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Liquid Crystalline Semiconductors for Organic Electronics

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Abstract

This research is based on the synthesis and evaluation of novel liquid crystalline materials with light-emitting and or charge-transporting properties. Some of the liquid crystals (LCs) synthesised incorporate photopolymerisable diene or methacrylate end groups, situated at the peripheries of the molecular core. These photoreactive liquid crystalline monomers are often termed reactive mesogens. The generation of linearly and circularly polarised light emission have been observed and a White-Light Organic Light-Emitting Diode (WOLED) fabricated from binary mixtures of LCs.

A series of fluorene-containing LCs have been synthesised for use as hole-transport, electron-transport and electroluminescent materials. Many of these materials exhibit nematic phases, which is beneficial for alignment due to the lower viscosity present in the nematic phase compared to the smectic phase. Columnar LCs with low melting points were synthesised by variation of the aliphatic groups at the 3,4,9,10-positions of a perylene tetracarboxylate. A fluorene-containing material with perfluorinated chains at the 9-position of the fluorene was synthesised, although the required LC phase was not observed. High electron-affinity nitrogen-containing smectic LCs have been synthesised with relatively low LC transition temperatures. These materials may prove useful as electron-transport materials. An electroluminescent chiral nematic LC was synthesised, which leads to the possibility of circularly polarised light. The possibility of a full-colour LC-Organic Light-Emitting Diode (OLED) has been demonstrated with the synthesis of a red-emitting material, a green-emitting material and a blue-emitting material. All three materials are LCs with high glass transition temperatures, which is important for device stability as these materials are not reactive mesogens. A White-Light OLED has been demonstrated by the mixing of two LCs. This nematic binary mixture when used as the emissive layer in an OLED emits white-light that is voltage independent and not due to Förster energy transfer. Consequently this mixture can be aligned and linearly polarised light emission has been generated with a 9:1 ratio. A series of perylene-containing LCs have been synthesised for use as electron-transport materials in OLEDs or electron-acceptors in organic photovoltaics.

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Publications

1. Introduction

Organic semiconductors are a class of organic materials that have found use in Organic Light-Emitting Diodes (OLEDs), Organic Field Effect Transistors (OFETs) and Organic Photovoltaics. Organic Light-Emitting Diodes are seen as an alternative display technology to Liquid Crystal displays.

The impetus behind the research in organic photovoltaics has been the search for costeffective photovoltaics. Polymer and oligomer organic photovoltaics could provide the alternative technology to inorganic solar cells.

This introductory chapter outlines the advantages and properties of organic semiconductors as the active component for OLEDs, OFETs and organic photovoltaics.

1.1 Fluorescence

The Joblonski diagram, ^[1] figure 1.01, shows the emission process when a molecule acquires excitation energy. The excitation energy can be from an electrical current (electroluminescence) or the absorption of photons (photoluminescence).



Figure 1.01 Jablonski diagram.

The S's represent singlet states (with net spin angular momentum 0) and the T's, triplet levels (with one unit of spin angular momentum). Each electronic level is made up of many vibrational and rotational levels. Since the energy difference between one rotational level and another is of the order of 0.01 eV, the energies of rotational transitions are too small for them to be observed. By contrast the energy differences between electronic states and between vibrational levels are several electron volts, and about 0.1 eV respectively. Thus at room temperature, those electrons which can participate in a transition leading to fluorescence (π -electrons) will be found populating the zero vibrational level. When the appropriate energy is absorbed by a molecule, an electron is raised from the zero vibrational level of the ground state to one of several vibrational levels of the first excited state $(S_0 \rightarrow S_1)$. In a condensed medium, a liquid or solid, an electron in a high vibrational level rapidly (10^{-12} sec) loses its excess vibrational energy in collisions with neighbouring molecules, a process called vibrational relaxation. Therefore highly-aggregated organic molecules, such as perylene-diimides, are unsuitable as emissive materials in organic light-emitting diodes (OLEDs). This is why many redemitting materials are unsuitable for OLEDs as they have large dipoles, which induce molecular aggregation. If the molecule can remain in its lowest excited state, S_1 , for 10^{-9} sec or longer and there are no competing processes, then the situation is favourable for this molecule to emit fluorescence radiation. The transition leading to fluorescence takes place from the zero vibrational level of the first excited state to one of the vibrational levels of the ground state. Excess vibrational energy in the ground state is lost by collisions with neighbouring molecules.

1.2 Phosphorescence

The transition $S_1 \rightarrow T_1$, shown in figure 1.01, represents another pathway of molecular deexcitation from the first excited state, via a metastable level. This process is called intersystem crossing, figure 1.01. A molecule with its excitation energy in its triplet level can remain in this condition for a relatively long period of time, as long as several seconds. Therefore this energy level is called a metastable level. On reverting to the ground state, $T_1 \rightarrow S_0$, the molecule may emit intercombination radiation, called

phosphorescence, figure 1.01. The process whereby a molecule undergoes a transition from a triplet state to a singlet state $T_1 \rightarrow S_0$, without luminescence, the excess energy being converted into heat, can also be called intersystem crossing.

 $S_0 + h\upsilon \rightarrow S_1 \rightarrow T_1 \rightarrow S_0 + h\upsilon$ Equation 1.01 Description of Intersystem Crossing resulting in Phosphorescence.

Where S is a singlet and T a triplet whose subscripts denote states (0 is the ground state, and 1 the excited state), equation 1.01. Transitions can also occur to higher energy levels from the ground state, S_o, but the first excited state is denoted for simplicity. In recent years cyclometallated metal complexes have been the subject of extensive studies as phosphorescent materials. Metal complexes have attracted attention because of their long-lived excited states and high luminescence quantum yields applicable to photoreductants, ^[2] oxygen sensors, ^[3] and emissive materials. ^[4] The strong spin-orbit coupling, caused by the presence of heavy metal ions incorporated in the complexes, results in efficient intersystem crossing from the singlet to the triplet excited state. Phosphorescent systems can be constructed by mixing a low concentration of a phosphorescent "guest" dopant in a fluorescent "host" material. The majority of the host's non-emissive triplet excitons can then be harvested either by Forster transfer to the singlet state of the guest complex followed by intersystