transition temperatures as demonstrated in Chapter 3. The data obtained from Comparison 4 is in
agreement with the previous series of comparisons. Again, a mixture of chains lowers the clearing temperature and has no consistent effect on the melting temperature. Also, the isomer $Q_{\text{wide}}A(6,10)$ clears at a higher temperature than $Q_{\text{long}}A(6,10)$, supporting the conclusion that the molecular shape has an effect on the mesogenic behaviour. The intermolecular distances obtained for these structural isomers are very similar, suggesting that there is interdigitation in the mesophase, without an obvious increase of stability. The broad ranges of liquid crystallinity may be caused by the lower symmetry of these compounds, as demonstrated in Chapter 3.

**Comparison 4**

<table>
<thead>
<tr>
<th>Compound</th>
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<th>I</th>
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</thead>
<tbody>
<tr>
<td>$Q(8,8)A(8)$</td>
<td>62</td>
<td>141</td>
<td>I</td>
</tr>
<tr>
<td>$Q_{\text{wide}}A(8)$</td>
<td>71</td>
<td>134</td>
<td>I</td>
</tr>
<tr>
<td>$Q_{\text{long}}A(8)$</td>
<td>66</td>
<td>122</td>
<td>I</td>
</tr>
<tr>
<td>$Q(8,8)A(6,10)$</td>
<td>48</td>
<td>137</td>
<td>I</td>
</tr>
<tr>
<td>$Q_{\text{wide}}A(6,10)$</td>
<td>34</td>
<td>126</td>
<td>I</td>
</tr>
<tr>
<td>$Q_{\text{long}}A(6,10)$</td>
<td>42</td>
<td>115</td>
<td>I</td>
</tr>
</tbody>
</table>

Figure 4.20: Comparison 4: $A(8)$ and $A(6,10)$ isomers.

Comparison 5 contains structural isomers having the same degree of symmetry but different distribution of the chains around the aromatic core. Compounds obtained with the quinone $Q(6,10)$ have been presented in Chapter 3 and will be compared to the compounds obtained with $Q_{\text{mix}}$ (see Figure 4.21). These three comparisons did not provide any useful information concerning the effect of the new substitution pattern on
the thermal behaviour of these new mesogens. Figure 4.22 shows the transition temperatures of the three series of new compounds ($Q_{\text{wide}}$, $Q_{\text{long}}$ and $Q_{\text{mix}}$).

**Comparison 5**

![Comparison 5 diagram]

<table>
<thead>
<tr>
<th>R</th>
<th>Cr 43 Col 130 I</th>
<th>Cr 41 Col 134 I</th>
<th>Cr 41 Col 134 I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = C_6H_{13}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R = C_8H_{17}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R = C_{10}H_{21}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.21: Comparison 5: unsymmetrical isomers obtained from the unsymmetrical quinones $Q(6,10)$ and $Q_{\text{mix}}$.

**Comparison 6**

![Comparison 6 diagram]

<table>
<thead>
<tr>
<th>R</th>
<th>Cr 70 Col 137 I</th>
<th>Cr 41 Col 134 I</th>
<th>Cr 60 Col 131 I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = C_6H_{13}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R = C_8H_{17}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R = C_{10}H_{21}$</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Figure 4.22: Comparison 6 of the mesogens obtained with $Q_{\text{wide}}$, $Q_{\text{long}}$ and $Q_{\text{mix}}$. 
From Figure 4.22, interesting trends emerged. Again, there is no consistent behaviour for the melting temperatures. The clearing temperature do, however follow an unexpected trend. The less symmetrical isomers ($Q_{\text{mix}}$) have clearing temperatures lower than their $Q_{\text{wide}}$ counter-part, as expected. The isomers decorated with the $Q_{\text{long}}$ quinone have clearing temperature lower than their less-symmetrical counter-part, which is contrary to Carnelley's rule. The inter-columnar distances obtained are all similar, indicating that the molecules have the ability to interdigitate. The elevated clearing temperatures of the less symmetrical isomers may be attributed to more stable mesophases from the intermolecular interactions between mesogens.

The quinone $Q_{\text{mix}}$ corresponds to a mixture of $Q_{\text{wide}}$ and $Q_{\text{long}}$. It has been established that the molecular shape of the quinones had a significant effect on the mesogenic behaviour. The compounds obtained with $Q_{\text{mix}}$ might represent the missing link between the elongated and widened molecular shapes. The low symmetry may have been overcome by the ability of the various chains to interdigitate.

4.5 Conclusion

This project involved the synthesis of 20 new compounds in order to assess the effect of the molecular shape on the mesogenic behaviour. The long and wide quinones were condensed with various diamines in the hope to create mesogens with new
properties or behaviour that would allow us to observe how the molecular structure of the molecules affects their properties. Interdigitation is present in all the mesophases, as suggested by the inter-columnar distances. It can however increase or decrease the stability of the mesophases.

Series 1 demonstrated that compounds with only four aliphatic chains do not form liquid crystalline phase despite their symmetry or substitution pattern. The introduction of strong electron-withdrawing groups on the core allows the formation of mesophases even with only four aliphatic chains. Compounds from Series 2 decorated with mixtures of chains (C₆H₁₃ and C₁₀H₂₁) have broader LC phases. It has been suggested that interdigitation was able to increase the stability of the mesophases.

Mesogens decorated with six aliphatic chains from Series 3, 4 and 5 have interesting behaviour. Structural isomers possessing similar molecular shapes but different distribution patterns show a decrease in clearing temperature. Isomers decorated with the mixture of chains, but at different position also show differences in thermal behaviour. Elongated molecules have lower clearing temperatures than more circular ones, confirming that molecular shape does have an effect on the mesogenic behaviour.

The following trend was observed for the clearing temperatures of all the compounds decorated with six aliphatic chains:
\[ T_c(Q(8,8)) > T_c(Q_{\text{wide}}) > T_c(Q_{\text{mix}}) > T_c(Q_{\text{long}}) \]

The chains distribution and the molecular shape of the mesogens has an important effect on the clearing temperature. This strategy could therefore be used to lower the clearing temperature of mesogens if that transition is also elevated. More work needs to be executed in order to fully understand the how the molecular shape affects the melting temperature.

Since the melting temperature is affected by the stability of both the crystal and the liquid crystal phase, various experiments could be performed on the crystalline solid in order to understand the effect of the distribution of the chains on the packing of the discs. Solid-State NMR and Scanning Tunneling Microscopy (STM) could provide valuable information. It has been attempted to obtain single crystals of the mesogens to understand the molecular assembly of this type of molecules. Unfortunately, the crystals obtained were too fragile and no XRD data was collected.

### 4.6 Experimental Section

Details on materials and experimental procedures are in Chapter 6, section 6.4.
CHAPTER 5: CONCLUSIONS AND FUTURE WORK

The research conducted in our research group has a complex but important goal: understanding structure/property relationships of organic materials. Specifically, we are gathering information on how molecular structure affects the properties of compounds forming liquid crystalline phases and developing tools that would allow for the rational design of liquid crystalline phases with desired properties. For the purpose of this thesis, strategies that would enable tailoring the mesogenic properties were investigated. To that end, the effect of molecular symmetry and shape on mesogenic properties was examined.

Results have shown that lowering the molecular symmetry was a useful tool to obtain mesophases in a lower range of temperatures. By breaking the molecular symmetry, the melting temperature was depressed to a greater extent than the clearing temperature, leading to a broader range of liquid crystalline behaviour. This information could be used with compounds already used in devices in order to improve their performance. Now that we have obtained various compounds with different degrees of symmetry, it would be interesting to try to measure the conductivity of these liquid crystalline phases. Our group has never executed such measurements but collaborations with other research groups could allow us to obtain data about the conductivity of our columnar phases. The compounds could be sandwiched between electrodes to measure
the conductivity of the liquid crystalline phases. It is also possible to modify the tip of an AFM to measure the conductivity along a column of molecules.

The project concerning the molecular shape of mesogens required the synthesis of new compounds. Various approaches were examined in order to obtain the quinones with the desired substitution pattern. The synthetic paths used previously in the laboratory were refined to provide us with the desired substitution pattern. The synthetic endeavours, shown in chapter 2, allowed us to improve the efficiency of some of our approaches. We are now able to obtain symmetrical benzil in only two steps compared to four when the benzoin condensation approach was used. This is also an improvement compared to previously published work. The Friedel-Crafts acylation also allows us to avoid using potassium cyanide, which is very toxic.

The results obtained from the shape project confirmed that the molecular shape has an influence on the mesogenic behaviour. The use of aliphatic chains of different length lowers the clearing temperatures. Elongated molecules also have lower clearing temperatures than their more circular counter-part. To support these results, more series of compounds could be synthesized in order to expand our understanding of how the molecular shape of the molecules influences the mesogenic behaviour. Figure 5.1 shows compounds bearing longer chains and more difference between the lengths of the chains. These compounds may give results that are more definitive concerning the effect of molecular shape on mesogenic behaviour.
The studies presented were mainly concerned with the distribution of the chains around the aromatic core. A new direction of the project could be to modify the nature of the core. The nitrogen atoms could be replaced by other atoms such as oxygen, sulphur and phosphorus. It could also be interesting to introduce more heteroatoms in the core and establish the effect on the mesogenic properties. Examples of such cores are shown in Figure 5.2. The nitrogen atoms could be replaced by others heteroatoms as shown in Figure 5.3.

Figure 5.1: Compounds with more discrepancy in the length of the chains appended to the quinone or the diamine portion of the molecule.

Figure 5.2: Mesogens with aromatic core containing more nitrogen atoms at various positions.
Figure 5.3: Aromatic cores with heteroatoms other than nitrogen.

It could also be pertinent to introduce some flexibility into the core and establish how it affects the mesogenic behaviour. Some examples are shown in Figure 5.4. Using a substituted 1,2-diaminocyclohexyl instead of a 1,2-diaminobenzene could lead to a large number of compounds to gather more information about structure/property relationships. Bridging to the benzene ring via a nitrogen atom, forming a carbazole moiety in the quinone could also provide useful information once it is allowed to react with various diamines. The addition of another chain might allow the quinone itself to be liquid crystalline.

Figure 5.4: Examples of more flexible cores: from the diamine (left) or the quinone (right) portion. X and Y can be H, halogens, -CN, aliphatic chains, -SR etc.
CHAPTER 6: EXPERIMENTAL SECTION

6.1 General experimental procedures

The characterization of the product was performed on a portion of the final pure compound. Unless stated otherwise, no further purification was performed prior to the mass spectroscopy, elementary analysis or NMR experiments. The same product was used to characterize the mesogenic behaviour (POM, DSC and VT-XRD). All new compounds were characterized by $^1$H and $^{13}$C NMR, mass spectroscopy, melting temperature and elemental analysis or High-Resolution mass spectroscopy (HR-MS).

6.1.1 Nuclear Magnetic Resonance

NMR spectra were obtained with various instruments: Varian Inova spectrometer at 500 MHz for $^1$H and 125 MHz for $^{13}$C; Bruker Avance at 600 MHz for $^1$H and 150 MHz for $^{13}$C and 400 MHz for $^1$H and 100 MHz for $^{13}$C. Chemical shifts ($\delta$) are expressed in ppm and were calculated from a reference solvent such as CDCl$_3$ ($\delta = 7.26$ ppm). In the analysis of the splitting of the peaks, the following symbols were used: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, quint = quintuplet, m = multiplet.
6.1.2 Mass Spectrometry

Mass spectrometry of small molecules (Mw < 500 g/mol) was performed using either a Varian 4000 GC/MS/MS equipped with a direct probe and ionization energy of 70 eV or a Hewlett-Packard 5985 mass spectrometer with EI of 70 eV. They were performed by technicians at Simon Fraser University: Simon Wong and Hongwen Chen.

Mass spectrometry of molecules with higher masses (Mw > 500 g/mol) was performed by MALDI-TOF with a Perspective Voyager-DE STR from PE Applied Biosystems using a nitrogen laser (337 nm) to desorb the analytes from the 2,5-dihydroxybenzoic acid matrix. High Resolution Mass Spectrometry (HR-MS) was performed on an Agilent 6210 TOF LC-MS with electrospray ionization (ESI).

6.1.3 Elemental Analysis

Elemental analysis was obtained from Mr. Miki Yang and Mr. Frank Haftbaradaran at Simon Fraser University using a EA1110 CHN CE Instrument with WO₃ as an accelerant. The analysis was performed on a small amount of product that was vacuum-dried for about 24 hours. The maximum accepted difference between the found and calculated values is set at ±0.4 % following the ACS (American Chemical Society) stipulations. In very few cases, the difference between the values was ±0.5 % and the
analysis was passed nonetheless since the other characterization methods indicated a high degree of purity.

6.1.4 Infrared Spectroscopy

IR spectra were recorded on a Thermo-Nicolet Nexus 670 FT-IR E.S.P. spectrometer using dried KBr pellets.

6.1.5 Melting Point

Melting points were measured on a Melt-Temp II apparatus from Laboratories Devices without correction or calibration using a mercury thermometer (-10 to 300 °C).

6.1.6 Differential Scanning Calorimetry (DSC)

DSC (differential scanning calorimetry) was used to establish the transition temperatures of our compounds (T\textsubscript{m}: crystal to liquid crystal; T\textsubscript{c}: liquid crystal to isotropic liquid). The analysis was performed on a Perkin Elmer DSC 7 and the values for the temperatures and enthalpies of transition were recorded on the first heating/cooling
cycle at a rate of 5 °C/min, then a second cycle was performed to assess the reproducibility of the phenomenon.

6.1.7 Polarized Optical Microscopy

The type of liquid crystalline phases observed was established using an Olympus BX50 polarized optical microscope equipped with a Linkam LTS350 heating stage. A sample was melted at a rate of 20 °C/min to form an isotropic phase, a cover slip was placed over the sample, which was then slowly cooled (0.5 to 1 °C/min) in order to observe textures that are characteristic of hexagonal columnar packing of the molecules.

6.1.8 Variable Temperature X-Ray Diffraction

Variable temperature X-ray diffraction experiments were performed using Rigaku RAXIS rapid diffractometer with a Cu Kα radiation, a graphite monochromator and a Fujifilm Co. Ltd. Curved image plate (460 mm x 256 mm). Samples were loaded into capillaries (~1 mm diameter) from the isotropic phase (using the hotstage of the POM) and were heated with the nitrogen heater that was provided with the diffractometer by Rigaku or using a home-made capillary furnace.220
6.2 Materials

Chemicals were used as purchased (Aldrich, Anachemia and Fisher Scientific) unless otherwise noted. Dichloromethane was dried by distillation over CaCl\textsubscript{2} and dimethylformamide was dried over 4 Å molecular sieves. Other solvents were used without further purifications. Nitrogen gas was purchased from Praxair. Silica (230-400 mesh) and TLC plates were bought from Silicycle Inc. Deuterated solvents (CDCl\textsubscript{3} and DMSO-d\textsubscript{6}) were purchased from Aldrich.

These solvents and reagents were purchased from Aldrich: BrCH\textsubscript{2}Cl, C\textsubscript{6}H\textsubscript{13}Br, C\textsubscript{8}H\textsubscript{17}Br, C\textsubscript{10}H\textsubscript{21}Br, ICl, LiOH-H\textsubscript{2}O, BF\textsubscript{3}•Et\textsubscript{2}O, VOF\textsubscript{3}, SnCl\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, BBr\textsubscript{3}, NBu\textsubscript{4}Br, butanone, (i-Pr)\textsubscript{2}NH, CuI, sulphuric acid, 2,3-diaminomaleonitrile, HNO\textsubscript{3}, veratrole, catechol, FeCl\textsubscript{3}, I\textsubscript{2}, HBr. These chemicals were purchased from VWR: DMF, THF, DCM, hexanes, ethyl acetate, DMSO, pyridine. These chemicals were purchased from Caledon Laboratories Ltd.: citric acid, K\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{2}SO\textsubscript{3}, NaCl, MgSO\textsubscript{4}, NaHCO\textsubscript{3}, NaOAc, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, methanol, acetic acid, HCl and acetic anhydride. Strem Chemicals Inc provided TMS-Acetylene, Pd(PPh\textsubscript{3})\textsubscript{4} and PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}. Eastman Kodak provided \textit{o}-phenylenediamine. Ethanol was obtained from Commercial alcohols Inc.
6.3 Synthesis Chapter 3

6.3.1 Synthesis of symmetrical quinones

Symmetrical quinones Q(6,6) and Q(8,8) were synthesized using literature procedures\(^{155,174}\). Q(10,10) was synthesized by Christine Lavigneur.

6.3.2 Synthesis of unsymmetrical quinones

Scheme 6.1: Synthesis of 1,2-dialkoxy-4-iodobenzene derivatives. \(i\) I\(_2\), H\(_2\)O\(_2\), H\(_2\)SO\(_4\) (cat), H\(_2\)O (3.7); \(ii\) BBr\(_3\), CH\(_2\)Cl\(_2\) (3.8); \(iii\) C\(_6\)H\(_{13}\)Br, K\(_2\)CO\(_3\), DMF (3.9a); C\(_8\)H\(_{17}\)Br, K\(_2\)CO\(_3\), DMF (3.9b).

\[
\begin{align*}
\text{OCH}_3 & \quad \text{OCH}_3 \\
\text{OCH}_3 & \quad \text{OCH}_3 \\
\text{OH} & \quad \text{OH} \\
\text{OR} & \quad \text{OR}
\end{align*}
\]

4-Iodo-1,2-dimethoxybenzene\(^{197}\) (3.7)

Veratrole (10.0 g, 72.4 mmol) was mixed with water (700 mL) and iodine (18.4 g, 72.4 mmol) in a two-necked round-bottom flask. The mixture was heated for five minutes at 50 °C. Hydrogen peroxide (2.46 g, 8.2 mL, 72.4 mmol) and sulphuric acid (four drops) were slowly added to the mixture that was heated at 50 °C overnight. The solution was cooled to room temperature and extracted with three portions of DCM (200 mL). The organic layers were combined and washed with a Na\(_2\)SO\(_3\)(sat) solution twice (200 mL),
water (200 mL) then brine (200 mL). The organic phase was dried over MgSO₄, filtered and evaporated to yield an amber oil that was used without further purification (17.54 g, 66.4 mmol, 92%). ¹H NMR (500 MHz, CDCl₃) δ 3.84 (s, 3H), 3.85 (s, 3H), 6.61 (d, 1H, J = 8.5 Hz), 7.11 (d, 1H, J = 2.0 Hz), 7.22 (dd, 1H, J = 8.5, 2.0 Hz).

1,2-Dihydroxy-4-iodobenzene¹⁹⁸ (3.8)

4-Iodo-1,2-dimethoxybenzene (10.0 g, 37.9 mmol) was mixed with dry CH₂Cl₂ in a flame-dried two-necked round-bottom flask. The solution was cooled in an acetone/dry ice bath and BBr₃ (28.5 g, 11.1 mL, 113 mmol) was added dropwise over about 25 minutes. The solution was allowed to warm up to room temperature overnight. Small pieces of ice were slowly added to the reaction mixture until no more effervescence was observed. Water (100 mL) was added and the mixture was extracted three times with DCM (75 mL). The organic layers were combined, washed with water (200 mL) three times, then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was purified by column chromatography: hexanes/ethyl acetate 80/20 to 50/50 to yield a clear oil (2.01 g, 8.51 mmol, 22%). ¹H NMR (500 MHz, CDCl₃) δ 5.24 (s, 1H), 5.30 (s, 1H), 6.63 (d, 1H, J = 8.5 Hz), 7.12 (dd, 1H, J = 8.5, 2.0 Hz), 7.19 (d, 1H, J = 2.0 Hz).
4-Iodo-1,2-dioctyloxybenzene<sup>221</sup> (3.9b)

4-Iodo-1,2-dihydroxybenzene (2.21 g, 9.37 mmol) was mixed with bromooctane (3.98 g, 20.6 mmol, 3.6 mL) in DMF (70 mL). Nitrogen was bubbled through the solution for 15 minutes. K<sub>2</sub>CO<sub>3</sub> (5.70 g, 41.2 mmol) was added, the solution was purged for another 10 minutes and heated at 90 °C for 24 hours. The solution was cooled to room temperature and water (200 mL) was added. The aqueous solution was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) four times, then with brine (150 mL). The solution was dried over MgSO<sub>4</sub>, filtered and evaporated. The product was purified by column chromatography (hexanes/ethyl acetate 9/1) and recrystallized in ethanol to yield a white solid (3.34 g, 7.26 mmol, 77%).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.89-0.91 (m, 6H), 1.26-1.40 (m, 16H), 1.43-1.50 (m, 4H), 1.78-1.84 (m, 4H), 3.96 (t, 4H, J = 6.75 Hz), 6.62 (d, 1H, J = 8.5 Hz), 7.14 (d, 1H, J = 2.5 Hz), 7.19 (dd, 1H, J = 8.5, 2.5 Hz).

Scheme 6.2: Formation of 1,2-dihexyloxy-4-iodobenzene. i) C<sub>6</sub>H<sub>13</sub>Br, K<sub>2</sub>CO<sub>3</sub>, DMF (3.10a); ii) I<sub>2</sub>, HIO<sub>3</sub>, AcOH, H<sub>2</sub>SO<sub>4</sub> (3.11a).

![Scheme 6.2: Formation of 1,2-dihexyloxy-4-iodobenzene.](image)

**3.10a:** R = C<sub>6</sub>H<sub>13</sub>  
**3.11a:** R = C<sub>6</sub>H<sub>13</sub>
1,2-Dihexyloxy-4-iodobenzene\textsuperscript{197} (3.11a)

1,2-Dihexyloxybenzene (5.00 g, 18.0 mmol) was mixed with iodine (2.37 g, 9.34 mmol) in water (25 mL), acetic acid (75 mL) and sulfuric acid (2.5 mL). Nitrogen was bubbled through the solution for 15 minutes. The solution was heated at 40 °C and a third of the iodic acid (1.01 g, 5.75 mmol) was added. The solution was stirred for 60 minutes and another portion was added. 60 minutes later the last portion was added and the reaction was heated for another two hours. The solution was allowed to cool to room temperature overnight and water (100 mL) was added. The solution was extracted three time with diethyl ether (100 mL). The organic layers were combined and washed with sodium bicarbonate (saturated solution, 150 mL) twice, water (150 mL), then brine (150 mL). The solution was dried over MgSO\textsubscript{4}, filtered and evaporated. The product was purified over a short silica column (100 % DCM) to yield a clear oil (4.55 g, 11.3 mmol, 63 %). $\textsuperscript{1}$H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 0.89-0.92 (m, 6H), 1.33-1.35 (m, 8H), 1.43-1.51 (m, 4H), 1.76-1.84 (m, 4H), 3.95 (t, 4H, $J=6.8$ Hz), 6.62 (d, 1H, $J=8.0$ Hz), 7.13 (d, 1H, $J=2.0$ Hz), 7.18 (dd, 1H, $J=8.0$, 2.0 Hz).
Scheme 6.3: i) TMS-acetylene, (i-Pr)2NH, CuI, PdCl2(PPh3)2, THF (3.12a); ii) K2CO3, MeOH, THF (3.13a); iii) CuI, Pd(PPh3)4, (i-Pr)2NH, THF (3.14); iv) I2, DMSO (3.15).

2-(3,4-Dihexyloxyphenyl)ethynyl-trimethylsilane (3.12a)

1,2-Dihexyloxy-4-iodobenzene (4.00 g, 9.89 mmol), CuI (0.565 g, 2.97 mmol) and (i-Pr)2NH (5 mL) were mixed in THF (100 mL) in a dry two-necked round-bottom flask. The solution was purged with nitrogen for 15 minutes. PdCl2(PPh3)2 (0.175 g, 0.250 mmol) and TMS-Acetylene (11.7 g, 17 mL, 199 mmol) were added and the solution was purged for another five minutes. The solution was heated at reflux for 24 hours. The solution was cooled to room temperature and filtered through a short silica column (washed with DCM). The organic solution was washed with HCl (20 %, 200 mL), water (200 mL) and then brine (200 mL). The solution was dried over MgSO4,
filtered and evaporated. The product was purified by column chromatography (98/2, hexanes/ethyl acetate) to yield a brownish oil that was used without further purification (2.34 g, 7.74 mmol, 78 %). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.24 (s, 9H), 0.89-0.92 (m, 6H), 1.32-1.36 (m, 8H), 1.43-1.56 (m, 4H), 1.78-184 (m, 4H), 3.96-4.00 (m, 4H), 6.77 (d, 1H, $J$ = 8.0 Hz), 6.96 (d, 1H, $J$ = 2.0 Hz), 7.03 (dd, 1H, $J$ = 8.0, 2.0 Hz).

4-Ethynyl-1,2-dihexyloxybenzene (3.13a)

(3,4-Dihexyloxyphenyl)-ethynyl-trimethylsilane (3.35 g, 11.1 mmol) was mixed in methanol (45 mL) and tetrahydrofuran (45 mL). K$_2$CO$_3$ (3.82 g, 27.7 mmol) was added and the reaction mixture was stirred at room temperature overnight. The solution was filtered through a short silica column (washed with DCM). The organic solution was washed with water (200 mL), then brine (200 mL). The solution was dried over MgSO$_4$, filtered and evaporated to yield an oil that was without further purification (2.65 g, 8.76 mmol, 79 %). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.89-0.92 (m, 6H), 1.33-1.36 (m, 8H), 1.44-1.51 (m, 4H), 1.78-184 (m, 4H), 3.99 (t, 4H, $J$ = 7.25 Hz), 6.79 (d, 1H, $J$ = 8.0 Hz), 6.99 (d, 1H, $J$ = 2.0 Hz), 7.06 (dd, 1H, $J$ = 8.0, 2.0 Hz).

3,4-Dihexyloxy-3',4'-dioctyloxydiphenylacetylene (3.14)

In a two-necked round-bottom flask, 1,2-dioctyloxy-4-iodobenzene (3.0 g, 6.5 mmol), 1,2-dihexyloxy-4-ethynylbenzene (2.7 g, 8.8 mmol) and CuI (0.37 g, 2.0 mmol) were mixed and the flask was purged (vacuum/N$_2$) three times. Pd(PPh$_3$)$_4$ (0.38 g, 0.33
mmol) was added and the flask was purged again twice before adding dry (i-Pr)₂NH (100 mL). The mixture was stirred at room temperature for 30 minutes and then heated at reflux overnight. The mixture was cooled to room temperature and aqueous HCl (10%) was added until pH was close to seven. The mixture was extracted three times with DCM (75 mL) and the organic extracts were combined prior to washing with water (200 mL) and brine (200 mL). The organic phase was dried over MgSO₄, filtered and evaporated. The product was purified by column chromatography (hexanes/dichloromethane, 1:1) to yield a white powder (2.6 g, 4.1 mmole, 63%) after recrystallization in hot hexanes; mp: 85-86 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.92 (m, 12H), 1.29-1.36 (m, 24H), 1.43-1.55 (m, 8H), 1.79-1.85 (m, 8H), 4.00 (t, 8 H, J = 4.5 Hz), 6.81 (d, 2H, J = 8.0 Hz), 7.02 (d, 2H, J = 1.5 Hz), 7.07 (dd, 2H, J = 8.0, 1.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 14.02, 14.10, 22.60, 22.67, 25.66, 25.68, 25.99, 26.01, 29.15, 29.20, 29.27, 29.36, 31.57, 31.81, 69.11, 69.16, 87.94, 113.19, 113.21, 115.58, 116.45, 116.47, 124.69, 148.65, 149.40 (17 carbon signals missing/overlapping); MALDI-TOF for [C₄₂H₆₆O₄]⁺ calculated (found) 634.50 (634.92); Elemental analysis (%) for C₄₂H₆₆O₄ calculated (found): C, 79.44 (79.07); H, 10.48 (10.76).

3,4-Dihexyloxy-3',4'-dioctyloxybenzil (3.15)

3,4-Dihexyloxy-3',4'-dioctyloxydiphenylacetylene (1.2 g, 1.9 mmol) and I₂ (0.96 g, 3.8 mmol) were dissolved in DMSO (40 mL) and the solution was heated at reflux overnight. The mixture was cooled down, water (200 mL) was added and the mixture was extracted with three portions of DCM (75 mL). The organic extracts were combined and
washed with large amounts of water (400 mL) three times, then with brine once (200 mL). The organic phase was dried over MgSO₄, filtered and evaporated. The product was recrystallized in hot hexanes to yield a white powder (0.97 g, 1.2 mmol, 77%). mp: 82-84 °C; \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 0.88-0.90 (m, 12H), 1.29-1.35 (m, 24H), 1.46-1.49 (m, 8H), 1.79-1.84 (m, 8H), 4.04-4.07 (m, 8H), 6.85 (d, 2H, \(J = 8.5\) Hz), 7.43 (dd, 2H, \(J = 8.5, 2.0\) Hz), 7.56 (d, 2H, \(J = 2.0\) Hz); \(^1^3\)C NMR (125 MHz, CDCl₃) \(\delta\) 13.97, 14.00, 14.08, 14.09, 22.55, 22.58, 22.64, 22.66, 25.57, 25.63, 25.90, 25.97, 28.87, 28.91, 29.01, 29.06, 29.22, 29.25, 29.28, 29.33, 31.48, 31.53, 31.77, 31.80, 69.10, 69.21, 69.22, 111.56, 112.26, 126.10, 126.18, 149.27, 154.96, 193.79 (one carbon signal missing/overlapping); MALDI-TOF for \([\text{C}_{42}\text{H}_{66}\text{O}_6-\text{H}]^+\) calculated (found): 667.49 (667.57); Elemental analysis (%) for \(\text{C}_{42}\text{H}_{66}\text{O}_6\) calculated (found): C, 75.63 (75.75); H, 9.97 (10.20).

Scheme 6.4: \(j\) VOF₃, BF₃•Et₂O, CH₂Cl₂.
2,3-Dihexyloxy-6,7-dioctyloxyphenanthrene-9,10-dione Q(6,8)

3,4-Dihexyloxy-3’,4’-dioctyloxybenzil (1.5 g, 2.3 mmol) was dissolved in dry CH₂Cl₂ (100 mL) under a nitrogen atmosphere in an ice/water bath. BF₃•Et₂O (0.72 g, 5.1 mmol, 0.64 mL) was added using a syringe and the mixture was allowed to stir for about ten minutes. VOF₃ (0.98 g, 7.9 mmol) was then added and the mixture was stirred for two hours. The reaction mixture was poured over an aqueous citric acid solution (10g/100 mL) and allowed to stir for another hour. The solution was extracted by dichloromethane (50 ml) three times and the extracts were combined and washed with water (200 mL) two times and brine once (150 mL). The organic phase was dried over MgSO₄, filtered and evaporated. The product was purified by column chromatography (DCM) to yield a red solid (1.1 g, 1.6 mmol, 73 %). mp: 86-88 °C. ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.93 (m, 12H), 1.29-1.38 (m, 24H), 1.47-1.53 (m, 8H), 1.81-1.91 (m, 4H), 4.04 (t, 4H, J = 6.5 Hz), 4.18 (t, 4H, J = 6.5 Hz), 7.05 (s, 2H), 7.47 (s, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 13.96, 13.99, 14.03, 14.05, 14.08, 22.56, 22.64, 25.59, 25.64, 25.93, 26.00, 28.07, 29.03, 29.10, 31.52, 31.78, 68.99, 69.01, 69.41, 106.86, 106.90, 112.71, 112.73, 112.75, 124.27, 124.31, 130.98, 131.00, 149.25, 149.29, 155.47, 179.05, 179.09 (six carbon signals missing/overlapping); MALDI-TOF for [C₄₂H₆₄O₆-H]⁺ calculated (found): 665.48 (665.45) ; Elemental analysis (%) for C₄₂H₆₄O₆ calculated (found): C, 75.86 (75.89); H, 9.70 (9.85).
Benzil 4.16 was synthesized by Johan Foster and oxidized to the corresponding quinone Q(8,10)

2,3-Didecyloxy-6,7-dioctyloxyphenanthrene-9,10-dione Q(8,10)

3,4-Didecyloxy-3’4’-dihexyloxybenzil (1.00 g, 1.28 mmol) was dissolved in dry CH₂Cl₂ (100 mL) under a nitrogen atmosphere in an ice/water bath. BF₃•Et₂O (0.410 g, 2.89 mmol, 0.39 mL) was added using a syringe and the mixture was allowed to stir for about ten minutes. VOF₃ (g, mmol) was then added and the mixture was stirred for two hours. The reaction mixture was poured over an aqueous citric acid solution (10g/100 mL) and allowed to stir for another hour. The solution was extracted by dichloromethane three times (75 mL) and the extracts were combined and washed with water (200 mL) two times and brine (150 mL) once. The organic phase was dried over MgSO₄, filtered and evaporated. The product was purified by column chromatography (DCM) to yield a red solid (0.810 g, 1.04 mmol, 81 %). mp: 79-81 °C. ¹H NMR (500 MHz, CDCl₃) δ 0.86-0.90 (m, 12H), 1.27-1.42 (m, 40H), 1.43-1.49 (m, 4H), 1.50-1.54 (m, 4H), 1.79-1.85 (m, 4H), 1.86-1.91 (m, 4H), 3.99 (t, 4H, J = 6.5 Hz), 4.15 (t, 4H, J = 6.3 Hz), 6.98 (s, 2H), 7.37 (s, 2H); MALDI-TOF for [C₅₀H₈₀O₆-H]⁺ calculated (found): 777.60 (777.88).
6.3.3 Synthesis of diamine derivatives

Scheme 6.5: Synthesis of symmetrical diamine derivatives. i) RBr, K$_2$CO$_3$, DMF (3.10a, 3.10b, 3.10c); ii) HNO$_3$ (3.17a, 3.17b, 3.17c); iii) SnCl$_2$, HCl, EtOH (3.18a, 3.18b, 3.18c).

\[
\begin{align*}
\text{HOH} & \xrightarrow{i} \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{H} \quad \text{N} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{OH} \\
\end{align*}
\]

3.10a: R = C$_6$H$_{13}$
3.10b: R = C$_6$H$_{17}$
3.10c: R = C$_{16}$H$_{31}$
3.17a: R = C$_6$H$_{13}$
3.17b: R = C$_6$H$_{17}$
3.17c: R = C$_{16}$H$_{31}$
3.18a: R = C$_6$H$_{13}$
3.18b: R = C$_6$H$_{17}$
3.18c: R = C$_{16}$H$_{31}$

A(6)

1,2-Dihexyloxybenzene (3.10a)

Catechol (10.0 g, 90.8 mmol) and bromohexane (30.0 g, 26 mL, 181 mmol) were mixed in DMF (200 mL) and nitrogen was bubbled through the solution for 15 minutes. K$_2$CO$_3$ (50.2 g, 363 mmol) was added and nitrogen was bubbled for another 10 minutes. The solution was heated at 130 °C for four days and then cooled to room temperature. Water (200 mL) was added and the solution was extracted three times with dichloromethane (75 mL). The organic layers were combined and washed with water (150 mL) three times, then brine (150 mL). The solution was dried over MgSO$_4$, filtered and evaporated. The product was purified by column chromatography (100 % hexanes to 100 % DCM) to yield a clear oil (26.0 g, 82.6 mmol, 91 %). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.89-0.93 (m, 6H), 1.33-1.37 (m, 8H), 1.47-1.50 (m, 4H), 1.81-1.84 (m, 4H), 3.97-4.04 (m, 4H), 6.90 (s, 4H); MS-EI for [C$_{18}$H$_{30}$O]$^+$ calculated (found) 278.2 (278.2)
1,2-Dihexyloxy-4,5-dinitrobenzene (Reaction performed by Cvijeta Stojanović)\textsuperscript{207} (3.17a)

1,2-Dihexyloxybenzene (19.9 g, 71.5 mmol) was mixed with nitric acid (90 mL) and cooled in an ice/water bath. The solution was stirred for 30 minutes, and then heated at 85 °C for two hours. The reaction mixture was cooled to room temperature and poured over a saturated solution of sodium bicarbonate (500 mL). Once the bubbling stopped, the precipitate was filtered, washed with water and air-dried. The product was recrystallized in hot ethanol to yield a yellow powder (20.5 g, 55.8 mmol, 78\%\).\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 0.90-0.92 (m, 6H), 1.33-1.37 (m, 8H), 1.46-1.51 (m, 4H), 1.84-1.89 (m, 4H), 4.10 (t, 4H, \(J = 6.6\) Hz), 7.29 (s, 2H); mp: 99-101 °C.

A(8)

1,2-Dioctyloxybenzene (3.10b)

Catechol (15.0 g, 136 mmol) and bromooctane (92.1 g, 82 mL, 477 mmol) were mixed in DMF (100 mL) and nitrogen was bubbled through the solution for ten minutes. \(\text{K}_2\text{CO}_3\) (75.2 g, 544 mmol) was added and nitrogen was bubbled for another five minutes. The solution was heated at 90 °C for 24 hours then cooled to room temperature. Water (100 mL) was added and the solution was extracted three times with dichloromethane (75 mL). The organic layers were combined and washed with water three times (150 mL), then brine (150 mL). The solution was dried over MgSO\textsubscript{4}, filtered and evaporated. The product was purified by column chromatography (100 % hexanes to 100 % DCM) to
yield a white solid (28.8 g, 86.2 mmol, 63 %); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.88-0.91 (m, 6H), 1.30-1.39 (m, 12H), 1.45-1.51 (m, 4H), 1.79-1.85 (m, 4H), 4.00 (t, 4H, $J = 6.8$ Hz), 6.89 (s, 4H).

1,2-Dioctyloxy-4,5-dinitrobenzene (3.17b)

1,2-Dioctyloxybenzene (5.28 g, 15.8 mmol) was mixed with nitric acid (75 mL) and cooled in an ice/water bath. The solution was stirred for 60 minutes, and then heated at 85 °C for 2 hours. The reaction mixture was cooled to room temperature and poured over a saturated solution of sodium bicarbonate (500 mL). Once the bubbling stopped, the precipitate was filtered, washed with water and air-dried. The product was recrystallized in hot ethanol to yield a yellow powder (4.69 g, 11.1 mmol, 70 %). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.87-0.90 (m, 6H), 1.26-1.38 (m, 16H), 1.45-1.49 (m, 4H), 1.84-1.90 (m, 4H), 4.10 (t, 4H, $J = 6.5$ Hz), 7.29 (s, 2H).

A(10) (3.10c)

Didecyloxybenzene was synthesized by Johan E. Foster and used without purification.

1,2-Didecyloxy-4,5-dinitrobenzene (3.17c)

1,2-Didecyloxybenzene (4.00 g, 10.2 mmol) was mixed with nitric acid and cooled in an ice/water bath. The solution was stirred for 60 minutes, and then heated at 85 °C for two hours. The reaction mixture was cooled to room temperature and poured over
a saturated solution of sodium bicarbonate (500 mL). Once the bubbling stopped, the precipitate was filtered, washed with water and air-dried. The product was recrystallized in hot ethanol to yield a yellow powder (3.13 g, 6.52 mmol, 64%). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.87-0.90 (m, 6H), 1.27-1.37 (m, 24H), 1.44-1.50 (m, 4H), 1.84-1.90 (m, 4H), 4.10 (t, 4H, $J$ = 6.5 Hz), 7.29 (s, 2H).

A(6,10)

Scheme 6.6: Synthesis of unsymmetrical diamine derivative A(6,10): i) C$_{10}$H$_{21}$Br, NBu$_4$Br, K$_2$CO$_3$, butanone (3.19); ii) C$_6$H$_{13}$Br, NBu$_4$Br, K$_2$CO$_3$, butanone (3.20); iii) HNO$_3$ (3.21); SnCl$_2$, HCl, EtOH (3.22).

Catechol (5.00 g, 45.4 mmol), tetrabutylammonium bromide (0.305 g, 0.946 mmol) and bromodecane (8.37 g, 37.8 mmol, 7.8 mL) were dissolved in butanone (200 mL) and N$_2$ was bubbled through the solution for 15 minutes. K$_2$CO$_3$ (5.18 g, 37.5 mmol) was added and the solution was purged for another ten minutes prior to be heated at reflux overnight. The solution was cooled to room temperature and HCl (20 %) was added until the effervescence stopped. Dichloromethane was added (150 mL) and the two
phases were separated. The aqueous phase was extracted twice with DCM (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was purified over silica (96/4 hexanes/ethyl acetate) to yield a clear oil (2.76 g, 11.0 mmol, 29%). ¹H NMR (500 MHz, CDCl₃) δ 0.89 (t, 3 H, J = 7 Hz), 1.28-1.39 (m, 12 H), 1.43-1.49 (m, 2 H), 1.79-1.84 (m, 2H), 4.03 (t, 2H, J = 6.8 Hz), 5.65 (s, 1H), 6.83-6.88 (m, 3H), 6.92-6.94 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.10, 22.66, 26.01, 29.24, 29.29, 29.36, 29.53, 29.55, 31.87, 68.87, 111.58, 114.39, 120.05, 121.26, 145.79, 145.95; MS-EI for [C₁₆H₂₆O₂] calculated (found): 250.2 (250.2); HR-MS for [C₁₆H₂₆O₂-H]⁺ calculated (found): 251.2007 (251.2011).

1-Decyloxy-2-hexyloxybenzene (3.20)

2-Decyloxyphenol (4.00 g, 16.0 mmol), bromohexane (3.43 g, 20.8 mmol) and tetrabutylammonium bromide (0.258 g, 0.80 mmol) were dissolved in butanone (100 mL) and N₂ was bubbled through the solution for 15 minutes. K₂CO₃ (5.74 g, 41.6 mmol) was added and the solution was purged for another ten minutes prior to being heated at reflux overnight. The solution was cooled to room temperature and HCl (20 %) was added until the effervescence stopped. DCM (100 mL) was added and the two phases were separated. The aqueous phase was extracted twice with DCM (50 mL) and the organic layers were combined. The organic phase was washed with water (150 mL) then brine (100 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was used without further purification as a clear oil (4.81 g, 14.4 mmol, 90%). ¹H NMR (500 MHz, CDCl₃)
δ 0.89-0.94 (m, 6H), 1.29-1.40 (m, 16H), 1.46-1.52 (m, 4H), 1.80-1.85 (m, 4H), 4.0-4.02 (m, 4H), 6.88-6.91 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 14.00, 14.08, 22.60, 22.66, 25.70, 26.03, 29.29, 29.33, 29.42, 29.55, 29.61, 31.60, 31.88, 69.21, 114.05, 120.95, 149.21 (5 carbon signals missing/overlapping); MS-EI for [C₂₂H₃₈O₂] calculated (found) 334.3 (334.4) M; HR-MS for [C₂₂H₃₈O₂-H]⁺ calculated (found): 335.2950 (335.2950).

1-Decyloxy-2-hexyloxy-4,5-dinitrobenzene (3.21)

1-Decyloxy-2-hexyloxybenzene (5.28 g, 15.8 mmol) was mixed with HNO₃ (50 mL), cooled in an ice/water bath and stirred for 90 minutes. The mixture was warmed to room temperature and stirred for 30 minutes. The reaction mixture was heated at 85 °C for two hours. The solution was cooled to room temperature and slowly poured over a NaHCO₃ saturated solution (500 mL) and stirred until the effervescence stopped. The solid was filtered, washed with water and air-dried. The yellow solid was purified by recrystallisation in hot anhydrous ethanol (4.44 g, 10.5 mmol, 66 %). ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.93 (m, 6H), 1.23-1.39 (m, 16H), 1.45-1.51 (m, 4H), 1.84-1.89 (m, 4H), 4.09-4.11 (m, 4H), 7.29 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 13.97, 14.12, 22.54, 22.69, 25.48, 25.82, 28.66, 28.71, 29.24, 29.33, 29.53, 29.54, 31.38, 31.90, 70.20, 107.87, 136.48, 151.80 (4 signals missing/overlapping); MS-EI for [C₂₂H₆₆N₂O₆] calculated (found) 424.3 (424.2); HR-MS for [C₂₂H₆₆N₂O₆-H]⁺ calculated (found): 425.2652 (425.2651).
6.3.4 Synthesis of hexaalkoxydibenzo[a,c]phenazine derivatives

General procedure for the formation of hexaalkoxydibenzo[a,c]phenazine derivatives:

1,2-Dialkoxy-4,5-dinitrobenzene (0.81 mmol) was reduced to the diamine by heating at 80 °C in 25 mL of ethanol with SnCl₂ (5.7 mmol) and concentrated HCl (4 mL) for six to eight hours. The solution was cooled to room temperature, poured over concentrated HCl (60 mL). The precipitate was filtered, washed with water and air-dried. The solid was immediately mixed with 2,3,6,7-tetrakis-alkoxy-phenanthrene-9,10-dione (0.15 mmol) and sodium acetate (3.0 mmol) in anhydrous ethanol (50 mL). The mixture was heated at reflux overnight. Once the mixture was cooled down, water (50 mL) was added and the mixture was extracted with DCM (40 mL) three times. The organic phases were combined and washed with water (100 mL) twice and then brine (100 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was purified by column chromatography (silica gel, 92:8 hexanes/ethyl acetate) to afford a yellow solid after recrystallization from CH₂Cl₂/MeOH.
Q(6,6)A(8): 2,3,6,7-tetrahexyloxy-11,12-dioctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene (0.530 g, 1.25 mmol) was reduced as above as the diamine and condensed with 2,3,6,7-tetrahexyloxyphenanthrene-9,10-dione (0.130 g, 0.214 mmol) to yield a yellow solid (0.147 g, 0.157 mmol, 73 %). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.91-0.97 (m, 18H), 1.33-1.43 (m, 60H), 1.55-1.59 (m, 12H), 1.94-1.97 (m, 12H), 4.20 (t, 4H, $J$ = 6.5 Hz), 4.23 (t, 4H, $J$ = 6.5 Hz), 4.31 (t, 4H, $J$ = 6.5 Hz), 7.46 (s, 2H), 7.67 (s, 2H), 8.67 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.06, 14.08, 14.12, 22.65, 22.67, 22.69, 25.82, 25.84, 26.09, 28.94, 29.29, 29.35, 29.38, 31.66, 31.68, 31.83, 69.03, 69.11, 69.62, 106.43, 106.73, 107.91, 124.18, 125.65, 139.11, 139.44, 149.31, 150.94, 152.72 (1 carbon signal missing/overlapping); MALDI-TOF for [C$_{60}$H$_{92}$N$_2$O$_6$H$^+$] calculated (found): 937.70 (937.03); Elemental analysis (%) for C$_{60}$H$_{92}$N$_2$O$_6$ calculated (found): C, 76.88 (76.56); H, 9.89 (9.89); N, 2.99 (3.28).

Q(6,8)A(6): 2,3,11,12-tetrahexyloxy-6,7-dioctyloxydibenzo[a,c]phenazine:

1,2-Dihexyloxy-4,5-dinitrobenzene (0.405 g, 1.10 mmol) was reduced as above as the diamine and condensed with 2,3-dihexyloxy-6,7-dioctyloxyphenanthrene-9,10-dione (0.130, 0.196 mmol) to yield a yellow solid (0.124 g, 0.132 mmol, 68 %). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.90 (t, 6H, $J = 6.8$ Hz), 0.93-0.96 (m, 12H), 1.32-1.45 (m, 32H), 1.55-1.59 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, $J = 6.8$ Hz), 4.35 (t, 4H, $J = 6.0$ Hz), 7.52 (s, 2H), 7.76 (s, 2H), 8.75 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.03, 14.05, 14.07, 14.11, 14.12, 22.62, 22.65, 22.66, 22.69, 22.70, 25.76, 25.81, 25.84, 26.15, 26.18, 28.90, 29.28, 29.33, 29.34, 29.35, 29.41, 29.46, 29.48, 31.58, 31.66, 31.68, 31.84, 31.85, 69.01,
69.03, 69.09, 69.61, 69.62, 106.40, 106.42, 106.71, 107.90, 107.92, 124.16, 125.64, 139.08, 139.41, 149.29, 150.93, 150.94, 152.70, 152.72 (12 carbon signals missing/overlapping); MALDI-TOF for [C₆₀H₉₂N₂O₆-H]⁺ calculated (found): 937.70 (937.24S); Elemental analysis (%) for [C₆₀H₉₂N₂O₆] calculated (found): C, 76.88, (76.50); H, 9.89, (9.82); N, 2.99, (3.32).

Q(8,8)A(6): 11,12-dihexyloxy-2,3,6,7-tetraoctyloxydibenzo[a,c]phenazine:

1,2-Dihexyloxy-4,5-dinitrobenzene (0.300 g, 0.814 mmol) was reduced as above as the diamine and condensed with 2,3,6,7-tetraoctyloxyphenanthrene-9,10-dione (0.107 g, 0.149 mmol) to yield a yellow solid (0.0922 g, 0.0928 mmol, 62 %). ¹H NMR (500 MHz, CDCl₃) δ 0.90-0.96 (m, 18H), 1.32-1.41 (m, 40H), 1.55-1.62 (m, 12H), 1.95-1.99 (m, 12H), 4.24-4.27 (m, 8H), 4.33 (t, 4H, J = 6.5 Hz), 7.52 (s, 2H), 7.75 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 14.28, 14.37, 22.87, 22.96, 26.02, 26.41, 26.44, 29.17, 29.60, 29.64, 29.69, 29.74, 29.76, 31.84, 32.12, 69.25, 69.32, 69.83, 106.60, 106.93, 108.15, 124.33, 125.86, 139.25, 139.58, 149.50, 151.16, 152.93 (4 carbon signals missing/overlapping); MALDI-TOF for [C₆₄H₁₀₀N₂O₆-H]⁺ calculated (found): 993.77 (994.45); Elemental analysis (%) for C₆₄H₁₀₀N₂O₆ calculated (found): C, 77.37 (77.05); H, 10.15 (10.44); N, 2.82 (3.10).
Q(6,8)A(8): 2,3-dihexyloxy-6,7,11,12-tetraoctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene (0.467 g, 1.10 mmol) was reduced as above as the diamine and condensed with 2,3-dihexyloxy-6,7-dioctyloxyphenanthrene-9,10-dione (0.132 g, 0.196 mmol) to yield a yellow solid (0.115 g, 0.116 mmol, 59%). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.90 (t, 12H, $J=7$Hz), 0.94 (t, 6H, $J=7.0$ Hz), 1.30-1.45 (m, 40H), 1.54-1.60 (m, 12H), 1.94-2.00 (m, 12H), 4.27 (t, 8H, $J=6.5$Hz), 4.35 (t, 4H, $J=6.5$Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 14.05, 14.07, 14.11, 14.15, 22.65, 22.66, 22.68, 22.69, 22.70, 25.81, 25.84, 26.09, 26.15, 26.18, 28.95, 29.29, 29.32, 29.34, 29.35, 29.37, 29.41, 29.46, 29.49, 29.51, 31.66, 31.68, 31.83, 31.84, 31.85, 69.00, 69.01, 69.03, 69.08, 69.59, 69.60, 106.38, 106.38, 106.40, 106.72, 107.89, 107.91, 124.16, 125.62, 139.08, 139.40, 149.26, 149.27, 150.91, 150.92, 152.68. (10 carbon signals missing/overlapping); MALDI-TOF for [C$_{64}$H$_{100}$N$_2$O$_6$-H]$^+$ calculated (found): 993.77 (994.33); Elemental analysis (%) for [C$_{64}$H$_{100}$N$_2$O$_6$] calculated (found): C, 77.37 (77.66); H, 10.15 (10.34); N, 2.89 (2.71).

Q(6,6)A(10): 11,12-didecyloxy-2,3,6,7-tetrahexyloxydibenzo[a,c]phenazine

1,2-Didecyloxy-4,5-dinitrobenzene was reduced as above as the diamine and condensed with 2,3,6,7-tetrahexyloxyphenanthrene-9,10-dione to yield a yellow solid (78%). $^1$H NMR (400 MHz, CDCl$_3$) δ 0.91-2.21 (m, 82H), 4.26 (t, 8H, $J=7.0$ Hz), 4.35 (t, 4H, $J=7.0$ Hz), 7.53 (s, 2H), 7.75 (s, 2H), 8.75 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ(ppm) 14.31, 14.33, 14.38, 22.90, 22.92, 22.95, 26.06, 26.09, 26.36, 29.19, 29.53, 29.59, 29.62, 29.67, 29.84, 29.89, 31.92, 31.93, 32.17, 69.32, 69.40, 69.86, 77.00, 77.26, 77.50,
106.63, 108.18, 149.59 (4 carbon signals missing/overlapping); MALDI-TOF for [C₄₄H₁₀₁N₂O₆-H]⁺ calculated (found): 994 (994); Elemental analysis (%) for [C₄₄H₁₀₁N₂O₆] calculated (found): C, 77.37 (77.14); H, 10.15 (10.05); N, 2.82 (2.90).

**Q(8,8)A(8): 2,3,6,7,11,12-hexaoctyloxydibenzo[a,c]phenazine**

1,2-Dioctyloxy-4,5-dinitrobenzene (0.470 g, 1.1 mmol) was reduced as above as the diamine and condensed with 2,3,6,7-tetraoctyloxyphenanthrene-9,10-dione (0.130 g, 0.180 mmol) to yield a yellow solid (0.147 g, 0.140 mmol, 78%). ¹H NMR (500 MHz, CDCl₃) δ 0.89-0.92 (m, 18H), 1.28-1.47 (m, 52H), 1.55-1.62 (m, 8H), 1.94-2.02 (m, 12H), 4.27 (t, 8H, J = 6.8 Hz), 4.35 (t, 4H, J = 6.8 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 14.02, 14.04, 14.06, 14.16, 22.69, 22.73, 26.10, 26.16, 26.17, 26.19, 28.96, 29.29, 29.34, 29.38, 29.43, 29.46, 31.76, 31.78, 31.83, 31.85, 31.86, 69.07, 69.11, 69.68, 124.23, 125.68, 139.13, 139.46, 149.35, 150.99, 152.75, 170.99. (2 carbon signals missing/overlapping); MALDI-TOF for [C₆₈H₁₀₈N₂O₆-H]⁺ calculated (found): 1049.83 (1049.84). Reported by Ong et al.²²²

**Q(6,8)A(10): 11,12-didecyloxy-2,3-dihexyloxy-6,7-dioctyloxydibenzo[a,c]phenazine**

1,2-Didecyloxy-4,5-dinitrobenzene (0.577 g, 1.2 mmol) was reduced as above as the diamine and condensed with 2,3-dihexyloxy-6,7-dioctyloxyphenanthrene-9,10-dione (0.131 g, 0.196 mmol) to yield a yellow solid (0.125 g, 0.119 mmol, 61%). ¹H NMR (500 MHz, CDCl₃) δ 0.88-0.96 (m, 12H), 0.94 (t, 6H, J = 7Hz), 1.26-1.43 (m, 40H),
1.54-1.63 (m, 12H), 1.94-2.01 (m, 12H), 4.26 (t, 8H, J = 5.5Hz), 4.34 (t, 4H, J = 6.5Hz), 7.52 (s, 2H), 7.76 (s, 2H), 8.75 (s, 2H); 13C NMR (125 MHz, CDCl3) δ 14.06, 14.07, 14.12, 22.65, 22.66, 22.70, 25.82, 25.84, 26.10, 26.18, 28.95, 29.29, 29.34, 29.35, 29.37, 29.41, 29.42, 29.46, 29.49, 29.59, 29.64, 31.66, 31.68, 31.85, 31.86, 31.93, 69.03, 69.10, 69.62, 69.64, 106.43, 106.45, 106.73, 107.91, 107.94, 124.18, 125.65, 139.11, 139.45, 149.30, 149.31, 150.94, 150.95, 152.72 (23 carbon signals missing/overlapping); MALDI-TOF for [C₆H₁₀₈N₂O₆-H]⁺ calculated (found): 1049.83 (1050.43); Elemental analysis (%) for [C₆₈H₁₁₆N₂O₆] calculated (found): C, 77.81, (78.10); H, 10.37, (10.65); N, 2.67, (2.93).

Q(8,8)A(10): 11,12-didecyloxy-2,3,6,7-tetraoctyloxydibenzo[a,c]phenazine

1,2-Didecyloxy-4,5-dinitrobenzene (0.450 g, 0.940 mmol) was reduced as above as the diamine and condensed with 2,3,6,7-tetraoctyloxyphenanthrene-9,10-dione (0.130 g, 0.180 mmol) to yield a yellow solid (0.108 g, 0.0974 mmol, 54 %). 1H NMR (500 MHz, CDCl3) δ 0.88-0.92 (m, 18H), 1.30-1.44 (m, 60H), 1.56-1.58 (m, 12H), 1.96-1.99 (m, 12H), 4.26 (t, 8H, J = 6.5 Hz), 4.34 (t, 4H, J = 6.5 Hz), 7.52 (s, 2H), 7.76 (s, 2H), 8.75 (s, 2H); 13C-NMR (125 MHz, CDCl3) δ 14.38, 22.96, 26.36, 26.42, 26.46, 29.24, 29.62, 29.65, 29.66, 29.71, 29.76, 29.78, 29.87, 29.92, 32.12, 32.13, 32.20, 69.22, 69.30, 69.80, 106.53, 106.94, 108.12, 124.33, 125.83, 139.24, 139.56, 149.45, 151.12, 152.88 (6 carbon signals missing/overlapping); MALDI-TOF for [C₇₂H₁₁₆N₂O₆-H]⁺ calculated
Q(8,10)A(8): 6,7-didecyloxy-2,3,11,12-tetraoctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene (0.300 g, 0.707 mmol) was reduced as above as the diamine and condensed with 2,3-didecyloxy-6,7-dioctyloxyphenanthrene-9,10-dione (0.100 g, 0.129 mmol) to yield a yellow solid (0.063 g, 0.0570 mmol, 44%). ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.92 (m, 18H), 1.25-1.47 (m, 60H), 1.54-1.61 (m, 12H), 1.93-2.01 (m, 12H), 4.26 (t, 8H, J = 6.5 Hz), 4.34 (t, 4H, J = 6.5 Hz), 7.52 (s, 2H), 7.75 (s, 2H), 8.75 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 14.12, 22.70, 26.09, 26.16, 26.18, 28.95, 29.29, 29.34, 29.36, 29.38, 29.42, 29.47, 29.49, 29.51, 29.54, 29.62, 29.69, 31.83, 31.84, 31.93, 69.05, 69.11, 69.63, 106.44, 106.69, 107.96, 124.09, 125.66, 149.31, 150.97, 152.74 (31 carbon signals missing/overlapping); MALDI-TOF for [C₇₂H₁₁₆N₂O₆H]⁺ calculated (found): 1105.89 (1105.84); Elemental analysis (%) for [C₇₂H₁₁₆N₂O₆] calculated (found): C, 78.21 (78.43); H, 10.57 (10.80); N, 2.53 (2.38).

Q(10,10)A(8): 2,3,6,7-tetradecyloxy-11,12-dioctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene (0.424 g, 1.0 mmol) was reduced as above as the diamine and condensed with 2,3,6,7-tetradecyloxyphenanthrene-9,10-dione (0.150 g, 0.180 mmol) to yield a yellow solid (0.0682 g, 0.0587 mmol, 33%). ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.92 (m, 18H), 1.28-1.47 (m, 68H), 1.54-1.62 (m, 20H), 1.94-2.02 (m,
12H), 4.27 (t, 8H, J = 6.5 Hz), 4.34 (t, 4H, J = 6.5 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 14.12, 22.69, 22.70, 26.09, 26.16, 26.18, 28.95, 29.29, 29.36, 29.38, 29.39, 29.42, 29.51, 29.55, 29.62, 29.69, 31.83, 31.93, 69.03, 69.09, 69.63, 106.44, 106.44, 106.73, 107.93, 124.17, 125.64, 139.09, 139.43, 149.30, 150.94, 152.70 (7 carbon signals missing/overlapping); MALDI-TOF for [C$_{76}$H$_{124}$N$_2$O$_{6}$-H$^+$] calculated (found): 1161.95 (1161.40); Elemental analysis (%) for [C$_{76}$H$_{124}$N$_2$O$_6$] calculated (found): C, 78.57 (78.77); H, 10.76 (10.91); N, 2.41 (2.38).

Q(8,10)A(10): 2,3,11,12-tetradecyloxy-6,7-dioctyloxydibenzo[a,c]phenazine.

1,2-Didecyloxy-4,5-dinitrobenzene (0.529 g, 1.10 mmol) was reduced as above as the diamine and condensed with 2,3-decyloxy-6,7-dioctyloxyphenanthrene-9,10-dione (0.139 g, 0.180 mmol) to yield a yellow solid (0.0746 g, 0.042 mmol, 36%). $^1$H NMR (500 MHz, CDCl$_3$) δ 0.87-0.91 (m, 18H), 1.26-1.47 (m, 68H), 1.54-1.62 (m, 20H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, J = 6.8 Hz), 4.35 (t, 4H, J = 6.5 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 14.12, 22.70, 26.10, 26.16, 26.18, 28.96, 29.34, 29.36, 29.37, 29.39, 29.43, 29.46, 29.49, 29.51, 29.54, 29.60, 29.62, 29.64, 29.69, 31.85, 31.86, 31.926, 31.933, 69.03, 69.10, 69.63, 106.45, 106.73, 107.93, 124.18, 125.64, 139.10, 139.43, 149.30, 150.94, 152.71 (23 carbon signals missing/overlapping); MALDI-TOF for [C$_{76}$H$_{124}$N$_2$O$_6$-H$^+$] calculated (found): 1161.95 (1161.41); Elemental analysis (%) for [C$_{76}$H$_{124}$N$_2$O$_6$] calculated (found): C, 78.57, (78.24); H, 10.76, (11.03); N, 2.41, (2.64).
Q(8,8)A(6,10): 12-decyloxy-11-hexyloxy-2,3,6,7-tetraoctyloxydibenzo[a,c]-phenazine.

1-Decyloxy-2-hexyloxy-4,5-dinitrobenzene was reduced as above as the diamine and condensed with 2,3,6,7-tetraoctyloxyphenanthrene-9,10-dione to yield a yellow solid (79%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 0.90 (m, 15H), 0.94 (t, 3H, $J = 7.2$ Hz), 1.25-1.46 (m, 48H), 1.54-1.62 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, $J = 6.6$ Hz), 4.34 (t, 4H, $J = 6.6$ Hz), 7.53 (s, 2H), 7.76 (s, 2H), 8.75 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 14.03, 14.11, 22.62, 22.69, 22.70, 25.76, 26.10, 26.16, 26.18, 28.90, 28.96, 29.33, 29.35, 29.41, 29.46, 29.48, 29.58, 29.63, 31.58, 31.84, 31.86, 31.91, 69.07, 69.13, 69.66, 106.49, 106.67, 107.98, 124.08, 125.70, 139.03, 139.37, 149.36, 151.03, 152.81 (7 carbon signals missing/overlapping); MALDI-TOF for [C$_{68}$H$_{108}$N$_2$O$_6$-H]$^+$ calculated (found) 1049.83 (1049.83); Elemental analysis (%) for [C$_{68}$H$_{108}$N$_2$O$_6$] calculated (found): C, 77.81 (77.47); H, 10.37 (10.22); N, 2.67 (2.71).
### 6.3.5 Statistical Calculations

\[ C.I. = \bar{x} \pm \frac{t(\alpha/2, n-1) \cdot s}{\sqrt{n}} \]

For a degree of confidence of 95\%, \( \alpha \) will be equal to 0.05, for a degree of confidence of 99\%, \( \alpha \) will be equal to 0.01. Therefore the values of \( \alpha/2 \) will be 0.025 and 0.005. For a series of 16 comparisons, \( n - 1 \) will be 15. Using an excel spreadsheet, the average and the standard deviation were calculated for \( \Delta T_m \), \( \Delta T_c \) and \( \Delta \text{Range} \). The values for \( t(\alpha/2, n-1) \) were obtained from statistical tables by entering the values for \( \alpha \) (0.025 and 0.005) and \( n-1 \) (15).

<table>
<thead>
<tr>
<th></th>
<th>( \Delta T_m ) (°C)</th>
<th>( \Delta T_c ) (°C)</th>
<th>ALC Range (°C)</th>
</tr>
</thead>
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<tr>
<td><strong>Average</strong></td>
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<td>-3.24</td>
<td>19.81</td>
</tr>
<tr>
<td><strong>Standard deviation (s)</strong></td>
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<td>15.63</td>
<td>21.25</td>
</tr>
<tr>
<td><strong>C.I. (95 %)</strong></td>
<td>-23.8 ± 7.3</td>
<td>-3.2 ± 8.3</td>
<td>19.8 ± 11.3</td>
</tr>
<tr>
<td><strong>C.I. (99 %)</strong></td>
<td>-23.8 ± 10.1</td>
<td>-3.2 ± 11.5</td>
<td>19.8 ± 15.7</td>
</tr>
</tbody>
</table>

\[ t_{(0.025, 15)} = 2.131, \ t_{(0.005, 15)} = 2.947 \]
6.4 Synthesis Chapter 4

6.4.1 Synthesis of the dialkoxyiodobenzene derivatives

Scheme 6.7: Synthesis of 2-decyloxy-1-hexyloxy-4-iodobenzene (4.5a) and 1-decyloxy-2-hexyloxy-4-iodobenzene (4.5b). i) C₆H₁₃Br, NBu₄Br, K₂CO₃, butanone (4.1a; 4.1b); ii) acetic anhydride, pyridine (4.2a; 4.2b); iii) ICl, CH₂Cl₂ (4.3a; 4.3b); iv) LiOH-H₂O, THF, MeOH, H₂O (4.4a; 4.4b); v) C₁₀H₂₁Br, NBu₄Br, K₂CO₃, butanone (4.5a; 4.5b).

6.4.1.1 2-Decyloxy-1-hexyloxy-4-iodobenzene (4.5a)

2-Hexyloxyphenol (4.1a)

Catechol (10.00 g, 90.8 mmol), bromohexane (15.00 g, 90.8 mmol, 12.8 mL) and tetrabutylammonium bromide (1.46 g, 4.54 mmol) were mixed in butanone and nitrogen was bubbled through the solution for ten minutes. K₂CO₃ (25.10 g, 180 mmol) was added and the solution was purged for an additional five minutes before being heated at reflux...
for 24 hours. The progress of the reaction was followed by TLC (hexanes/ethyl acetate, 96:4) until completion. The mixture was cooled to room temperature, water (150 mL) was added and the phases separated. The organic layer was washed with water (150 mL) twice and then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was purified over silica (hexanes/ethyl acetate: 96/4) to yield a light yellow oil (9.12 g, 47.0 mmol, 52 %). $^1$H NMR (CDCl₃) δ 0.90-0.93 (m, 3H), 1.33-1.37 (m, 4H), 1.44-1.47 (m, 2H), 1.82 (quint. , 2H, $J = 7.1$ Hz), 4.04 (t, 2H, $J = 6.5$ Hz), 5.65 (s, 1H), 6.81-6.88 (m, 3H), 6.92-6.94 (m, 1H); MS-CI for $[C_{12}H_{18}O_2-Cl]^{+}$ calculated (found): 195.1 (195.1).

2-Hexyloxyphenyl acetate (4.2a)

2-Hexyloxyphenol (7.00 g, 36.1 mmol), pyridine (15 mL) and acetic anhydride (15 mL) were mixed and the mixture was heated at reflux overnight. The solution was cooled to room temperature, water was added and the solution was cooled in a water bath for 20 minutes. The aqueous phase was extracted with three portions of dichloromethane (75 mL) and the organic phases were combined. The organic phase was washed with HCl(aq) 10 % until the aqueous phase remained acidic, then with water (150 mL) and brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated to yield a brownish oil (7.97 g, 33.8 mmol, 94 %) that was used without further purification. $^1$H NMR (CDCl₃) δ 0.89-0.92 (m, 3H), 1.31-1.36 (m, 2H), 1.41-1.46 (m, 2H), 1.76 ( quint, 2H, $J = 7.0$ Hz), 2.30 (s, 3H), 3.97 (t, 2H, $J = 6.5$ Hz), 6.91-6.96 (m, 2H), 7.03 (dd, 1H, $J$
= 7.8, 1.5 Hz), 7.46 (dedoubled triplet, 1H, J = 7.8, 1.5 Hz); MS-Cl for [C_{14}H_{20}O_{3}-H]^+ calculated (found): 237.1 (237.1).

2-Hexyloxy-5-iodophenyl acetate (4.3a)

2-(Hexyloxy)phenyl acetate (5.27 g, 22.3 mmol) was mixed in dichloromethane (40 mL) and cooled in an ice/water bath. A solution of iodine monochloride (ICl, 3.98 g, 24.5 mmol, 1.23 mL) in dichloromethane (25 mL) was added slowly to the reaction mixture which was allowed to warm to room temperature and stirred at room temperature for 3 hours. The solution was poured over cold Na$_2$S$_2$O$_3$ (sat) (100 mL) and stirred until the red color disappeared. The phases were separated and the aqueous phase was extracted twice with dichloromethane (50 mL). The organic phases were combined and washed with water (150 mL) twice and then brine (150 mL). The solution was dried over MgSO$_4$, filtered and evaporated to yield a yellow oil (7.28 g, 20.1 mmol, 90%) which was used without further purification. $^1$H NMR (500 MHZ, CDCl$_3$) δ 0.90 (t, 3H, J = 7 Hz), 1.31-1.35 (m, 2H), 1.38-1.44 (m, 2H), 1.74 ( quint, 2H, J = 7.1 Hz), 2.28 (s, 3H), 3.94 (t, 2H, J = 6.5 Hz), 6.70 (d, 1H, J = 8.5 Hz), 7.33 (d, 1H, J = 2 Hz), 7.46 (dd, 1H, J = 8.5, 2 Hz); MS-Cl for [C_{14}H_{19}I_{3}-H]^+ calculated (found): 363.0 (363.0).

2-Hexyloxy-5-iodophenol (4.4a)

2-Hexyloxy-5-iodophenyl acetate (7.20 g, 19.9 mmol) was dissolved in methanol (25 mL), THF (25 mL) and H$_2$O (10) and LiOH•H$_2$O (2.62 g, 62.5 mmol) was added in
one portion. The mixture was allowed to stir at room temperature for four hours. The
solution was poured over cold 10 % HCl (aq) to obtain a solution having pH lower than
seven and the aqueous phase was extracted with three portions of DCM (150 mL). The
organic phases were combined and washed with water (200 mL) and then brine (200
mL). The solution was dried over MgSO₄, filtered and evaporated to yield a brownish oil
(6.11 g, 19.1 mmol, 96 %) that was used without further purification. ¹H NMR (500
MHZ, CDCl₃) δ 0.89-0.92 (m, 3H), 1.32-1.35 (m, 2H), 1.43-1.46 (m, 2H), 1.80 ( quint,
2H, J = 7.1 Hz), 4.00 (t, 2H, J = 6.8 Hz), 5.61 (s, 1H), 6.58 (d, 1H, J = 8.5 Hz), 7.13 (dd,
1H, J = 8.5, 2 Hz), 7.23 (d, 1H, J = 2 Hz); MS-CI for [C₁₂H₁₇I₂O₂] calculated (found):
320.0 (320.0).

2-Decyloxy-1-hexyloxy-4-iodobenzene (4.5a)

2-Hexyloxy-5-iodophenol (6.11 g, 19.1 mmol), bromodecane (4.65 g, 21.0 mmol,
4.35 mL) and tetrabutylammonium bromide (0.50 g, 1.55 mmol) were mixed in butanone
(90 mL) and nitrogen was bubbled through the solution for ten minutes. K₂CO₃ (7.65 g,
42.3 mmol) was added and nitrogen was bubbled for another five minutes before heating
the reaction mixture at reflux overnight. The mixture was cooled to room temperature,
water and CH₂Cl₂ were added (50 mL each) and the phases were separated. The aqueous
phase was extracted twice with DCM (75 mL), the organic phases were combined and the
solution was washed with water (200 mL) and then brine (200 mL). The solution was
dried over MgSO₄, filtered and evaporated to yield a white solid that was recrystalised
from EtOH (7.06 g, 15.3 mmol, 80 %). mp 40-41 °C; ¹H NMR (500 MHz, CDCl₃) δ
0.87-0.91 (m, 6H), 1.27-1.35 (m, 16H), 1.42-1.48 (m, 4H), 1.76-1.83 (m, 4H), 3.93-3.96 (m, 4H), 6.61 (d, 1H, \( J = 8.5 \) Hz), 7.12 (d, 1H, \( J = 2 \) Hz), 7.17 (dd, 1H, \( J = 8.5, 2 \) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 14.00, 14.09, 22.58, 22.65, 25.63, 25.95, 29.12, 29.14, 29.24, 29.31, 31.55, 31.79, 69.32, 69.39, 82.48, 115.66, 122.60, 129.77, 149.20, 150.10; MS-CI for \([C_{22}H_{37}I_{2}O]^{-}\) calculated (found): 461.2 (460.9); Elemental Analysis (%) for \([C_{22}H_{37}I_{2}O]^{-}\) calculated (found): C, 57.39 (57.58); H, 8.10 (8.08).

6.4.1.2 1-Decyloxy-2-hexyloxy-4-iodobenzene (4.5b)

2-Decyloxyphenol (4.1b)

Catechol (5.00 g, 45.4 mmol), NBu\(_4\)Br (0.305 g, 0.946 mmol) and bromodecane (8.37 g, 37.8 mmol, 7.8 mL) were dissolved in butanone (200 mL) and \( N_2 \) was bubbled through the solution for 15 minutes. \( K_2CO_3 \) (5.18 g, 37.5 mmol) was added and the solution was purged for another ten minutes prior to be heated at reflux overnight. The solution was cooled to room temperature and HCl (20 %) was added until the effervescence stopped. Dichloromethane (150 mL) was added and the two phases were separated. The aqueous phase was extracted twice with DCM (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO\(_4\), filtered and evaporated. The product was purified over silica (hexanes/ethyl acetate: 96/4) to yield a clear oil (2.76 g, 11.0 mmol, 29 %). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 0.89 (t, 3 H, \( J = 7 \) Hz), 1.28-1.39 (m, 12 H), 1.43-
1.49 (m, 2 H), 1.79-1.84 (m, 2H), 4.03 (t, 2H, J = 6.8 Hz), 5.65 (s, 1H), 6.83-6.88 (m, 3H), 6.92-6.94 (m, 1H); 13C NMR (150 MHz, CDCl3) δ 14.10, 22.66, 26.01, 29.24, 29.29, 29.36, 29.53, 29.55, 31.87, 68.87, 111.58, 114.39, 120.05, 121.26, 145.79, 145.95; MS-EI for [C16H26O2] calculated (found): 250.2 (250.2); HR-MS for [C16H26O2-H]+ calculated (found): 251.2007 (251.2011).

2-Decyloxyphenyl acetate (4.2b)

2-Decyloxyphenol (2.17 g, 8.70 mmol) was mixed in acetic anhydride (5 mL), pyridine (5 mL) and heated at reflux overnight. The mixture was cooled to room temperature, water (100 mL) was added and the solution was cooled in a room temperature water bath. The aqueous solution was extracted three times with CH2Cl2 (75 ml) and the phases were combined. The organic layer was washed with large amounts of water (400 mL) twice, then brine (200 mL). The solution was dried over MgSO4, filtered and evaporated to yield an amber oil (2.43 g, 8.32 mmol, 96 %) that was used without further purification. 1H NMR (CDCl3, 600 MHz) δ 0.90 (t, 3H, J = 7.2 Hz), 1.29-1.39 (m, 12H), 1.41-1.46 (m, 2H), 1.74-1.79 (m, 2H), 2.31 (s, 3H), 3.97 (t, 2H, J = 6.3 Hz), 6.91-6.97 (m, 2H), 7.03 (dd, 1H, J = 7.8, 1.8 Hz), 7.18 (m, 1H); 13C NMR (150 MHz, CDCl3) δ 14.10, 20.59, 22.67, 25.90, 29.18, 29.31, 29.33, 29.54, 29.58, 31.89, 68.63, 113.40, 120.56, 122.66, 126.78, 140.06, 150.60, 169.03; MS-EI for [C18H28O3] calculated (found): 292.2 (292.1); HR-MS for [C18H28O3-H]+ calculated (found): 293.2116 (293.2119).
2-Decyloxy-5-iodophenyl acetate (4.3b)

2-Decyloxyphenyl acetate (2.11 g, 7.24 mmol) was dissolved in CH₂Cl₂ (15 mL) and the solution was cooled with an ice bath. A mixture of iodine monochloride (ICl, 1.29 g, 7.96 mmol, 0.4 mL) in CH₂Cl₂ (10 mL) was added using a dropping funnel over about 30 minutes. The solution was allowed to warm to room temperature overnight. The reaction mixture was poured over a cold saturated solution of Na₂S₂O₃ (100 mL) and stirred until the red color disappeared. The phases were separated and the aqueous phase was extracted twice with CH₂Cl₂ (75 mL). The organic phases were combined and washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield a yellow oil that was used without further purification (2.93 g, 7.02 mmol, 97 %). ¹H NMR (CDCl₃, 600 MHz) δ 0.88 (t, 3H, J = 7.2 Hz), 1.27-1.34 (m, 12H), 1.38-1.45 (m, 2H), 1.72-1.76 (m, 2H), 2.05 (s, 3H), 3.93 (t, 2H, J = 6.3 Hz), 6.70 (d, 1H, J = 8.4 Hz), 7.33 (d, 1H, J = 2.4 Hz), 7.46 (dd, 1H, J = 8.4, 2.4 Hz);¹³C NMR (CDCl₃, 150 MHz) δ 14.10, 20.44, 22.66, 25.82, 29.02, 29.28, 29.30, 29.52, 29.55, 31.88, 68.81, 81.04, 115.20, 131.46, 135.60, 140.74, 150.81, 168.55; MS-EI for [C₁₈H₂₇IO₃] calculated (found): 418.1 (418.1) ; HR-MS found for [C₁₈H₂₇IO₃-H]⁺ calculated (found): 419.1083 (419.1076).

2-Decyloxy-5-iodophenol (4.4b)

2-Decyloxy-5-iodophenyl acetate (2.77 g, 6.62 mmol) was dissolved in a mixture of MeOH (10 mL), THF (10 mL) and H₂O (5 mL). LiOH•H₂O (0.97 g, 23.16 mmol) was added in one portion and the mixture was stirred at room temperature overnight. HCl (20
% was added until the pH was acidic and the aqueous solution was extracted three times with CH₂Cl₂ (75 mL). The organic layers were combined and washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield a yellow oil that was used without further purification (2.01 g, 5.35 mmol, 81%).

¹H NMR (CDCl₃, 600 MHz) δ 0.88 (t, 3H, J = 6.9 Hz), 1.27-1.37 (m, 12 H), 1.41-1.47 (m, 2H), 1.77-1.82 (m, 2H), 4.0 (t, 2H, J = 6.6 Hz), 5.6 (s, 1H), 6.58 (d, 1H, J = 8.4 Hz), 7.13 (dd, 1H, J = 8.4, 2.4 Hz), 7.23 (d, 1H, J = 2.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 14.10, 22.66, 25.93, 29.07, 29.28, 29.31, 29.51, 29.55, 31.86, 69.06, 82.75, 113.34, 123.32, 128.96, 146.03, 146.71; MS-EI for [C₁₆H₂₅I₂O₂] calculated (found) 376.1 (376.1); HR-MS for [C₁₆H₂₅I₂O₂-H]+ calculated (found): 377.0977 (377.0977).

1-Decyloxy-2-hexyloxy-4-iodobenzene (4.5b)

2-Decyloxy-5-iodophenol (6.11 g, 16.2 mmol), NBu₄Br (0.262 g, 0.811 mmol) and bromohexane (4.02 g, 24.3 mmol, 3.4 mL) were dissolved in butanone (200 mL) and N₂ was bubbled through the solution for 15 minutes. K₂CO₃ (6.73 g, 48.7 mmol) was added and the solution was purged for another ten minutes prior to being heated at reflux overnight. The solution was cooled to room temperature and 20% HCl was added until the effervescence stopped. Dichloromethane (100 mL) was added and the two phases were separated. The aqueous phase was extracted twice with CH₂Cl₂ (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was recrystallized with ethanol, filtered and air-dried to yield a white solid (5.38 g, 11.7
mmol, 72 %). mp: 38-40 °C; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 0.87-0.92 (m, 6H), 1.26-1.36 (m, 16H), 1.42-1.49 (m, 4H), 1.76-1.82 (m, 4H), 3.95 (t, 4H, \(J = 6.6\) Hz), 6.61 (d, 1H, \(J = 8.4\) Hz), 7.12 (d, 1H, \(J = 1.8\) Hz), 7.18 (dd, 1H, \(J = 8.4, 1.8\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 14.01, 14.10, 22.59, 22.68, 25.63, 25.97, 29.11, 29.17, 29.33, 29.38, 29.55, 29.59, 31.53, 31.89, 69.33, 69.40, 82.48, 115.67, 122.61, 129.78, 149.22, 150.11; MS-EI for [C\(_{22}\)H\(_{37}\)O\(_2\)I] calculated (found): 460.2 (460.3); HR-MS for [C\(_{22}\)H\(_{37}\)I0\(_2\)-H\(^+\)] calculated (found): 461.1916 (461.1911).

### 6.4.2 Synthesis of the quinones

#### 6.4.2.1 Synthesis acetylene precursors 4.7a and 4.7b

Scheme 6.8: Formation of the free acetylene from the 1,2-dialkoxy-4-iodobenzene derivatives 4.5a and 4.5b. i) TMS-acetylene, CuI, PdCl\(_2\)(PPh\(_3\))\(_2\), (i-Pr\(_2\))\(_2\)NH, THF (4.6a; 4.6b); ii) K\(_2\)CO\(_3\), THF, MeOH (4.7a; 4.7b).

\[\text{R}_1 = \text{C}_6\text{H}_{13}, \quad \text{R}_2 = \text{C}_6\text{H}_{13}\]

\[\text{R}_1 = \text{C}_6\text{H}_{13}, \quad \text{R}_2 = \text{C}_6\text{H}_{13}\]

\[\text{R}_1 = \text{C}_6\text{H}_{13}, \quad \text{R}_2 = \text{C}_6\text{H}_{13}\]

\[\text{R}_1 = \text{C}_6\text{H}_{13}, \quad \text{R}_2 = \text{C}_6\text{H}_{13}\]

\[\text{R}_1 = \text{C}_6\text{H}_{13}, \quad \text{R}_2 = \text{C}_6\text{H}_{13}\]

\[\text{R}_1 = \text{C}_6\text{H}_{13}, \quad \text{R}_2 = \text{C}_6\text{H}_{13}\]
2-(3-Decyloxy-4-hexyloxyphenyl)ethynyl-trimethylsilane (4.6a)

2-Decyloxy-1-hexyloxy-4-iodobenzene (4.00 g, 8.69 mmol), CuI (0.497 g, 2.61 mmol) and PdCl₂(PPh₃)₂ (0.153, 0.217 mmol) were mixed in a round bottom flask and submitted to three cycles of vacuum/N₂. (i-Pr)₂NH (85 mL) and TMS-Acetylene (10.2 g, 104 mmol, 14.7 mL) were added to the solids and N₂ was bubbled for 15 minutes. The reaction mixture was heated at 60 °C for 24 hours, and then cooled to room temperature. H₂O and HCl_(conc.) were added until the pH was acidic. The aqueous phase was extracted with CH₂Cl₂ (100 mL) three times and the organic phases were combined, washed with water (200 mL) and brine (200 mL). The organic phase was dried over MgSO₄, filtered and evaporated. The crude black oil was purified over silica (hexanes/ethyl acetate: 96:4) to yield a brownish oil that was used without further purification (3.30 g, 7.66 mmol, 88 %). ¹H NMR (500 MHz, CDCl₃) δ 0.24 (s, 9H), 0.87-0.91 (m, 6H), 1.27-1.36 (m, 16H), 1.42-1.48 (m, 4H), 1.81 (quint., 4 H, J = 7.1 Hz), 3.96-3.99 (m, 4H), 6.76 (d, 1H, J = 8 Hz), 6.96 (d, 1H, J = 2Hz), 7.03 (dd, 1H, J = 8, 2 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 0.06, 14.01, 14.11, 22.59, 22.68, 25.64, 25.99, 29.12, 29.20, 29.33, 29.38, 29.56, 29.60, 31.57, 31.90, 69.07, 69.17, 92.04, 105.47, 112.98, 115.12, 116.88, 125.40, 148.53, 149.83; MS-Cl for [C₂₇H₄₆O₂Si-H]⁺ calculated (found): 431.5 (431.3); HR-MS for [C₂₇H₄₆O₂Si-H]⁺ calculated (found): 431.3345 (431.3343).

3-Decyloxy-1-ethynyl-4-hexyloxybenzene (4.7a)

2-(3-Decyloxy-4-hexyloxyphenyl)ethynyltrimethylsilane (3.13 g, 7.69 mmol) was dissolved in MeOH (45 mL) and THF (45 mL). K₂CO₃ (2.66 g, 19.2 mmol) was added
and the mixture was stirred at room temperature for three hours and TLC (hexanes 100 %) indicated total conversion of the starting material. The reaction mixture was poured over silica, washed with DCM and evaporated to yield a dark brown oil that was used without further purification in the next step (2.65 g, 7.39 mmol, 74 %). \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 0.87-0.92 (m, 6H), 1.27-1.36 (m, 16H), 1.43-1.49 (m, 4H), 1.79-1.83 (m, 4H), 2.98 (s, 1H), 3.96-4.00 (m, 4H), 6.79 (d, 1H, \( J = 8.5 \) Hz), 6.99 (d, 1H, \( J = 2 \) Hz), 7.06 (dd, 1H, \( J = 8.5, 2 \) Hz); \( ^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 14.1, 22.66, 22.68, 26.10, 26.04, 29.24, 29.29, 29.33, 29.35, 29.36, 29.53, 29.55, 31.87, 31.91, 68.87, 69.27, 111.58, 114.09, 114.39, 120.05, 120.98, 121.26, 145.79, 145.95; MS-CI for \([\text{C}_{24}\text{H}_{38}\text{O}_2]\) calculated (found): 358.3 (358.4); HR-MS for \([\text{C}_{24}\text{H}_{38}\text{O}_2-\text{H}]^+\) calculated (found): 359.2950 (359.2941).

2-(4-Decyloxy-3-hexyloxybenzene)ethynyl-trimethylsilane (4.6b)

4-Decyloxy-3-hexyloxyiodobenzene (3.62 g, 7.86 mmol), trimethylsilaneacetylene (7.47 g, 76.0 mmol, 10.7 mL) and \((\text{i-Pr})_2\text{NH}\) (19.2 g, 190 mmol, 27 mL) were mixed in THF (100 mL). N\(_2\) was bubbled through for ten minutes at room temperature. Cul (0.435 g, 2.29 mmol) and \(\text{PdCl}_2(\text{PPh}_3)_2\) (0.133 g, 0.190 mmol) were added and the solution was purged with \(\text{N}_2\) for another ten minutes. The solution was stirred at room temperature for one hour, and then heated at 80 °C for 24 hours. The mixture was cooled to room temperature and poured onto a short silica column that was then washed with DCM. The organic phase was washed twice with water (150 mL), then brine (200 mL). The solution was dried over MgSO\(_4\), filtered and evaporated. The
product was purified by column chromatography (hexanes/ethyl acetate; 98/2) to yield a brown oil (3.34 g, 7.75 mmol, 98 %). $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 0.18 (s, 9H), 0.78-0.90 (m, 6H), 1.17-1.55 (m, 20 H), 1.69-1.80 (m, 4H), 3.86-3.98 (m, 4H), 6.65-7.15 (m, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 0.10, 14.05, 14.14, 22.64, 22.71, 25.69, 26.00, 29.18, 29.36, 29.43, 29.51, 29.58, 29.62, 31.59, 31.93, 69.10, 69.20, 92.08, 105.50, 113.00, 115.15, 116.90, 125.43, 148.56, 149.86; MS-EI for [C$_{27}$H$_{46}$O$_2$Si-H]$^+$ calculated (found): 431.3 (431.5); HR-MS for [C$_{27}$H$_{46}$O$_2$Si-H]$^+$ calculated (found): 431.3345 (431.3347).

1-Decyloxy-4-ethynyl-2-hexyloxybenzene (4.7b)

2-Trimethylsilaneethynyl-4-decyloxy-3-hexyloxybenzene (3.25 g, 7.55 mmol) was dissolved in MeOH (50 mL) and THF (50 mL). K$_2$CO$_3$ (2.61 g, 18.88 mmol) was added in one portion and the mixture was stirred at room temperature overnight and TLC (98/2, hexanes/Ethyl acetate) showed completion of the reaction. The mixture was filtered on silica and washed with DCM. The product was obtained as a brown oil (2.41 g, 6.71 mmol, 89 %) that was used as is in the next step. $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 0.87-0.92 (m, 6H), 1.22-1.37 (m, 16H), 1.43-1.49 (m, 4H), 1.79-1.83 (m, 4H), 2.98 (s, 1H), 3.96-4.00 (m, 4H), 6.79 (d, 1H, $J = 7.8$ Hz), 6.99 (d, 1H, $J = 1.8$ Hz), 7.06 (dd, 1H, $J = 7.8, 1.8$ Hz); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 14.00, 14.09, 22.59, 22.67, 25.65, 25.97, 29.12, 29.14, 29.32, 29.38, 29.54, 29.58, 31.55, 31.89, 69.08, 69.21, 83.96, 113.04, 114.01, 117.06, 125.48, 148.61, 150.04; MS-EI for [C$_{24}$H$_{38}$O$_2$-H]$^+$ calculated (found): 359.3 (359.3); HR-MS for [C$_{24}$H$_{38}$O$_2$-H]$^+$ calculated (found): 359.2946 (359.2950).
6.4.2.2 Synthesis of $Q_{\text{wide}}$ and $Q_{\text{long}}$

Scheme 6.9: Synthesis of $Q_{\text{wide}}$ and $Q_{\text{long}}$. i) CuI, Pd(PPh$_3$)$_4$, (i-Pr)$_2$NH, THF (4.8a = 46%; 4.8b = 82%); ii) I$_2$, DMSO (4.9a = 91%; 4.9b = 92%); iii) VOF$_3$, BF$_3$-Et$_2$O, CH$_2$Cl$_2$ ($Q_{\text{wide}}$ = 69%; $Q_{\text{long}}$ = 72%).

3,3'-Didecyloxy-4,4'-dihexyloxydiphenylacetylene (4.8a)

2-Decyloxy-4-ethynyl-1-hexyloxybenzene (1.21 g, 3.36 mmol), 2-decyloxy-1-hexyloxy-4-iodobenzene (1.70 g, 3.70 mmol) and CuI (0.194 g, 1.02 mmol) were put in a round-bottom flask (250 mL) and subjected to three vacuum/nitrogen cycles. Pd(PPh$_3$)$_4$ (0.196 g, 0.170 mmol) was added, the flask was purged twice with nitrogen and (i-Pr)$_2$NH (70 mL, previously degassed with N$_2$) was added. The mixture was stirred for 30
minutes at room temperature and then at reflux overnight. The solution was cooled to room temperature and HCl\textsubscript{(conc.)} was added until the pH of the solution was acidic. DCM (100 mL) was added and the two phases were separated. The aqueous phase was extracted twice with DCM (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) and then brine (200 mL). The solution was dried over MgSO\textsubscript{4}, filtered and evaporated. Column chromatography (hexanes/dichloromethane: 50/50) and recrystallization with hot hexanes afforded a beige solid (1.07 g, 1.55 mmol, 46 %). mp: 85-87 °C; \textsuperscript{1}H NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 0.87-0.92 (m, 12H), 1.24-1.38 (m, 32H), 1.44-1.51 (m, 8H), 1.82 (quint., 8H, \(J = 7.1\) Hz), 3.98-4.02 (m, 8H), 6.81 (d, 2H, \(J = 8.5\) Hz), 7.02 (d, 2H, \(J = 2\) Hz), 7.07 (dd, 2H, \(J = 8.5, 2\) Hz); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 14.01, 14.10, 22.60, 22.68, 25.66, 26.01, 29.15, 29.21, 29.34, 29.40, 29.56, 29.61, 31.58, 31.90, 69.13, 69.19, 87.94, 113.25, 115.61, 116.51, 124.70, 148.69, 149.42; MALDI-TOF for \([C_{46}H_{74}O_{4}-H]^+\) calculated (found) 691.57 (691.59).

Elemental Analysis (%) for \([C_{46}H_{74}O_{4}]\) calculated (found): C, 79.95 (80.02); H, 10.79 (10.43).

3,3'-Didecyloxy-4,4'-dihexyloxybenzil (4.9a)

3,3'-Decyloxy-4,4'-dihexyloxydiphenylacetylene (1.00 g, 1.45 mmol) and I\textsubscript{2} (0.735 g, 2.89 mmol) were dissolved in DMSO (40 mL) and the mixture was heated at reflux for three hours, then allowed to cool down to room temperature overnight. The mixture was poured over a saturated solution of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (300 mL) and stirred until the solution was cool and the red colour disappeared. The aqueous phase was extracted three
times with DCM (75 mL) and the organic phases were combined. The organic phase was washed with large amounts of water (350 mL) three times and then with brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was recrystallized in hot hexanes to yield a light yellow solid (1.03 g, 1.42 mmol, 91 %). mp: 100 °C (DSC: 95-103 ° C) ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.91 (m, 12H), 1.27-1.37 (m, 32 H), 1.44-1.50 (m, 8H), 1.81-1.87 (m, 8H), 4.04-4.07 (m, 8H), 6.84 (d, 2H, J = 8.5 Hz), 7.43 (dd, 2H, J = 8.5, 2 Hz), 7.56 (d, 2H, J = 2 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 13.98, 14.08, 22.56, 22.65, 25.56, 25.63, 25.89, 25.96, 28.88, 29.02, 29.23, 29.30, 31.50, 31.79, 69.10, 69.20, 111.55, 112.23, 126.11, 126.16, 149.27, 154.96, 193.81; MALDI-TOF for [C₄₆H₇₄O₆] calculated (found): 722.55 (722.65); Elemental Analysis (%) for [C₄₆H₇₄O₆] calculated (found): C, 76.41 (76.78); H, 10.32 (10.24).

2,7-Didecyloxy-3,6-dihexyloxyphenanthrene-9,10-dione (Qwide)

In a dry two-necked round-bottom flask, 3,3’-didecyloxy-4,4’-dihexyloxybenzil (2.00 g, 2.77 mmol) was dissolved in dry dichloromethane (150 mL) and cooled to 0 °C. BF₃•Et₂O (0.883 g, 0.79 mL, 6.22 mmol) was added with a syringe and the mixture was allowed to stir for 5 minutes. VOF₃ (1.20 g, 9.68 mmol) was then added and the reaction mixture was stirred at room temperature for 60 minutes. The solution was then poured over a citric acid aqueous solution (10 g, 100 mL) and allowed to stir for 15 minutes then poured in a separatory funnel. The organic phase was removed and the aqueous layer was extracted with dichloromethane (75 mL). The organic phases were combined, washed with water (200 mL) and brine (200 mL). The solution was dried over MgSO₄, filtered
and evaporated. The solid obtained was purified over silica (93/7; dichloromethane/hexanes) to remove any remaining starting material. The product was recrystallized in hot hexanes to yield a red solid (1.38 g, 1.91 mmol, 69 %). mp: 80-81 °C; 1H NMR (500 MHz, CDCl₃) δ 0.87-0.94 (m, 12H), 1.27-1.38 (m, 32 H), 1.41-1.56 (m, 8H), 1.81-1.93 (m, 8H), 4.04 (t, 4H, J = 6.5 Hz); 4.07 (t, 4H, J = 6.5 Hz), 7.10 (s, 2H), 7.52 (s, 2H); 13C NMR (150 MHz, CDCl₃) δ 14.01, 14.13, 22.60, 22.70, 25.67, 25.98, 29.04, 29.08, 29.36, 29.38, 29.57, 29.61, 31.55, 31.92, 69.20, 69.58, 107.26, 113.06, 124.55, 131.19, 149.57, 179.25; MALDI-TOF for [C₄₆H₇₂O₆-H]+ calculated (found): 721.54 (721.67); Elemental Analysis (%) for [C₄₆H₇₂O₆] calculated (found): C, 76.62 (76.31); H, 10.06 (10.08).

4,4'-didecyloxy-3,3'-dihexyloxydiphenylacetylene (4.8b)

4-Decyloxy-1-ethynyl-3-hexyloxybenzene (2.26 g, 6.31 mmol), 1-decyloxy-2-hexyloxy-4-iodobenzene (3.49 g, 7.57 mmol) and CuI (0.361 g, 1.89 mmol) were mixed with tetrahydrofuran (100 mL) and (i-Pr)₂NH (4 mL) in a 2-necked round-bottom flask (250 mL). Nitrogen was bubbled through the solution for 15 minutes. Pd(PPh₃)₄ (0.365 g, 0.316 mmol) was added and the nitrogen was bubbled for another ten minutes. The solution was heated at reflux 24 hours. The solution was cooled to room temperature and filtered on silica (washed with CH₂Cl₂). The solution was poured in a separatory funnel and the organic phase was washed with HCl (20 %) until the pH of the aqueous phase remained acidic. The organic layer was then washed with water (200 mL) twice, then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid
was recrystallized with hexanes to afford a beige solid (3.55 g, 5.14 mmol, 82%). mp: 94-95 ºC; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 0.87-0.92 (m, 12H), 1.27-1.37 (m, 32H), 1.44-1.50 (m, 8H), 1.79-1.85 (m, 8H), 4.00 (t, 8H, \(J = 6.6\) Hz), 6.82 (d, 2H, \(J = 8.4\) Hz), 7.02 (d, 2H, \(J = 1.8\) Hz), 7.07 (dd, 2H, \(J = 8.4, 1.8\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 14.05, 14.14, 22.64, 22.71, 25.71, 26.02, 29.20, 29.23, 29.36, 29.44, 29.59, 29.63, 31.60, 31.93, 69.16, 69.22, 87.97, 113.28, 115.64, 116.54, 124.73, 148.71, 149.46; MALDI-TOF for [C\(_{46}\)H\(_{74}\)O\(_4\)-H]\(^+\) calculated (found): 691.57 (691.56); Elemental Analysis (%) for [C\(_{46}\)H\(_{74}\)O\(_4\)] calculated (found): C, 79.95 (80.12); H, 10.79 (10.67).

**4,4'-Didecyloxy-3,3'-dihexyloxybenzil (4.9b)**

4,4'-Didecyloxy-3,3'-dihexyloxydiphenylacetylene (2.03 g, 2.94 mmol) and I\(_2\) (1.49 g, 5.87 mmol) were dissolved in DMSO (100 mL). The mixture was heated at reflux for three hours and allowed to cool down to room temperature overnight. Water (100 mL) and CH\(_2\)Cl\(_2\) (100 mL) were added in order to dissolve the solid formed. The two phases were separated and the organic phase was washed with a Na\(_2\)S\(_2\)O\(_3\) (200 mL) saturated solution, then with large amounts of water (350 mL) three times, and then brine (200 mL). The solution was dried over MgSO\(_4\), filtered and evaporated. The product was recrystallized in hot hexanes to yield a white solid (1.96 g, 2.71 mmol, 92%). mp: 90-91 ºC; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 0.87-0.92 (m, 12H), 1.26-1.37 (m, 32H), 1.44-1.50 (m, 8H), 1.81-1.86 (m, 8H), 4.04-4.07 (m, 8H), 6.85 (d, 2H, \(J = 8.4\) Hz), 7.43 (dd, 2H, \(J = 8.4, 2.4\) Hz), 7.56 (d, 2H, \(J = 2.4\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 14.01, 14.10, 22.59, 22.67, 25.63, 25.90, 28.91, 29.00, 29.32, 29.52, 29.56, 31.53, 31.88, 69.10, 69.21,
111.55, 112.23, 126.11, 126.17, 149.27, 154.96, 193.81 (1 carbon signal missing/overlapping); MALDI-TOF for [C_{46}H_{74}O_{6}-H]^+ calculated (found): 723.56 (723.57); Elemental Analysis (%) for [C_{46}H_{74}O_{6}] calculated (found): C, 76.41 (76.51); H, 10.32 (10.32).

3,6-didecyloxy-2,7-dihexyloxyphenanthrene-9,10-dione (Q_{long})

4,4'-Didecyloxy-3,3'-dihexyloxybenzil (1.31 g, 1.81 mmol) was dissolved in dry CH_2Cl_2 (150 mL) in a two-necked round-bottom flask under nitrogen. The mixture was cooled down in an ice/water bath and BF_3•Et_2O (0.64 g, 4.52 mmol, 0.81 mL) was added with a syringe. The solution was allowed to stir for about ten minutes and VOF_3 (0.78 g, 6.32 mmol) was added. The reaction was allowed to stir at room temperature for 90 minutes. The solution was poured over a citric acid solution (10 g for 100 mL of water) and stirred for 20 minutes. The two phases were separated and the organic layer was washed with water (150 mL) twice, then water (150 mL). The solution was dried over MgSO_4, filtered and evaporated. The solid was purified on a silica column (100 % DCM) and recrystallized in hot acetone to yield a red solid (0.94 g, 1.30 mmol, 72 %). mp: 79-80 °C; ^1H NMR (CDCl_3, 600 MHz) δ 0.87-0.93 (m, 12H), 1.27-1.42 (m, 32H), 1.48-1.54 (m, 8H), 1.82-1.87 (m, 4H), 1.88-1.92 (m, 4H), 4.07 (t, 4H, J = 6.6 Hz), 4.19 (t, 4H, J = 6.3 Hz), 7.11 (s, 2H), 7.54 (s, 2H); 13C NMR (CDCl_3, 150 MHz) δ 14.01, 14.10, 22.59, 22.68, 25.62, 26.00, 28.97, 29.12, 29.34, 29.39, 29.55, 29.60, 31.52, 31.89, 69.16, 69.55, 107.22, 113.02, 124.51, 131.16, 149.50, 155.58, 179.24; MS-ESI for [C_{46}H_{72}O_{6}-H]^+
calculated (found) 721.5 (721.5); Elemental Analysis (%) for [C_{46}H_{72}O_6] calculated (found): C, 76.62 (76.31); H, 10.06 (10.08).

6.4.2.3 Synthesis of \( Q_{\text{mix}} \)

Scheme 6.10: Synthesis of \( Q_{\text{mix}} \). i) CuI, Pd(PPh_3)_4, (i-Pr)NH, THF (4.8c); ii) I_2, DMSO (4.9c); iii) VOF_3, BF_3-Et_2O, CH_2Cl_2 (\( Q_{\text{mix}} \)).
3,4'-Didecyloxy-3',4-dihexyloxydiphenylacetylene (4.8c)

1-Decyloxy-4-ethynyl-2-hexyloxybenzene (2.55 g, 7.10 mmol), 2-decyloxy-1-hexyloxy-4-iodobenzene (3.95 g, 8.58 mmol) and CuI (0.412 g, 2.16 mmol) were mixed with tetrahydrofuran (100 mL) and (i-Pr)₂NH (three mL) in a two-necked round-bottom flask (250 mL). Nitrogen was bubbled through the solution for 15 minutes. Pd(PPh₃)₄ (0.410 g, 0.355 mmol) was added and the nitrogen was bubbled for another ten minutes. The solution was heated at reflux for 24 hours. The solution was cooled to room temperature and filtered on silica (washed with CH₂Cl₂). The solution was poured in a separatory funnel and the organic phase was washed with 20 % HCl until the pH of the aqueous phase remained acidic. The organic layer was then washed with water (200 mL) twice, then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was recrystallized with hexanes to afford a beige solid (3.80 g, 5.50 mmol, 77%). mp: 84-85 °C; ¹H NMR (CDCl₃, 400 MHz) δ 0.87-0.92 (m, 32H), 1.27-1.36 (m, 32H), 1.44-1.50 (m, 8H), 1.79-1.84 (m, 8H), 4.01 (t, 8H, J = 4.4 Hz), 6.82 (d, 2H, J = 5.6 Hz), 7.02 (d, 2H, J = 1.2 Hz), 7.07 (dd, 2H, J = 5.6, 1.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 14.02, 14.11, 22.60, 22.61, 22.68, 25.67, 25.68, 26.00, 26.01, 29.16, 29.17, 29.20, 29.22, 29.34, 29.41, 29.57, 29.60, 29.61, 31.58, 31.90, 69.14, 69.19, 87.95, 113.26, 115.61, 116.52, 124.71, 148.69, 149.43 (10 carbon signals missing/overlapping); MS-ESI for [C₄₆H₇₄O₄-H]⁺ calculated (found): 691.6 (691.8); HR-MS for [C₄₆H₇₄O₄-H]⁺ calculated (found): 691.5665 (691.5679).
3,4'-Didecyloxy-3',4-dihexyloxybenzil (4.9c)

3,4'-Didecyloxy-3',4-dihexyloxydiphenylacetylene (3.02 g, 4.38 mmol) and I₂ (2.23 g, 8.79 mmol) were dissolved in DMSO (100 mL). The mixture was heated at reflux for three hours and allowed to cool down to room temperature overnight. Water and CH₂Cl₂ were added in order to dissolve the solid formed. The two phases were separated and the organic phase was washed with a Na₂S₂O₃ (250 mL) saturated solution, then with large amounts of water (350 mL) three times then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was recrystallized in hot hexanes to yield a white solid (2.66 g, 3.68 mmol, 84%). mp: 87-88 °C; ¹H NMR (CDCl₃, 400 MHz) δ 0.87-0.92 (m, 12H), 1.27-1.38 (m, 32H), 1.44-1.50 (m, 8H), 1.81-1.87 (m, 8H), 4.04-4.07 (m, 8H), 6.85 (d, 2H, J = 5.6 Hz), 7.43 (dd, 2H, J = 5.6, 1.2 Hz), 7.56 (d, 2H, J = 1.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.98, 14.01, 14.10, 14.11, 22.56, 22.60, 22.67, 22.68, 25.57, 25.64, 25.91, 25.98, 28.86, 28.91, 29.01, 29.06, 29.32, 29.34, 29.38, 29.53, 29.56, 29.60, 31.49, 31.54, 31.88, 31.90, 69.10, 69.21, 111.55, 112.22, 112.24, 126.12, 126.17, 149.27, 149.28, 154.96, 193.81 (9 carbon signals missing/overlapping); MS-ESI for [C₄₆H₇₄O₆-H]⁺ calculated (found): 723.6 (723.0); HR-MS for [C₄₆H₇₄O₆-H]⁺ calculated (found): 723.5564 (723.5574).

2,6-Didecyloxy-3,7-dihexyloxyphenanthrene-9,10-dione (Qₘᵢₓ)

3,4'-Didecyloxy-3',4-dihexyloxybenzil (2.24 g, 3.10 mmol) was dissolved in dry CH₂Cl₂ (200 mL) in a two-necked round-bottom flask under nitrogen. The mixture was cooled down in an ice/water bath and BF₃•Et₂O (1.10 g, 7.75 mmol, 1.4 mL) was added.
with a syringe. The solution was allowed to stir for about ten minutes and VOF₃ (1.44 g, 11.6 mmol) was added. The reaction was allowed to stir at room temperature for 90 minutes. The solution was poured over a citric acid solution (10 g for 100 mL of water) and stirred for 20 minutes. The two phases were separated and the organic layer was washed with water (150 mL) twice then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was purified on a silica column (100 % DCM) and recrystallized in hot acetone to yield a red solid (1.75 g, 2.43 mmol, 79 %). mp: 69-70 ºC; ¹H NMR (CDCl₃, 400 MHz) δ 0.87-0.89 (m, 6H), 0.90-0.94 (m, 6H), 1.28-1.41 (m, 32H), 1.48-1.55 (m, 8H), 1.82-1.87 (m, 4H), 1.88-1.92 (m, 4H), 4.05-4.08 (m, 4H), 4.17-4.20 (m, 4H), 7.10 (s, 2H), 7.53 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.00, 14.10, 22.58, 22.67, 25.62, 25.65, 25.96, 26.00, 28.97, 29.02, 29.06, 29.12, 29.33, 29.37, 29.39, 29.55, 29.59, 29.60, 31.52, 31.53, 31.89, 69.15, 69.54, 107.20, 112.99, 124.49, 131.14, 149.49, 155.57, 179.22 (9 carbon signals missing/overlapping); MS-ESI for [C₄₆H₇₂O₆-H]⁺ calculated (found): 721.5407 (721.5432); HR-MS for [C₄₆H₇₂O₆-H]⁺ calculated (found): 721.5407 (721.5398).
6.4.2.4 Synthesis of Q(6,10)

Q(6,10) was synthesized from the 4-ido-1,2-dialkoxybenzene derivatives synthesized by Jonathan Sypal-Kohout and Johan E. Foster

Scheme 6.11: Synthesis of Q(6,10): i) CuI, Pd(PPh₃)₄, (i-Pr)₂NH, THF (4.12); ii) I₂, DMSO (4.13); iii) VOF₃, BF₃·Et₂O, DCM (Q(6,10)). Compounds 4.10 and 4.11 were synthesized by Johan Foster.

3,4-Didecyloxy-3',4'-dihexyloxy-diphenylacetylene (4.12)

4-Iodo-1,2-didecyloxybenzene (2.63 g, 5.09 mmol), 1,2-dihexyloxy-4-ethynylbenzene (1.85 g, 6.11 mmol), CuI (0.291 g, 1.53 mmol) and (i-Pr)₂NH (2.0 mL) were mixed in THF (100 mL) in a dry two-necked round-bottom flask. Nitrogen was bubbled through for 15 minutes. Pd(PPh₃)₄ (0.294 g, 0.255 mmol) was added and the solution was purged for another ten minutes. The reaction mixture was heated at reflux for 24 hours then cooled to room temperature. The solution was passed through a short silica column and washed with DCM. The organic solution was washed with 10 % HCl,
water (150 mL) and then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was recrystallized with hexanes to yield a beige solid (1.47 g, 2.13 mmol, 42%). ¹H NMR (400 MHz, CDCl₃) δ 0.87-0.92 (m, 12H), 1.27-1.37 (m, 32H), 1.43-1.53 (m, 8H), 1.77-1.85 (m, 8H), 4.00 (t, 4H, J = 6.8 Hz), 6.82 (d, 1H, J = 8.0 Hz), 7.02 (d, 1H, J = 2.0 Hz), 7.07 (dd, 1H, J = 8.0, 2.0 Hz).

3,4-Didecyloxy-3',4'-dihexyloxybenzil (4.13)¹⁷⁸

3,4 Didecyloxy-3',4'-dihexyloxy-diphenylacetylene (1.46, 2.11 mmol) was mixed with iodine (1.07 g, 4.22 mmol) in DMSO (80 mL). The mixture was heated at reflux for two hours and allowed to cool to room temperature overnight. Water (150 mL) was added and the aqueous solution was extracted three times with DCM (75 mL). The organic layers were combined and washed with a Na₂S₂O₃ saturated solution (150 mL), with water (150 mL) three times then with brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was recrystallized with hexanes to yield a beige solid (1.19 g, 1.64 mmol, 78%). ¹H NMR (400 MHz, CDCl₃) δ 0.86-0.93 (m, 12H), 1.27-1.38 (m, 32H), 1.43-1.51 (m, 8H), 1.80-1.88 (m, 8H), 4.05 (t, 8H, J = 6.6 Hz), 6.85 (d, 2H, J = 8.4 Hz), 7.43 (dd, 2H, J = 8.4, 2.0 Hz), 7.56 (d, 2H, J = 2.0 Hz).

2,3-Didecyloxy-6,7-dihexyloxyphenanthrene-9,10-dione (Q(6,10))¹⁷⁸

3,4-Didecyloxy-3’,4’-dihexyloxybenzil (1.16 g, 1.61 mmol) was dissolved in dry CH₂Cl₂ (100 mL) under a nitrogen atmosphere in a ice/water bath BF₃•Et₂O (0.571 g,
4.02 mmol, 0.72 mL) was added using a syringe and the mixture was allowed to stir for about ten minutes. VOF₃ (0.698 g, 5.63 mmol) was then added and the mixture was stirred for two hours. The reaction mixture was poured over an aqueous citric acid solution (10g/100 mL) and allowed to stir for another hour. The solution was extracted by dichloromethane (75 mL) three times and the extracts were combined and washed with water (200 mL) two times and brine (150 mL). The organic phase was dried over MgSO₄, filtered and evaporated. The product was purified by column chromatography (dichloromethane) to yield a red solid (0.821 g, 1.14 mmol, 71%). Melting point: 67-69 °C. ¹H NMR (500 MHz, CDCl₃) δ 0.86-0.94 (m, 12H), 1.27-1.40 (m, 32H), 1.44-1.55 (m, 8H), 1.80-1.93 (m, 8H), 4.06 (t, 4H, J = 6.6 Hz), 4.19 (t, 4H, J = 6.4 Hz), 7.09 (s, 2H), 7.52 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.98, 14.09, 14.10, 22.57, 22.67, 25.62, 25.65, 25.96, 26.00, 28.98, 29.03, 29.07, 29.13, 29.34, 29.37, 29.39, 29.56, 29.60, 29.61, 31.52, 31.53, 31.90, 69.16, 69.55, 107, 225, 107.231, 107.25, 113.02, 113.04, 124.51, 131.14, 149.50, 155.59, 179.22 (12 carbon signals missing/overlapping); MS-ESI for [C₄₂H₆₄O₆-H]⁺ calculated (found): 721.54 (721.54). HR-MS for [C₄₂H₆₄O₆-H]⁺ calculated (found): 721.5407 (721.5446).
6.4.3 Synthesis of the final compounds

General procedure for the preparation of tetraalkoxydibenzo[a,c]phenazine derivatives:

Tetraalkoxyphenanthrene-9,10-dione and o-phenylenediamine were dissolved in acetic acid (15 mL) and the mixture was heated at reflux overnight. The solution was cooled to room temperature; the solid formed was filtered and washed with a large amount of water (300 mL). The solid was dried under vacuum and recrystallized from DCM/MeOH to yield a bright yellow solid. Amounts used are specified for each compound in the characterization section.

Qwide-A(Ph): 2,7-Didecyloxy-3,6-dihexyloxydibenzo[a,c]phenazine

2,7-Didecyloxy-3,6-dihexyloxyphenanthrene-9,10-dione: 0.115 g, 0.160 mmol; o-phenylenediamine: 0.0690 g, 0.640 mmol; Final product: 0.105 g, 0.133 mmol, 83 %; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 0.87-0.90 (m, 6H), 0.93-0.96 (m, 6H), 1.25-1.47 (m, 32H), 1.60 (quint., 8H, \(J = 7.5\) Hz), 1.95-2.01 (m, 8H), 4.28 (t, 4 H, \(J = 6.5\) Hz), 4.36 (t, 4H, \(J = 6.5\) Hz), 7.75 (s, 2H), 7.79-7.81 (m, 2H), 8.30-8.32 (m, 2H), 8.81 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 14.05, 14.12, 22.65, 22.70, 25.81, 26.17, 29.30, 29.32, 29.38, 29.49, 29.61, 29.68, 31.67, 31.92, 69.15, 69.64, 106.48, 108.74, 123.88, 126.53, 128.97, 129.17, 141.58, 141.91, 149.43, 151.74; MALDI-TOF for [C\(_{52}\)H\(_{76}\)N\(_2\)O\(_4\)-H]\(^+\) calculated (found) 793.6 (793.97); Elemental Analysis (%) for [C\(_{52}\)H\(_{76}\)N\(_2\)O\(_4\)] calculated (found): C, 78.74 (78.80); H, 9.66 (9.55); N, 3.53 (3.34).
**Q_{longA}(Ph): 3,6-Didecyloxy-2,7-dihexyloxydibenzo[a,c]phenazine**

3,6-Didecyloxy-2,7-dihexyloxyphenanthrene-9,10-dione: 0.110 g, 0.153 mmol; *o*-phenylenediamine: 0.0780 g, 0.721 mmol; Final product: 0.0757 g, 0.0954 mmol, 63 %; 

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 0.88 (t, 6H, $J = 7.2$ Hz), 0.995 (t, 6H, $J = 7.2$ Hz), 1.28-1.47 (m, 32H), 1.55-1.63 (m, 8H), 1.95-2.01 (m, 8H), 4.28 (t, 4H, $J = 6.6$ Hz), 4.36 (t, 4H, $J = 6.6$ Hz), 7.74 (s, 2H), 7.80-7.81 (m, 2H), 8.31-8.32 (m, 2H), 8.81 (s, 2H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 14.08, 14.12, 22.67, 22.69, 25.83, 26.15, 29.23, 29.36, 29.37, 29.52, 29.60, 29.67, 31.66, 31.92, 69.12, 69.59, 106.38, 108.65, 123.83, 126.51, 128.98, 129.15, 141.56, 141.89, 149.38, 151.71; MS-ESI for [C$_{52}$H$_{78}$N$_2$O$_4$-H]$^+$ calculated (found): 793.59 (793.59); Elemental Analysis (%) for [C$_{52}$H$_{78}$N$_2$O$_4$] calculated (found): C, 78.74 (79.01); H, 9.66 (9.68); N, 3.53 (3.71).

**Q_{mixA}(Ph): 3,7-Didecyloxy-2,6-dihexyloxydibenzo[a,c]phenazine**

2,6-Didecyloxy-3,7-dihexyloxyphenanthrene-9,10-dione: 0.123 g, 0.171 mmol; *o*-phenylenediamine: 0.0738 g, 0.683 mmol; Final product: 0.113 g, 0.142 mmol, 83 %; 

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 0.89 (t, 6H, $J = 6.9$ Hz), 0.94-0.96 (m, 6H), 1.28-1.47 (m, 32H), 1.58-1.64 (m, 8H), 1.95-2.02 (m, 8H), 4.28 (m, 4H), 4.35 (t, 4H, $J = 6.6$ Hz), 7.74 (s, 2H), 7.79-7.81 (m, 2H), 8.30-8.32 (m, 2H), 8.81 (s, 2H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 14.05, 14.07, 14.12, 22.66, 22.67, 22.69, 25.81, 25.84, 26.15, 26.17, 29.25, 29.30, 29.32, 29.38, 29.50, 29.52, 29.60, 29.61, 29.68, 31.66, 31.67, 31.915, 31.924, 69.14, 69.63, 106.44, 106.46, 108.72, 123.86, 126.52, 128.96, 129.17, 141.57, 141.90, 149.42,
151.74 (16 carbon signals missing/overlapping); MS-ESI for \([C_{52}H_{76}N_2O_4-H]^+\) calculated (found): 793.5883 (793.5856); Elemental Analysis (%) for \([C_{52}H_{76}N_2O_4]\) calculated (found): C, 78.74 (78.44); H, 9.66 (9.73); N, 3.53 (3.82).

Q(8,8)A(Ph): 2,3,6,7-Tetraoctyloxydibenzo[a,c]phenazine

2,3,6,7-Tetraoctyloxyphenanthrene-9,10-dione: 0.0775 g, 0.108 mmol; \(o\)-phenylenediamine: 0.0512 g, 0.473 mmol; Final product: 0.0810 g, 0.102 mmol, 95 %; 
\(^1\)H NMR (CDCl₃, 600 MHz) \(\delta\) 0.89-0.92 (m, 12H), 1.32-1.40 (m, 24H), 1.41-1.47 (m, 8H), 1.57-1.63 (m, 8H), 1.95-2.01 (m, 8H), 4.28 (t, 4H, \(J = 6.6\) Hz), 4.36 (t, 4H, \(J = 6.6\) Hz), 7.74 (s, 2H), 7.80-7.81 (m, 2H), 8.31-8.32 (m, 2H), 8.81 (s, 2H); \(^13\)C NMR (CDCl₃, 150 MHz) \(\delta\) 14.11, 14.12, 22.69, 22.70, 26.15, 26.17, 29.30, 29.33, 29.34, 29.38, 29.46, 29.47, 31.84, 31.86, 69.15, 69.64, 106.48, 108.74, 123.87, 126.53, 128.96, 129.17, 141.91, 149.43, 151.75; MS-ESI for \([C_{52}H_{76}N_2O_4-H]^+\) calculated (found): 793.6 (793.2): Elemental Analysis (%) for \([C_{52}H_{76}N_2O_4]\) calculated (found): C, 78.74 (78.39); H, 9.66 (9.61); N, 3.53 (3.71).

Q(6,10)A(Ph): 2,3-Didecyloxy-6,7-dihexyloxydibenzo[a,c]phenazine

2,3-Didecyloxy-6,7-dihexyloxyphenanthrene-9,10-dione: 0.119 g, 0.165 mmol; \(o\)-phenylenediamine: 0.0786 g, 0.727 mmol; Final product: 0.118 g, 0.148 mmol, 90 %; 
\(^1\)H NMR (CDCl₃, 400 MHz) \(\delta\) 0.87-0.90 (m, 6H), 0.93-0.97 (m, 6H), 1.29-1.48 (m, 32 H), 1.55-1.65 (m, 8 H), 1.94-2.02 (m, 8H), 4.28 (t, 4 H, \(J = 6.2\) Hz), 4.36 (t, 4 H, \(J = 6.4\) Hz),
7.74 (s, 2H), 7.79-7.81 (m, 2H), 8.30-8.33 (m, 2H), 8.81 (m, 2H); $^{13}$C NMR (CDCl₃, 150 MHz) δ 14.04, 14.05, 14.10, 14.11, 22.65, 22.66, 22.69, 25.81, 25.84, 26.16, 26.18, 29.26, 29.31, 29.33, 29.34, 29.38, 29.39, 29.50, 29.52, 29.61, 29.62, 29.68, 29.69, 31.66, 31.67, 31.93, 31.94, 69.17, 69.18, 69.66, 69.67, 106.56, 108.82, 123.91, 126.56, 128.96, 128.97, 129.01, 129.18, 141.60, 141.92, 149.46, 151.78 (5 carbon signals missing/overlapping); MS-ESI for [C₅₂H₇₆N₂O₄] calculated (found): 792.6 (792.9); Elemental Analysis (%) for [C₅₂H₇₆N₂O₄] calculated (found): C, 78.74 (78.67); H, 9.66 (9.73); N, 3.53 (3.81).

**General procedure for the preparation of tetraalkoxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile:**

2,3,6,7-Tetraalkoxyphenanthrene-9,10-dione and diaminomaleonitrile were mixed in acetic acid (25 mL) and nitrogen was bubbled for 15 minutes. The mixture was heated at reflux for 24 hours and then cooled down to room temperature. The solution was poured over ice, water was added and the solution was stirred until the ice was melted. The aqueous solution was extracted with CHCl₃ (50 mL) three times and the layers were combined. The organic phase was washed with water (50 mL) twice, then with brine (75 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was purified on a short silica column (CH₂Cl₂) and TLC showed the presence of only one product. The solid was recrystallized from hot acetone to yield an orange solid. Amounts used are specified for each compound in the characterization section.
**Q widened A (CN):** 6,11-Didecyloxy-7,10-dihexoxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile

2,7-Didecyloxy-3,6-dihexxyloxyphenanthrene-9,10-dione: 0.122 g, 0.169 mmol; diaminomaleonitrile: 0.183 g, 1.69 mmol; Final product: 0.0401 g, 0.0506 mmol, 30 %;  ¹H NMR (CDCl₃, 600 MHz) δ 0.88 (t, 6 H, J = 6.8 Hz), 0.94 (t, 6 H, J = 7 Hz), 1.25-1.46 (m, 24 H), 1.55-1.63 (m, 16 H), 1.94-2.02 (m, 8 H), 4.26 (t, 4 H, J = 6.5 Hz), 4.30 (t, 4 H, J = 6.5 Hz), 7.66 (s, 2 H), 8.40 (s, 2 H) ¹³C NMR (CDCl₃, 150 MHz) δ 14.05, 14.14, 22.65, 22.72, 25.79, 26.13, 29.14, 29.16, 29.40, 29.61, 29.67, 31.63, 31.94, 69.29, 69.51, 105.06, 107.92, 114.45, 120.99, 128.03, 128.28, 141.16, 150.07, 153.81; MALDI-TOF for [C₅₀H₇₂N₄O₄-H]⁺ calculated (found): 793.56 (793.28); Elemental Analysis (%) for [C₅₀H₇₂N₄O₄] calculated (found): C, 75.72 (75.28); H, 9.15 (9.17); N, 7.06 (6.68).

**Q lengthened A (CN):** 3,6-Didecyloxy-2,7-dihexxyloxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile

3,6-Didecyloxy-2,7-dihexxyloxyphenanthrene-9,10-dione: 0.118 g, 0.164 mmol; diaminomaleonitrile: 0.177 g, 1.64 mmol; Final product: 0.0490 g, 0.0618 mmol, 38 %; ¹H NMR (CDCl₃, 600 MHz) δ 0.89 (t, 6 H, J = 6.9 Hz), 0.95 (t, 6 H, J = 6.9 Hz), 1.25-1.47 (m, 32 H), 1.58-1.62 (m, 8 H), 1.95-2.02 (m, 8 H), 4.22 (t, 4 H, J = 6.6 Hz), 4.28 (t, 4 H, J = 6.3 Hz), 7.58 (s, 2 H), 8.28 (s, 2 H); ¹³C NMR (CDCl₃, 150 MHz) δ 14.04, 14.11, 22.64, 22.69, 25.77, 26.14, 29.09, 29.20, 29.37, 29.50, 29.60, 29.66, 31.64, 31.92, 69.22, 69.41, 104.80, 107.69, 114.40, 120.77, 127.89, 128.07, 140.86, 149.91, 153.70;
MS-ESI for \([C_{50}H_{72}N_4O_4-Na]^+\) calculated (found): 815.5 (815.2); Elemental Analysis (%) for \([C_{50}H_{72}N_4O_4]\) calculated (found): C, 75.72 (75.89); H, 9.15 (9.28); N, 7.06 (6.85);

\[\text{Q}_{\text{mix}}A(\text{CN}): 3,6-\text{Didecyloxy-2,7-dihexoxydibenzo}[f,h]\text{quinoidaline2,3-dicarbonitrile}\]

3,6-Didecyloxy-2,7-dihexoxyphenanthrene-9,10-dione: 0.1248 g, 0.173 mmol; diaminomaleonitrile: 0.187 g, 1.73 mmol; Final compound: 0.0169 g, 0.021 mmol, 12 %; 

\(^1\text{H NMR}\) (CDCl\(_3\), 600 MHz) \(\delta\) 0.89 (t, 6 H, \(J = 7.2\) Hz), 0.95 (t, 6 H, \(J = 7.2\) Hz), 1.25-1.46 (m, 32 H), 1.57-1.62 (m, 8 H), 1.95-2.02 (m, 8 H), 4.23-4.25 (m, 4 H), 4.30 (t, 4 H, \(J = 6.6\) Hz), 7.63 (s, 2 H), 8.35 (s, 2 H); \(^13\text{C NMR}\) (CDCl\(_3\), 150 MHz) \(\delta\) 14.03, 14.11, 22.64, 22.69, 25.76, 25.78, 26.11, 26.12, 29.08, 29.13, 29.15, 29.19, 29.365, 29.374, 29.48, 29.59, 29.65, 30.93, 31.62, 31.91, 69.25, 69.45, 104.93, 107.80, 114.41, 120.88, 127.95, 128.17, 141.01, 149.98, 149.99, 153.75 (18 carbon signals missing/overlapping); 

MS-ESI for \([C_{49}H_{68}N_4O_4]^+\) calculated (found): 776.5241 (776.2273); Elemental Analysis (%) for \([C_{50}H_{72}N_4O_4]\) calculated (found): C, 75.72 (75.73); H, 9.15 (9.16); N, 7.06 (6.73).

**General procedure for the preparation of hexaalkoxydibenzo[a,c]phenazine:**

1,2-Alkoxyl-4,5-dinitrobenzene was reduced to the diamine by heating at 80 °C in ethanol (15 mL) with SnCl\(_2\) and concentrated HCl (5 mL) for six to eight hours. The solution was poured over concentrated HCl (80 mL), the precipitate was filtered, washed with water and vacuum dried. The solid was immediately mixed with 2,3,6,7-tetraalkoxyphenanthrene-9,10-dione and sodium acetate in anhydrous ethanol (20 mL).
The mixture was heated at reflux overnight. Once the mixture was cooled down, water (50 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (50 mL) three times. The organic layers were combined and washed with water (100 mL) twice and then brine (100 mL). The solution was dried over MgSO$_4$, filtered and evaporated. The product was purified by column chromatography (silica gel: hexanes/ethyl acetate: 98/2) to afford a yellow solid after recrystallization from CH$_2$Cl$_2$/MeOH. Amounts used are specified for each compound in the characterization section.

**QwideA(6): 2,7-Didecyloxy-3,6,11,12-tetrahexyloxydibenzo[a,c]phenazine**

1,2-Dihexyloxy-4,5-dinitrobenzene: 0.328 g, 0.890 mmol; SnCl$_2$: 1.18 g, 5.7 mmol; 2,7-didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.110 g, 0.153 mmol; sodium acetate: 0.415 g, 3.05 mmol; Final product: 0.083 g, 0.0838 mmol, 55 %; $^1$H NMR (CDCl$_3$, 600 MHz) δ 0.87-0.90 (m, 6H), 0.93-0.95 (m, 12H), 1.25-1.46 (m, 40H), 1.56-1.62 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, $J = 6.6$ Hz), 4.34 (t, 4H, $J = 6.6$ Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 14.03, 14.05, 14.11, 22.62, 22.66, 22.69, 25.76, 25.82, 26.19, 28.91, 29.36, 29.38, 29.50, 29.61, 29.68, 31.58, 31.69, 31.92, 69.05, 69.11, 69.66, 106.51, 106.75, 107.98, 124.21, 125.67, 139.12, 139.46, 149.35, 150.98, 152.75 (1 carbon signal missing/overlapping); MALDI-TOF for [C$_{64}$H$_{100}$O$_6$N$_2$-H]$^+$ calculated (found): 993.766 (993.773); Elemental analysis (%) for [C$_{64}$H$_{100}$O$_6$N$_2$] calculated (found): C, 77.37 (76.99); H, 10.15 (10.10); N, 2.82 (3.06).
Q_{long}A(6): 3,6-Didecyloxy-2,7,11,12-tetrahexyloxydibenzo[a,c]phenazine

1,2-Dihexyloxy-4,5-dinitrobenzene: 0.345 g, 0.937 mmol; SnCl₂: 1.24 g, 6.56 mmol; 3,6-didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.106 g, 0.147 mmol; sodium acetate: 0.401 g, 2.95 mmol; Final product: 0.114 g, 0.115 mmol, 78 %; \(^1\)H NMR (CDCl₃, 600 MHz) \(\delta\) 0.88-0.90 (m, 6H), 0.93-0.96 (m, 12H), 1.29-1.46 (m, 40H), 1.55-1.64 (m, 12H), 1.93-2.02 (m, 12H), 4.27 (t, 8H, \(J = 6.6\) Hz), 4.35 (t, 4H, \(J = 6.6\) Hz), 7.52 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); \(^1^3\)C NMR (CDCl₃, 150 MHz) \(\delta\) 14.02, 14.04, 14.10, 22.62, 22.67, 22.69, 25.77, 25.85, 26.17, 28.92, 29.30, 29.37, 29.43, 29.54, 29.61, 29.68, 31.58, 31.67, 31.92, 69.08, 69.13, 69.69, 106.57, 106.79, 108.05, 124.24, 125.70, 139.14, 139.48, 149.37, 151.01, 152.77; MS-ESI for [C₆₄H₁₀₀N₂O₆-H]⁺ calculated (found): 993.77 (993.76); Elemental Analysis (%) for [C₆₄H₁₀₀N₂O₆] calculated (found): C, 77.37 (77.33); H, 10.15 (10.09); N, 2.82 (3.07);

Q_{mix}A(6): 2,6-Didecyloxy-3,7,11,12-tetrahexyloxydibenzo[a,c]phenazine

1,2-Hexyloxy-4,5-dinitrobenzene: 0.3445 g, 0.935 mmol; SnCl₂: 1.237 g, 6.54 mmol; 2,6-didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.113 g, 0.157 mmol; sodium acetate: 0.4265 g, 3.13 mmol; Final product: 0.0570 g, 0.574 mmol, 37 %; \(^1\)H NMR (CDCl₃, 400 MHz) \(\delta\) 0.87-0.90 (t, 6H, \(J = 6.8\) Hz), 0.92-0.96 (t, 12H, \(J = 7.2\) Hz), 1.29-1.44 (m, 40 H), 1.55-1.62 (m, 12 H), 1.93-2.02 (m, 12 H), 4.27 (t, 8H, \(J = 6.6\) Hz), 4.35 (t, 4 H, \(J = 6.6\) Hz), 7.53 (s, 2 H), 7.77 (s,2H), 8.76 (s, 2 H); \(^1^3\)C NMR (CDCl₃, 100 MHz) \(\delta\) 14.02, 14.05, 14.07, 14.10, 22.61, 22.66, 22.67, 25.76, 25.82, 25.85, 26.16,
26.19, 28.91, 29.30, 29.37, 29.42, 29.50, 29.53, 29.60, 29.67, 31.58, 31.67, 31.69, 31.92, 69.06, 69.07, 69.12, 69.685, 69.690, 69.70, 106.57, 106.78, 106.80, 108.03, 108.04, 124.23, 124.26, 125.69, 139.14, 139.48, 139.54, 139.55, 151.01, 152.76 (15 carbon signals missing/overlapping); MS-ESI for \([C_{64}H_{100}N_2O_6-H]^+\) calculated (found): 993.77 (993.76); Elemental Analysis (%) for \([C_{64}H_{100}N_2O_6]\) calculated (found): C, 77.37 (77.20); H, 10.15 (10.14); N, 2.82 (3.02).

Q\textsubscript{wide}A(8): 2,7-Didecyloxy-3,6-dihexyloxy-11,12-dioctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene: 0.345 g, 0.811 mmol; SnCl\textsubscript{2}: 1.06 g, 5.60 mmol; 2,7-didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.100 g, 0.139 mmol; sodium acetate: 0.378 g, 2.77 mmol; Final product: 0.0978 g, 0.0932 mmol, 67%; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz) \(\delta\) 0.87-0.92 (m, 12H), 0.93-0.95 (m, 6H), 1.28-1.46 (m, 48H), 1.56-1.63 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, \(J = 6.6\) Hz), 4.35 (t, 4H, \(J = 6.6\) Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 150 MHz) \(\delta\) 14.06, 14.11, 22.66, 22.68, 22.69, 25.82, 26.10, 26.19, 28.95, 29.29, 29.36, 29.38, 29.50, 29.61, 29.68, 31.69, 31.83, 31.92, 69.06, 69.12, 69.67, 106.76, 107.99, 124.22, 125.68, 139.13, 139.47, 149.36, 150.98, 152.75 (4 carbon signals missing/overlapping); MALDI-TOF for \([C_{68}H_{108}N_2O_6]\) calculated (found): 1048.821 (1048.820); Elemental Analysis (%) for \([C_{68}H_{108}N_2O_6]\) calculated (found): C, 77.81 (77.79); H, 10.37 (10.21); N, 2.67 (2.42).
Q_{long}(8): 6-Didecyloxy-2,7-dihexyloxy-11,12-dioctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene: 0.545 g, 1.28 mmol; SnCl\textsubscript{2}: 1.11 g, 5.88 mmol; 3,6-didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.118 g, 0.163 mmol; sodium acetate: 0.445 g, 3.27 mmol; Final product: 0.0545 g, 0.0519 mmol, 32 %; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz) δ 0.87-0.92 (m, 12H), 0.95 (t, 6H, J = 6.9 Hz), 1.26-1.46 (m, 46H), 1.55-1.63 (m, 16H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.6 Hz), 7.52 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 150 MHz) δ 14.07, 14.11, 22.67, 22.68, 25.84, 26.09, 26.17, 28.95, 29.29, 29.37, 29.42, 29.53, 29.60, 31.67, 31.83, 69.06, 69.12, 69.66, 106.49, 106.76, 107.98, 124.21, 125.67, 139.13, 139.46, 149.34, 150.98, 152.74 (3 carbon signals missing/overlapping); MS-ESI for [C\textsubscript{68}H\textsubscript{108}N\textsubscript{2}O\textsubscript{6}-H]\textsuperscript{+} calculated (found): 1049.8286 (1049.8228); Elemental Analysis (%) for [C\textsubscript{68}H\textsubscript{108}N\textsubscript{2}O\textsubscript{6}] calculated (found): C, 77.81 (77.33); H, 10.37 (10.36); N, 2.67 (3.11).

Q_{mix}(8): 3,6-Didecyloxy-2,7-dihexyloxy-11,12-dioctyloxydibenzo[a,c]phenazine

1,2-Dioctyloxy-4,5-dinitrobenzene: 0.3491 g, 0.822 mmol; SnCl\textsubscript{2}: 1.10 g, 5.76 mmol; 3,6-didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.113 g, 0.157 mmol; sodium acetate: 0.419 g, 3.08 mmol; Final product: 0.0932 g, 0.0888 mmol, 57 %; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 0.87-0.96 (m, 18 H), 1.25-1.45 (m, 48 H), 1.54-1.65 (m, 12 H), 1.93-2.02 (m, 12 H), 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.4 Hz), 7.53 (s, 2 H), 7.77 (s,2H), 8.35 (s, 2 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ 14.05, 14.10, 22.66, 22.67, 22.68, 22.69, 25.83, 25.85, 26.10, 26.17, 26.20, 28.96, 29.29, 29.37, 29.50, 29.55.
29.53, 29.61, 29.68, 31.67, 31.69, 31.83, 31.92, 69.09, 69.13, 69.70, 69.71, 106.57, 106.80, 108.065, 108.073, 124.25, 124.26, 125.49, 125.70, 139.15, 139.49, 149.38, 149.40, 149.51, 151.01, 151.02, 152.77 (12 carbon signals missing/overlapping); MS-ESI for \([C_{68}H_{108}N_2O_6-H]^+\) calculated (found): 1049.83 (1049.81); Elemental Analysis (%) for \([C_{68}H_{108}N_2O_6]\) calculated (found): C, 77.81 (77.71); H, 10.37 (10.28); N, 2.67 (3.07).

\[Q_{longA(6,10)}: 3,6,11-Tridecyloxy-2,7,12-trihexyloxydibenzo[a,c]phenazine\]

1-Decyloxy-2-hexyloxy-4,5-dinitrobenzene: 0.547 g, 1.29 mmol; SnCl\(_2\): 1.70 g, 9.00 mmol; 3,6-didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.116 g, 0.160 mmol; sodium acetate: 0.436 g, 3.20 mmol; Final product: 0.0945 g, 0.0900 mmol, 56 %; \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 0.87-0.90 (m, 9H), 0.94-0.96 (m, 9H), 1.28-1.46 (m, 48H), 1.55-1.63 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, \(J = 6.6\) Hz), 4.35 (t, 4H, \(J = 6.6\) Hz), 7.52 (s, 2H), 7.76 (s, 2H), 8.76 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 14.03, 14.07, 14.11, 22.63, 22.67, 22.69, 25.76, 25.84, 26.10, 26.17, 28.90, 28.96, 29.29, 29.36, 29.37, 29.42, 29.54, 29.58, 29.60, 29.23, 29.68, 31.58, 31.67, 31.92, 69.05, 69.11, 69.65, 106.48, 106.75, 107.97, 124.20, 125.67, 139.12, 139.45, 149.33, 150.97, 152.74 (5 carbon signals missing/overlapping); MS-ESI for \([C_{68}H_{108}N_2O_6-H]^+\) calculated (found): 1049.8286 (1049.8235); Elemental Analysis (%) for \([C_{68}H_{108}N_2O_6]\) calculated (found): C, 77.81 (77.92); H, 10.37 (10.41); N, 2.67 (3.00).
QWideA(6,10): 2,7,11- Tridecyloxy-3,6,12-trihexyloxydibenzo[a,c]phenazine

1-Decyl-2-hexyloxy-4,5-dinitrobenzene: 0.342 g, 0.806 mmol; SnCl₂: 1.06 g, 5.61 mmol; 2,7-didecyloxy-3,6-dihexyloxy-phenanthrene-9,10-dione: 0.108 g, 0.150 mmol; sodium acetate: 0.380 g, 2.77 mmol; Final product: 0.122 g, 0.116 mmol, 77 %; 

¹H NMR (CDCl₃, 600 MHz) δ 0.87-0.90 (m, 9H), 0.93-0.95 (m, 9H), 1.28-1.46 (m, 48H), 1.55-1.62 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.6 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 14.11, 14.05, 14.11, 22.63, 22.66, 22.69, 25.76, 25.81, 26.11, 26.19, 28.90, 28.96, 29.36, 29.38, 29.42, 29.50, 29.58, 29.61, 29.63, 29.68, 31.58, 31.69, 31.92, 69.05, 69.11, 69.66, 106.51, 106.76, 107.98, 124.22, 125.67, 139.13, 139.46, 149.35, 150.97, 152.74 (6 aliphatic carbon signals missing/overlapping); MALDI-TOF for [C₆₃H₁₀₈N₂O₆] calculated (found): 1049.829 (1049.860); Elemental Analysis (%) for [C₆₃H₁₀₈N₂O₆] calculated (found): C, 77.81 (77.68); H, 10.37 (10.30); N, 2.67 (2.74).

QWideA(10): 2,7,11,12-Tetradecyloxy-3,6-dihexyloxydibenzo[a,c]phenazine

1,2-Didecyloxy-4,5-dinitrobenzene: 0.408 g, 0.850 mmol; SnCl₂: 1.12 g, 5.95 mmol; 2,7-didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.108 g, 0.150 mmol; sodium acetate: 0.378 g, 2.77 mmol; Final product: 0.0637 g, 0.0576 mmol, 42 %; ¹H NMR (CDCl₃, 600 MHz) δ 0.87-0.90 (m, 12H), 0.93-0.95 (m, 6H), 1.26-1.46 (m, 56H), 1.56-1.62 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.6 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 14.06, 14.12,
22.66, 22.69, 25.82, 26.10, 26.19, 28.96, 29.36, 29.38, 29.42, 29.50, 29.59, 29.61, 29.64, 29.68, 31.69, 31.92, 69.06, 69.12, 69.67, 106.52, 106.77, 107.99, 124.23, 125.68, 139.14, 139.47, 149.36, 150.99, 152.76 (5 carbon signals missing/overlapping); MALDI-TOF for 
$[C_{72}H_{116}N_2O_6-H]^+$ calculated (found): 1105.891 (1105.900); Elemental Analysis (%) for 
$[C_{72}H_{116}N_2O_6]$ calculated (found): C, 78.21 (78.14); H, 10.57 (10.45); N, 2.53 (2.32).

$Q_{long A}(10)$: 3,6,11,12-Tetradecyloxy-2,7-dihexyloxydibenzo[a,c]phenazine

1,2-Didecyloxy-4,5-dinitrobenzene: 0.437 g, 0.910 mmol; SnCl$_2$: 1.20 g, 6.37 mmol; 3,6-didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.107 g, 0.149 mmol; sodium acetate: 0.405 g, 2.97 mmol; Final product: 0.0584 g, 0.0528 mmol, 36 %; $^1$H NMR (CDCl$_3$, 600 MHz) δ 0.89 (t, 12H, $J = 6.8$ Hz), 0.95 (t, 6H, $J = 7.2$ Hz), 1.29-1.45 (m, 56H), 1.54-1.64 (m, 12H), 1.93-2.02 (m, 12H), 4.27 (t, 8H, $J = 6.6$ Hz), 4.35 (t, 4H, $J = 6.6$ Hz), 7.52 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 14.05, 14.09, 22.67, 22.69, 25.86, 26.11, 26.18, 28.98, 29.32, 29.36, 29.37, 29.42, 29.46, 29.54, 29.59, 29.61, 29.64, 29.68, 31.68, 31.92, 69.12, 69.15, 69.74, 106.67, 106.85, 108.17, 124.29, 125.73, 139.16, 139.50, 149.41, 151.06, 152.80 (3 carbon signals missing/overlapping); MS-ESI for $[C_{72}H_{116}N_2O_6-H]^+$ calculated (found): 1105.8912 (1105.8862); Elemental Analysis (%) for $[C_{72}H_{116}N_2O_6]$ calculated (found): C, 78.21 (78.20); H, 10.57 (10.54); N, 2.53 (2.75).
Q_{mix}A(10): 3,6,11,12-Tetradecyloxy-2,7-dihexyloxydibenzo[a,c]phenazine

1,2-Didecyloxy-4,5-dinitrobenzene: 0.4378 g, 0.911 mmol; SnCl\textsubscript{2}: 0.861 g, 4.55 mmol; 3,6-Didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.110 g, 0.153 mmol; sodium acetate: 0.416 g, 3.06 mmol; Final product: 0.0805 g, 0.0728 mmol, 48 %; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \delta 0.87-0.90 (m, 12 H), 0.95 (t, 6H, J = 7.0 Hz), 1.29-1.48 (m, 58 H), 1.53-1.65 (m, 12 H), 1.93-2.03 (m, 12 H), 4.27 (t, 8H, J = 6.4 Hz), 4.35 (t, 4 H, J = 6.6 Hz), 7.52 (s, 2 H), 7.76 (s,2H), 8.76 (s, 2 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \delta 13.97, 14.10, 22.67, 22.69, 25.85, 26.10, 26.17, 28.97, 29.31, 29.36, 29.37, 29.42, 29.44, 29.54, 29.59, 29.61, 29.64, 29.68, 31.67, 31.92, 69.08, 69.12, 69.13, 69.69, 106.57, 106.78, 106.80, 108.06, 124.25, 125.70, 139.14, 139.48, 149.37, 151.01, 152.77 (23 carbon signals missing/overlapping); MS-ES for [C\textsubscript{72}H\textsubscript{116}N\textsubscript{2}O\textsubscript{6}-H\textsuperscript{+}] calculated (found): 1105.8912 (1105.8997); Elemental Analysis (%) for [C\textsubscript{72}H\textsubscript{116}N\textsubscript{2}O\textsubscript{6}] calculated (found): C, 78.21 (78.26); H, 10.57 (10.55); N, 2.53 (2.80);

Q(10,10)A(4): 11,12-Dibutyloxy-2,3,6,7-tetradecyloxydibenzo[a,c]phenazine

1,2-Dibutyloxy-4,5-dinitrobenzene: 0.331 g, 1.06 mmol; SnCl\textsubscript{2}: 1.40 g, 7.42 mmol; 2,3,6,7-Tetradecyloxyphenanthrene-9,10-dione: 0.122 g, 0.147 mmol; sodium acetate: 0.399 g, 2.93 mmol; Final product: 0.066 g, 0.0629 mmol, 43 %; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 0.87-0.90 (m, 12 H), 1.06 (t, 6H, J = 7.4 Hz), 1.29-1.45 (m, 48H), 1.57-1.64 (m, 12H), 1.95-2.01 (m, 12H), 4.25-4.30 (m, 8H), 4.35 (t, 4H, J = 6.6 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 13.90, 14.11, 19.34,
22.69, 26.17, 26.19, 29.37, 29.38, 29.43, 29.50, 29.54, 29.62, 29.69, 31.00, 31.93, 68.85, 69.09, 69.71, 106.60, 106.81, 108.07, 124.25, 125.71, 139.14, 139.49, 149.39, 151.02, 152.78 (6 carbon signals missing/overlapping); MS-ESI for [C₆₈H₁₀₈N₂O₆-H]⁺ calculated (found): 1049.8 (1049.4); Elemental analysis (%) for [C₆₈H₁₀₈N₂O₆] calculated (found):
C: 77.81 (77.98); H: 10.37 (10.42); N: 2.67 (2.87).
APPENDIX 1: OXIDATIVE AND ELECTROCHEMICAL SYNTHESIS OF TRIPHENYLENE DERIVATIVES

Introduction

This chapter describes a study that was carried out in our laboratory and published in 2008 in Macromolecules (Macromolecules, 2008, 41, 2994-2997). This study was prompted by a paper published in 2006 by Xu and co-workers in which they reported the synthesis of polymers obtained electrochemically from 1,2-methylenedioxybenzene (MDB). Based on spectroscopic evidence (NMR, UV-Vis, Fluorescence and FT-IR), the authors claimed that the product they obtained was the poly-orthophenylene derivative (PMDB) from electropolymerisation of MDB as shown in Figure A.1.1. As we will demonstrate, PMDB was not the product obtained by anodic oxidation.

Figure A.1.1: Proposed synthesis of polymethylenedioxybenzene (PMDB) from methylenedioxybenzene (MDB).
Conjugated polymers (CPs) such as PMDB have attracted attention as lightweight and flexible semiconductors that can be readily modified to tune their electrical and optical properties. Polythiophene and polypyrrole CPs have been widely studied but they tend to exhibit limited stability, especially to oxidation. Polymers obtained from benzene derivatives possess good conductivity and are less susceptible to degradation from ambient air than other conjugated polymers. Poly(p-phenylene) and poly(m-phenylene) have been synthesized and characterized, but poly(o-phenylene) CPs have yet to be synthesized and characterized. The polymer that Xu and co-workers claimed to have prepared would have been a potentially significant innovation in the field of conjugated polymers.

The product obtained by Xu et al. exhibited limited solubility compared to the starting material. The product peaks in the \(^1\)H NMR spectrum, which were shifted downfield (larger chemical shift) upon reaction, suggested an increase in conjugation, upon formation of polymeric material. Only three the peaks were observed in the \(^{13}\)C NMR spectrum of the final product. The failure to observe four peaks, as would be expected for this material, was attributed to a reduced peak intensity from losing the attached hydrogen upon polymerization.

The UV-Vis spectrum of MDB showed a maximum absorption at 282 nm. This peak is also present in the spectrum of the obtained product, along with another broad peak at a longer wavelength (300 to 360 nm). This red-shift is an indication that the final
product is more conjugated, consistent with the formation of a polymeric material. The photoluminescence spectra show a peak at 320 nm for the monomer and another at around 400 nm for the final product. This shift is also consistent with a more conjugated system being formed upon anodic oxidation.

Xu and co-workers also presented the FT-IR of the starting materials and of the doped product (PMDB\(^{+}\))(BF\(_4\)). The main features of the spectra of the final products are the presence of peaks confirming the formation of 1,2,4,5-tetrasubstituted benzene rings, which is consistent with the formation of PMDB.

While these pieces of evidence did suggest that the product obtained was PMDB, other crucial characterization data were not reported. The characterization of polymeric material normally includes experiments such as MADLI-TOF, size exclusion chromatography or vapour pressure osmometry to assess the average molecular weight. Xu and co-workers did not present any experiments of this type and some of the results presented were not consistent with the formation of a polymeric material.

The \(^1\)H NMR spectrum presented by Xu and co-workers was characterized by very sharp and well-defined peaks. High molecular weight polymers are known to exhibit proton spectra with broad peaks. Small molecular weight polymers, or oligomers, would produce even broader peaks and the end groups would appear at a distinct chemical shift from the rest of the polymer. Since polymers can adopt a variety of three-dimensional
conformations, the repeating units are found in chemical environments that are slightly different, which will lead to broad peaks. Moreover, oligo-\(\sigma\)-phenylenes tend to adopt helical structures in solution. This type of three-dimensional organization would lead to an upfield shift of the aromatic hydrogen peaks related to MDB. Xu and co-workers reported a downfield shift of the aromatic peaks for the obtained product.

Taken together, these observations suggest that the product Xu et al. obtained was a discrete low molecular weight compound. The most likely candidate is the triphenylene shown in Figure A.1.2, which would arise from the cyclic trimerization of MDB. Triphenylene derivatives have been known for decades and are among the first disc-shaped compounds found to exhibit liquid crystalline phases. Also, it is widely known that catechol (1,2-dihydroxybenzene) derivatives such as MDB can form triphenylene by appropriate chemical or electrochemical oxidation as shown in Figure A.1.3. Platinum and palladium electrodes can favour the electrochemical formation of triphenylene cores. In fact, Simonet and co-workers reported that anodic oxidation of MDB yields a highly insoluble material that they were unable to fully characterize.
The formation of a triphenylene moiety would also be accompanied by an increased conjugation, which would lead to peaks with downfield shifts in the $^1$H NMR spectrum. The peaks in the $^1$H and $^{13}$C NMR spectra reported by Xu et al. are therefore in agreement with the formation of a triphenylene derivative, as are the red shifts observed in the UV-Visible absorption and fluorescence spectra. Triphenylene derivatives previously reported in the literature have properties that are similar to the ones reported by Xu and co-workers.
The same research group subsequently reported the synthesis of an apparently polymeric material via anodic oxidation of \(\text{o-dihydroxybenzene (o-DHB)}\) in a Lewis acid solution (BF\(_3\)-Et\(_2\)O).\(^{252}\) The characterization carried out on this product yielded similar results to those obtained for PMDB. These results were again taken as evidence to confirm the formation of a polymeric material (red shifts in the UV-Vis and fluorescence spectra). Again, some of the key elements of the NMR spectra are not consistent with the formation of a polymeric material, and the lack of mass spectrometry data precludes arguments that a high molecular weight material was formed. Again, the evidence pointed toward the formation of a triphenylene derivative. In this case, the likely product is A.1.1, a common precursor in the synthesis of triphenylene mesogens.\(^{253}\) To establish with certainty whether triphenylene derivatives were formed, we undertook the synthesis of triphenylenes A.1.1 and A.1.2 shown in Figure A.1.4.

![Figure A.1.4: Structure of Triphenylene A.1.1 and A.1.2.](image)

A.1.1

A.1.2

Figure A.1.4: Structure of Triphenylene A.1.1 and A.1.2.
Synthesis of Compounds A.1.1 and A.1.2

Compound A.1.1 is widely known from the literature since it is an important intermediate in the synthesis of hexaalkoxytriphenylene derivatives and was prepared according to literature methods.\textsuperscript{253,254} Veratrole (1,2-dimethoxybenzene) was oxidized in presence of FeCl\textsubscript{3} to obtain 2,3,6,7,10,11-hexamethoxytriphenylene. NMR and mass spectrometry of the resulting solid match the literature values available for this intermediate.\textsuperscript{253} Deprotection in a mixture of acetic acid and hydrobromic acid at reflux produced compound A.1.1 in 82\% yield over 2 steps (Scheme A.1.1). Its identity was confirmed by NMR (\textsuperscript{1}H and \textsuperscript{13}C), MS and FT-IR. The data obtained matches the data reported in the literature.\textsuperscript{152}

Scheme A.1.1: Synthesis of compound A.1.1. \textit{i}) FeCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, 86 \%; \textit{ii}) AcOH/HBr, 95 \%.

As already noted, the detailed characterization of A.1.2 has not previously been reported. We therefore undertook its synthesis using three different approaches. Compound A.1.2 was obtained in 54 \% yield via alkylation of A.1.1 with BrCH\textsubscript{2}Cl in presence of K\textsubscript{2}CO\textsubscript{3} in DMF as the solvent (route A).\textsuperscript{255-257} 1,2-Methylenedioxybenzene
(MDB) was also treated with FeCl₃ in CH₂Cl₂ and a black solid was obtained. On the basis of its NMR spectra and mass spectrometry, it was confirmed that the product formed was the same as that obtained by route A. By this route (B), the desired product was obtained in 25 % yield as shown in Scheme A.1.2.

Scheme A.1.2 Synthesis of compound A.1.2. Conditions: i) BrCH₂Cl, K₂CO₃, DMF, 54 %; ii) FeCl₃, CH₂Cl₂, 25 %.

The final route was the attempted electrochemical synthesis of A.1.2 by reproducing as closely as possible the experiments reported by Xu and co-workers. The detailed experimental procedure can be found at the end of the appendix. Upon application of an electrical potential of 1.4 mV, a black solid deposited on the platinium electrode. The product was collected by scraping it off the electrode surface, washing it with acetonitrile and vacuum-drying. ¹H and ¹³C NMR, as well as MS, indicated that route C afforded a product with identical spectroscopic properties as the products obtained via routes A and B.

Compounds A.1.1 and A.1.2 were characterized by the same methods used by Xu and co-workers: ¹H and ¹³C NMR, FT-IR, UV-vis and fluorescence spectroscopy.
MALDI-TOF and HR-MS mass spectrometry confirmed that the molecular weight of the products obtained by routes A, B and C are in fact that of the triphenylene derivative. Despite repeated efforts, compound A.1.2 could not be thoroughly purified and remained a dark brown/black solid with traces of impurities observed in the $^1$H NMR spectrum.\textsuperscript{258} The poor solubility of this compound made its purification difficult. The colour of the compound we obtained does not match what was reported by Xu and co-workers. They reported that PMDB was a baby blue solid and P-o-DHB was light green.\textsuperscript{225,252}

**Characterization of compounds A.1.1 and A.1.2 by $^1$H NMR**

$^1$H NMR spectra were recorded for compounds A.1.1 and A.1.2 and were compared with those presented by Xu and co-workers and with the data reported in the literature. The data obtained is summarized in Table A.1.1, along with the data presented by Xu and co-workers. All the spectra were recorded in DMSO-$d_6$. 

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Figure A.1.5: $^1$H NMR of synthesized compound A.1.1.

Figure A.1.6: $^1$H NMR spectrum of compound A.1.2.
The $^1$H NMR spectrum of compound A.1.1 was recorded in deuterated DMSO and shows the presence of two peaks that are in accordance with the literature: $\delta$ 7.60 (s, 6H) and 9.28 (s, 6H) ppm (Figure A.1.5). The peak at 7.60 ppm is in agreement with the data presented by Xu and co-workers. The broad peak at 9.28 ppm corresponds to the phenolic hydrogens of the triphenylene. Xu et al. did not report this region of the spectrum and it is therefore difficult to comment about this peak. As a general rule, this type of hydrogen has a chemical shift that can vary according to the experimental conditions such as the concentration of the analyte or the amount of water present.\textsuperscript{259} It is also possible that they did not observe this peak, which would explain why no comments about that peak were made and this region of the spectrum was not shown. However, the chemical shift for this peak is in accordance with what has been reported for compound A.1.1, further suggesting that the product obtained is the triphenylene derivative.\textsuperscript{253}

Compound A.1.2 was only slightly soluble in DMSO, but it was possible to record a spectrum possessing two peaks at 6.17 ppm (s, 6H) and 8.17 ppm (s, 6H), as shown in Figure 2.6. The results are the same for the products obtained via routes A, B and C. Route A afforded A.1.2 from the known compound A.1.1, hence confirming that the product obtained is a triphenylene derivative. The $^1$H NMR peaks for compounds A.1.1 and A.1.2 are listed in Table A.1.1.
Table A.1.1: $^1$H NMR data collected for compounds A.1.1 and A.1.2.

<table>
<thead>
<tr>
<th>Compound A.1.1</th>
<th>Compound A.1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xu et al. $^{260}$</td>
<td>Voisin et al.</td>
</tr>
<tr>
<td>δ (ppm)</td>
<td>δ (ppm)</td>
</tr>
<tr>
<td>400 MHz</td>
<td>500 MHz</td>
</tr>
<tr>
<td>7.65</td>
<td>7.60, 9.28</td>
</tr>
</tbody>
</table>

Characterization of compounds A.1.1 and A.1.2 by $^{13}$C NMR

The $^{13}$C NMR spectrum was recorded for compound A.1.1 and three peaks were observed at 107.7, 121.7 and 145.2 ppm (Figure A.1.7). The peaks are in accordance with the literature for hexahydroxytriphenylene and with the results presented by Xu and co-workers.$^{260}$ Again, all the spectra were recorded in deuterated DMSO.
Because compound A.1.2 was only slightly soluble in deuterated DMSO, obtaining a $^{13}$C NMR spectrum was more difficult. A 600 MHz NMR spectrometer equipped with a cryoprobe was used to obtain spectra with a better signal-to-noise ratio than the spectrum presented by Xu et al.. They reported a $^{13}$C NMR spectrum for the starting material (MDB) with a good signal-to-noise ratio while the “polymerized” material exhibited a very poor signal to noise ratio. Any conclusions from their spectral data therefore should be treated with caution. The proton decoupled $^{13}$C NMR spectrum obtained for compound A.1.2 had four peaks: 101.3, 101.9, 124.5 and 147.4 ppm (see Figure A.1.8). This spectrum was compared to the data presented by Xu and co-workers. (see Table A.1.2).
Figure A.1.8: $^{13}$C NMR of compound A.1.2 (C-H decoupled)

Table A.1.2: $^{13}$C NMR (DMSO-$d_6$) of compounds A.1.1 and A.1.2

<table>
<thead>
<tr>
<th>Compound A.1.1</th>
<th>Compound A.1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Xu et al.$</td>
<td>$Voisin et al.$</td>
</tr>
<tr>
<td>$\delta$ (ppm)</td>
<td>$\delta$ (ppm)</td>
</tr>
<tr>
<td>100 MHz</td>
<td>150 MHz</td>
</tr>
<tr>
<td>107.8, 121.9, 145.0</td>
<td>107.7, 121.7, 145.2</td>
</tr>
</tbody>
</table>
Our $^{13}$C NMR results are partially in agreement with the data presented by Xu and co-workers. They reported peaks at 101, 109 and 147 ppm but no second peak at 101 ppm and no peak at 124.5 ppm. The low signal-to-noise ratio on the spectrum presented could account for the absence of the peak at 124 ppm. It could also explain why they only reported one peak around 101 while we observed two (101.3 and 101.9 ppm). The peak at 109 ppm was only observed in the spectrum presented by Xu and co-workers. Given these discrepancies, we decided to investigate further in order to confirm our identification.

C-H decoupled and C-H coupled $^{13}$C NMR, Attached Proton Test (ATP) and Heteronuclear Single Quantum Coherence (HSQC) experiments were carried out to further characterize compound A.1.2. The same spectrometer (600 MHz, equipped with a cryoprobe) and the same solvent (DMSO-$d_6$) were used to perform all the NMR experiment. The experiments were conducted on MDB and on the triphenylene A.1.2. Carbons belonging to the starting materials and the triphenylene were labelled as shown in Figure A.1.9.
Figure A.1.9: Structure of MDB and Triphenylene A.1.2. Each atom has been labelled for the NMR experiments.

The proton coupled $^{13}$C NMR spectrum shown in Figure A.1.10 indicated the number of hydrogen attached to each of the carbons of the starting material. The triplet at 100.6 ppm corresponds to carbon a (two hydrogens) while the singlet at 147.1 ppm correspond to carbon b, which has no hydrogens. Based on their relative chemical shifts, it is possible to assign the peak at 108.6 ppm as carbon c, with the remaining peak at 121.7 ppm assigned to carbon d. The oxygen on the acetal moiety will donate electron density to carbon c, making it more shielded than carbon d. This assignment is different than the one presented by Xu and co-workers, but the more detailed experiments confirmed our assignment. The peak at 101 ppm was assigned to carbon a, the peak at 109 ppm was assigned to carbon c and the peak at 145 ppm to carbon b. The missing peak was assigned to carbon d, which loses its hydrogen upon reaction and hence produces a peak of lower intensity.
Figure A.1.10: $^{13}$C NMR spectrum of MDB. Left: Proton-decoupled $^{13}$C NMR spectrum; Right: $^{13}$C NMR spectrum with C-H coupling. Chemical shifts: 100.6, 108.6, 121.7 and 147.1 ppm.

The attached proton test (APT) provides a spectrum where primary (-CH$_3$-) and tertiary (-CH-) carbons will be negative while secondary (-CH$_2$-) and quaternary (-C-) carbons are positive (Figure A.1.11). The spectrum obtained shown in Figure A.1.10 confirms the assignment previously made with the $^{13}$C NMR spectrum (C-H coupled).
The last experiment, Heteronuclear Single Quantum Correlation (HSQC), was used to obtain the coupling through one bond between carbons and hydrogens nuclei. As shown in Figure A.1.12, the two hydrogens of the acetal moiety give rise to a peak at about 6.0 ppm, which couples with the carbon peak at 100.6 ppm. The carbon b (147.1 ppm) is the most deshielded by the oxygen atoms and is not bonded to any hydrogen. Hydrogens on carbon c are expected to be the most deshielded and therefore were assigned to the peak at 7.0 ppm. The correlation experiment shows that they are bonded to the carbon at 108.6 ppm. The remaining hydrogens (d) are at 6.8 ppm on the $^1$H spectrum and are coupled to the carbon atom at 121.7 ppm. The data obtained from the
NMR experiments on the starting material helped characterizing the final product, compound A.1.2.

Figure A.1.12: HSQC of 1,3-methylenedioxybenzene.

HSQC was carried out on compound A.1.2 and is shown in Figure A.1.13. The peak at 6.17 ppm in the $^1$H spectrum corresponds to the hydrogens of the acetal moiety. The HSQC spectrum indicates that these hydrogens couple with the carbon at 101.3 ppm. The other peak in the proton spectrum (8.17 ppm) couples with the peak at 101.9 ppm on the carbon spectrum, carbon c of the triphenylene. The two remaining peaks in the $^{13}$C spectrum correspond to carbons b and d, which do not bear any hydrogens. The signal at
147.4 ppm was assigned to carbon b, which is expected to be strongly deshielded by the attached oxygen. This carbon on the starting material (MDB) shows up at 147.1 ppm. By process of elimination the remaining peak at 124.5 is assigned to carbon d.

The attached proton test (APT) of A.1.2, shown in Figure A.1.14 differentiates secondary and quaternary carbons (positive peaks) from tertiary and primary (negative peaks). Only one carbon has a negative intensity, which is consistent with the proposed triphenylene that has one primary, one tertiary and two quaternary carbons. It is therefore possible to confirm our previous assignment from the HSQC that the peak at 101.3 ppm is the secondary carbon (a) whereas the peak at 101.9 ppm corresponds to the tertiary carbon (c). The quality of the ATP spectrum is poorer than the proton decoupled $^{13}$C-NMR spectrum and more peaks, arising from impurities that we were not able to remove,
are observed. These however do not impair our ability to establish the number of carbons attached the various carbon atoms.

\[ a \] 

\[ \begin{align*} 
\text{b} & \quad 147.4 \text{ ppm} \\
\text{d} & \quad 124.5 \text{ ppm} \\
\text{c} & \quad 101.9 \text{ ppm} \\
\text{a} & \quad 101.3 \text{ ppm} 
\end{align*} \]

\[ 13 \text{C NMR} \]

\[ \text{CH}_2 \]

\[ \text{CH} \]

Figure A.1.14 $^{13}$C and ATP spectra obtained with compound A.1.2 synthesized by Voisin et al.

Characterization of compounds A.1.1 and A.1.1 by mass spectrometry

Matrix Assisted Laser Desorption/Ionisation-Time-Of-Flight (MALDI-TOF) was used to determine the molecular weights of the products obtained. In both cases, we were able to obtain the exact mass of the triphenylenes A.1.1 and A.1.2, as summarized in Table A.1.3. No peaks were observed for high molecular weight materials, showing that the triphenylene is the obtained product, rather than polymeric materials. The error on the molecular weights obtained with the MALDI-TOF are bigger than expected (up to $\pm 0.55$
g/mol). The MALDI-TOF was not calibrated and the errors on the values obtained were greater than normally observed.

Table A.1.3 Mass spectrometry obtained for compounds A.1.1 and A.1.2.

<table>
<thead>
<tr>
<th>Compound A.1.1</th>
<th>Compound A.1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>Voisin et al.</td>
</tr>
<tr>
<td>Calculated</td>
<td>Voisin et al.</td>
</tr>
<tr>
<td></td>
<td>(route A)</td>
</tr>
<tr>
<td>324.063</td>
<td>324.580</td>
</tr>
<tr>
<td>360.063</td>
<td>360.288</td>
</tr>
<tr>
<td>360.298</td>
<td>360.298</td>
</tr>
<tr>
<td>360.1</td>
<td></td>
</tr>
</tbody>
</table>

*The mass spectrometry was performed by EI because the MALDI-TOF was unavailable at the time of the experiment.

Characterization of compounds A.1.1 and A.1.2 by FTIR

FT-IR spectra of compounds A.1.1 and A.1.2 are shown in Figure A.1.16 and Figure A.1.17 respectively. For both compounds, the peaks observed are similar to the ones reported by Xu and co-workers, although these researcher reported only the IR spectra of the oxidized radical cations \((A.1.1^+)\)( BF_4^-) and \((A.1.2^+)\)( BF_4^-). Because the IR spectra that were obtained were for the neutral forms of these molecules, it is anticipated that the spectral properties should not be in complete accordance.

The spectrum obtained for compound A.1.1 shows a strong and broad peak centered at 3280 cm\(^{-1}\) that corresponds to the –OH stretch. The C-H stretch around 3100
cm\(^{-1}\) is hidden in that peak. The carbon-carbon stretches for the aromatic ring were found at 1603 and 1448 cm\(^{-1}\). The overtone region (2000-1670 cm\(^{-1}\)) was not observable in the spectrum recorded. However, the C-H out-of-plane bending of sp\(^2\) carbons was observed at 852 and 794 cm\(^{-1}\). The peaks found around 1635 and 852 cm\(^{-1}\) in the spectrum recorded confirmed the 1,2,4,5 substitution pattern on the benzene rings.\(^{263}\)

The spectra recorded for compounds A.1.2 obtained via routes A and B were identical. The spectra showed the presence of the two C-O-C strong stretches at 1035 and 1243 cm\(^{-1}\) and two weak at 1094 and 1161 cm\(^{-1}\). The two strong peaks indicate that the oxygen is bonded to two different carbons (primary and quaternary) and the total of four peaks in this region indicate a cyclic acetal.\(^{263}\) The C-H stretch was found at 2897 cm\(^{-1}\) and the C=C bonds stretches at 1604 and 1440 cm\(^{-1}\). The C-H out-of-plane bending (sp\(^2\)) was found at 932 and 852 cm\(^{-1}\). The C-H bend for the sp\(^3\) carbons was found at 1455 cm\(^{-1}\). The overtone region is hidden in the broad peak at 1604 cm\(^{-1}\).
Figure A.1.15: FT-IR of compound A.1.1.

Figure A.1.16: FT-IR of compound A.1.2.
Characterization of compounds A.1.1 and A.1.2 by UV-Vis and Fluorescence Spectroscopy

The UV-Visible absorption and emission spectra of compounds A.1.1 and A.1.2 were recorded in DMSO. The results are similar but only the results obtained with compound A.1.2 are shown. Solutions of various concentrations (see Table A.1.5) were prepared and the UV-Vis spectra were recorded (see Figure A.1.17). The maximum absorbance ($\lambda_{\text{max}}$) was 280 nm and was used as the excitation wavelength for the emission spectra. Fluorescence was recorded for four of the solutions ranging from $6.2 \times 10^{-6}$ M to $2.6 \times 10^{-5}$ M (see Figure A.1.18) and the maximum emission was observed at 387 nm. The results obtained are in accordance with what was presented in the various papers by Xu and co-workers. In addition, those results are strikingly similar to UV-Vis and fluorescence spectra reported for hexaalkoxytriphenylene derivatives.$^{264,265}$
Figure A.1.17: UV-Vis absorption spectra of solutions of compound A.1.2 in DMSO.

Figure A.1.18: Emission spectra of solutions of compound A.1.2 in DMSO.
Conclusions

Compounds A.1.1 and A.1.2 were synthesized and shown to be triphenylene derivatives. The data obtained from the various characterization experiments are consistent with the data reported in the literature for various triphenylene-derived compounds. Our data are also consistent with what Xu and co-workers presented in their papers, therefore confirming that they had not obtained a polymeric material as claimed.

Experimental Section

Details on materials and instruments used are listed in chapter 6 (Sections 6.1 and 6.2).

Synthesis of Compound A.1.1

Scheme A.1.3: Synthesis of compound A.1.1. Conditions: i) FeCl₃, CH₂Cl₂; ii) AcOH/HBr.
2,3,6,7,10,11-Hexamethoxytriphenylene

Dimethoxybenzene (10.0 g, 72.0 mmol) was dissolved in dry dichloromethane (400 mL) and nitrogen was bubbled through the solution for 20 minutes. While the mixture was still under nitrogen, FeCl₃ (35 g, 217 mmol) was slowly added and the mixture was stirred at room temperature for 90 minutes. The reaction mixture was poured over methanol (600 mL) and allowed to settle overnight in the refrigerator. The solid formed was filtered and washed with large amounts of methanol (400 mL) and ethanol (400 mL) before being vacuum-dried to yield a light pink powder (8.5 g, 21 mmol, 86%); ¹H NMR (500 MHz, CDCl₃) δ 4.05 (s, 18H), 8.02 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 56.0, 104.0, 123.1, 148.6; MALDI-TOF for [C₂₄H₂₄O₆]⁺ calculated (found) 408.157 (408.046); mp > 300°C.

2,3,6,7,10,11-Hexahydroxytriphenylene, A.1.1

2,3,6,7,10,11-Hexamethoxytriphenylene (2.02 g, 4.95 mmol) was suspended in a 1:1 mixture of HBr and AcOH (120 mL) and the solution was heated at reflux for 24 hours (the solid dissolved upon heating). The mixture was allowed to cool to room temperature. The precipitate formed was filtered, washed with a large amounts of water (until the pH of the water was neutral (~7), about 1.5 liter) and then vacuum-dried. Recrystallization from boiling water afforded a dark purple solid (1.61 g, 4.70 mmol, 95%). ¹H NMR (500 MHz, DMSO-δ₆) δ 7.60 (s, 6H), 9.28 (s, 6H); ¹³C NMR (125 MHz, DMSO-δ₆) δ 107.7, 121.7, 145.2; MALDI-TOF for [C₁₈H₁₂O₆]⁺ calculated (found)
324.06 (324.58); FT-IR (KBr): 1256 cm\(^{-1}\) (C-O stretch), 3280 cm\(^{-1}\) (O-H stretch); mp > 300 °C.

**Synthesis of Compound A.1.2**

Scheme A.1.4: Synthesis of compound A.1.2. Route A: BrCH\(_2\)Cl, K\(_2\)CO\(_3\), DMF; Route B) FeCl\(_3\), CH\(_2\)Cl\(_2\); Route C: electrochemical oxidation with platinum electrode.

A.1.2-Route A:

A.1.1 (0.081 g, 0.25 mmol) was dissolved in dry DMF (0.75 mL) and nitrogen was bubbled through the solution for one hour. K\(_2\)CO\(_3\) (0.21 g, 1.5 mmol) was added and the mixture was degassed for another ten minutes. CH\(_2\)BrCl (0.11 g, 0.82 mmol, 53.5 μL) was added and the mixture was heated at 80 °C for 20 hours. The mixture was cooled to room temperature, methanol (50 mL) and water (50 mL) were added. The resulting solid was filtered and washed with large amounts of water (200 mL), methanol (200 mL) and THF (200 mL) to yield and brown powder (0.046 g, 0.13 mmol, 51 %). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 6.17 (s, 6H), 8.17 (s, 6H); \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \(\delta\) 101.3,
A.1.2-Route B:

1,2-Methylenedioxybenzene (MDB) (2.00 g, 16 mmol) was dissolved in dry chloroform (50 mL) and nitrogen was bubbled through the solution for ten minutes. FeCl₃ (8.0 g, 5 mmol) was added slowly and the mixture was purged with nitrogen for an additional two minutes. The reaction mixture was stirred at room temperature for 90 minutes and poured over methanol (150 mL). The mixture was stored in the refrigerator overnight. The solid was filtered and washed with methanol (200 mL), water (200 mL), aqueous ammonia (10 %, 200 mL), water (200 mL) and then methanol (200 mL) to afford a brown solid (0.48 g, 1.3 mmol, 25 %). 

\[ ^1H\text{ NMR (500 MHz, DMSO-}_d^6\text{) } \delta \text{ 6.17 (s, 6H), 8.17 (s, 6H); } \]

\[ ^{13}C\text{ NMR (150 MHz, DMSO-}_d^6\text{) } \delta \text{ 101.3, 101.9, 124.5, 147.4; } \]

MALDI-TOF for \([C_{21}H_{12}O_6]^+\) calculated (found) 360.06 (360.29); FT-IR (KBr): 1245 cm⁻¹, 1037 cm⁻¹ (C-O stretch); mp > 300 °C.

A.1.2-Route C:

Using dry spectrograde acetonitrile (MeCN), a solution of MDB (0.2 mol·L⁻¹) containing NBut₄PF₆ (0.1 mol·L⁻¹) was prepared. A flask equipped with platinum electrodes (working, reference and counter) in the solution was degassed with nitrogen.
for 15 minutes prior to application of a constant potential of 1.4 mV for ten minutes. The
dark solid that deposited on the working electrode was collected, the solution changed
and degassed again. The process was repeated until enough solid had been collected to
perform characterization experiments. The solid was washed with acetonitrile (20 mL)
and vacuum-dried. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 6.17 (s, 6H), 8.17 (s, 6H); $^{13}$C
NMR (150 MHz, DMSO-$d_6$) $\delta$ 101.3, 101.9, 124.5, 147.4; MS-EI for [C$_{21}$H$_{12}$O$_6$]$^+$
calculated (found) 360.1 (360.1); mp $> 300$ °C.

**UV-Vis and Fluorescence spectroscopy**

Compound A.1.1 is known so we did not recorded UV-visible or fluorescence
spectra. Compound A.1.2 was dissolved in spectrograde DMSO at a starting
concentration of 2.58 mol-L$^{-1}$ (solution A). Dilutions afforded six solutions of various
concentrations listed in Table A.1.4. UV-Vis and Fluorescence spectra were recorded
using 1 x 1 cm quartz cuvettes. Prior to record the fluorescence spectra, the solutions
were filtered with syringe filter (Fisherbrand fliter, 0.45 μm, PTFE).
Table A.1.4: Solution prepared for UV-Vis and fluorescence spectroscopic measurements.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Concentration (mol·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.03 x 10⁻⁶</td>
</tr>
<tr>
<td>B</td>
<td>5.15 x 10⁻⁶</td>
</tr>
<tr>
<td>C</td>
<td>6.18 x 10⁻⁶</td>
</tr>
<tr>
<td>D</td>
<td>8.24 x 10⁻⁶</td>
</tr>
<tr>
<td>E</td>
<td>1.03 x 10⁻⁵</td>
</tr>
<tr>
<td>F</td>
<td>2.58 x 10⁻⁵</td>
</tr>
</tbody>
</table>
APPENDIX 2: DEMONSTRATION OF X-RAY CALCULATIONS

For a given compound, an X-ray diffraction pattern is recorded and values for 2θ are obtained. Using Bragg's law (Equation A.2.1), it is possible to obtain d, which corresponds to the distance in angstroms (Å) between various objects in the ordered phases. The formula used is:

\[ n\lambda = 2dsin\theta \]  \quad \text{Equation A.2.1}

for which, \( \lambda = 1.54 \) Å and \( n = 1 \). The calculations will be shown with compound Q(8,8)A(8), recorded at 120 °C (Figure A.2.1)
Figure A.2.1: Diffractogram of Q(8,8)A(8) recorded at 120 °C for 30 minutes.

The values obtained are: 4.15, 7.20, 19.97, 24.26. Those values will be divided in two to get $\theta$ in degrees. This value will be converted into radians using equation A.2.2 shown below:

$$\frac{\theta \text{ (degrees)} \pi}{180} = \theta \text{ (radians)}$$  
Equation A.2.2
<table>
<thead>
<tr>
<th>Peaks observed</th>
<th>Value in Angströms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance between 100 planes</td>
<td>21.27 Å</td>
</tr>
<tr>
<td>Distance between 110 planes</td>
<td>12.26 Å</td>
</tr>
<tr>
<td>Alkyl halo</td>
<td>4.44 Å</td>
</tr>
<tr>
<td>π-π Stacking</td>
<td>3.66 Å</td>
</tr>
</tbody>
</table>

With the values for 100 and 110, it is possible to calculate \( a \), the lattice constant.

To confirm the presence of a hexagonal 2D lattice of the columns, the ratio for 2θ of 110/100 must be 1.73. Peaks were indexed as 110 for ratios between 1.72 and 1.75 in order to account for small distortions of the hexagonal 2D lattice. In some cases, however, the 110 peak is not observable.

To find \( a \), the trigonometric equalities must be considered:

\[
2(110)/(\sin 90) = (a/2)/(\sin 30) = 100/(\sin 60)
\]

Also:

\[
\sin 90 = 1; \; \sin 60 = (\sqrt{3})/2; \; \sin 30 = 1/2
\]
From these, we can conclude that \( a = 2(110) = 2(100)/(\sqrt{3}) \), which implies that \( a = 24.5 \) Å for Q(8,8)A(8) at 120 ° C.

Figure A.2.2: Representation of the lattice and the various planes obtained via VT-XRD.
APPENDIX 3: NMR EXPERIMENTS FOR SELECTIVE IODINATION OF 2-DECYLOXYPHENYL ACETATE.

Scheme A.3.1: Selective EAS of 2-decyloxyphenyl acetate.

2-Decyloxyphenyl acetate was selectively iodinated with iodine monochloride in presence of dichloromethane to afford 5-iodo-2-decyloxyphenyl acetate (Scheme A.3.1). A small sample was purified by column chromatography (silica gel) with a hexanes/ethyl acetate mixture (97/3) to afford a purer compound that we could analyze by $^1$H and $^{13}$C NMR, HMBC (Heteronuclear Multiple Bond Correlation) and HMQC (Heteronuclear Multiple Quantum Correlation). These experiments allowed us to confirm that the electrophilic aromatic substitution took place para to the alkoxy chain and make the distinction between the two possibilities shown in Figure A.3.1.
Figure A.3.1: Possible products from the iodination of 2-decyloxyphenyl acetate.

The $^1$H spectrum NMR is shown in Figure A.3.2 and the assignment is shown on the spectrum. The more shielded peak is a triplet at 0.88 ppm and corresponds to the methyl group (hydrogens a) at the end of the decyloxy chain. Hydrogens labelled b, c and d are shown by various multiplets between 1.27 and 1.76 ppm. The singlet at 2.26 ppm corresponds to the methyl group of the acetate group labelled f. The triplet at 3.93 ppm corresponds to the first methylene (-CH$_2$-) group of the alkoxy chain, labelled e. To assign the hydrogens in the aromatic region, their chemical shifts and splitting pattern were used. In the aromatic ring, the values of the coupling constants decrease as the distance between the hydrogens increases: $^2$J $>$ $^3$J. It is therefore possible to establish the substitution pattern of the benzene ring by analyzing the splitting of the peaks observed in the aromatic region. The iodine atom will have a deshielding effect on the hydrogens on the vicinal carbons. The acetate will also have a deshielding effect since it is an electron-withdrawing group. The alkoxy chain will have a shielding effect from its electron-donating behaviour.
The more deshielded peak labelled h is a doublet of doublets, indicating that it is close to the iodine atom and coupling with two different hydrogens atoms. The coupling constants of 8.4 Hz and 2.4 Hz indicate that one of the hydrogen is para while the second one is meta to h. The doublet observed at 7.33 ppm has a coupling constant of 2.4 Hz that indicates that it is able to couple with an hydrogen in the meta position. This peak corresponds to hydrogen i. That hydrogen can be next to the acetate group, which would increase its chemical shift, or the decyloxy chain, which would decrease it chemical shift. Since it is not the lowest peak in the aromatic region, that hydrogen is most likely to be next to the acetate group. The last hydrogen, g, produces a doublet at 6.70 ppm with a coupling constant of 8.4 Hz since its coupling with hydrogen h. This analysis is consistent with the formation of 5-iodo-2-decyloxyphenylacetate (Figure A.3.1, molecule I).

Figure A.3.2: $^1\text{H}$ NMR spectrum of 5-iodo-2-alkoxyphenyl acetate. Full $^1\text{H}$ spectrum on the left and expanded aromatic region on the right.
In order to confirm this assignment, other experiments were conducted. The HSQC allowed us to assign carbons bearing hydrogens since the spectrum shows the coupling between the hydrogens and the carbons they are attached to as shown in Figure A.3.4. We mainly focused on the carbons and hydrogens in the aromatic region where the reaction took place. Hydrogen $g$ couples with carbon $g$ at 115.20 ppm, hydrogen $i$ with carbon $i$ at 131.46 ppm and hydrogen $h$ with carbon $h$ at 135.60 ppm. The hydrogens $e$ couple with carbon $e$ at 68.81 ppm and the hydrogens $f$ of the acetate group couple with the carbon $f$ at 20.44 ppm. The triplet observed at 3.93 ppm corresponds to hydrogens $e$ coupling with the carbon peak at 68.81 ppm also labelled $e$. The triplet at 0.88 ppm corresponds to hydrogens $a$ that couple with the carbon peak at 14.01 ppm labelled $a$ as well.

Figure A.3.4: HSQC of 5-iodo-2-decyloxyphenylacetate.
From the $^{13}$C NMR spectrum, it is possible to assign unambiguously some of the carbons signals as shown in Figure A.3.5. The peaks observed between 14.10 and 31.88 ppm correspond to the carbons of the decyloxy chain (a, b, c and d). The carbon of the methyl group (f) of the acetate functional group is also in that region, at 20.44 ppm according to the HSQC. The remaining carbons are j, k, l and m. The carbon of the carbonyl group of the acetate function (m) is the most deshielded at 168.55 ppm. The carbon bearing the iodine atom (j) will be more shielded than the other aromatic carbons and observed at 81.04 ppm. Further experiments were required to assign with certitude carbons k and l.

![Figure A.3.5: $^{13}$C NMR spectrum of 5-iodo-2-decyloxyphenyl acetate with the assignment of most of the peaks.](image)

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The results of the HMBC allowed the assignment of carbons k and l as well as confirming the substitution pattern of the iodinated product of the reaction shown in Scheme A.3.1. This type of experiment has the ability to show the coupling between nuclei separated by two or three bonds, hence with much smaller coupling constants. The first information obtained with the HMBC (Figure A.3.6) allowed the assignment of carbons k and l. The triplet observed for hydrogens e shows a strong coupling with atoms that are three bonds away ($^3J$): carbon d (aliphatic chain) and carbon k (aromatic ring) at 150.81 ppm. There is also a very weak coupling with carbon e ($^1J$). The singlet observed for hydrogens f couples strongly with carbon m at 168.55 ppm ($^2J$). A small coupling is also observed with carbon l at 140.73 ppm ($^4J$). From these informations, carbon k bears the acetate group while carbon l bears the decyloxy chain. A complete assignment of the $^{13}$C NMR spectrum is shown in Figure A.3.7. Further analysis of the HMBC revealed the relative position of these groups with respect to the iodine atom.
Figure A.3.6: Assignment of peaks for carbons k and l using the HMBC spectrum.

Figure A.3.7: $^{13}$C NMR spectrum fully assigned.
The second purpose of the HMBC experiment is to confirm that the substitution pattern obtained upon iodination corresponds to compound I shown in Figure A.3.1. The aromatic region of the spectrum was expanded and the long-range coupling analyzed using the assignment established with the previous experiments performed. The stronger correlation peaks are associated with coupling through two or three bonds. As the distance increase, the intensity of the correlation peaks decreases. Most of the peaks in the aromatic region do not give enough information to make the distinction between the two possible substitution patterns I and II. However, two peaks do confirm that the acetate is in the meta position of the iodine.

It has been established that hydrogen g is between the hydrogen h and one of the groups appended to the benzene ring (acetate or alkoxy chain). Strong correlation peaks (i and ii) show that carbons j and l are three bonds away from hydrogen g, confirming substitution pattern I. This hydrogen also shows a weaker correlation peak with carbon k (iii), which is two bonds away. Hydrogen h has the iodine atom and hydrogen g as neighbours. The strong correlation peaks (iv and v) indicate that carbons k and i are three bonds away, also consistent with substitution pattern I. From the correlation peaks obtained with hydrogen i (vi and vii), carbons h and k are three bonds away, confirming the substitution pattern I. The last correlation peak (viii) is weak but demonstrates correlation between the carbon m of the acetate and hydrogen i, separated by four bonds. Figure A.3.8 shows the HMBC spectrum along with the correlation peaks mentioned earlier.
Figure A.3.8: Portion of the HMBC showing correlation between carbons and hydrogens used to confirm the substitution pattern of the iodinated compound.
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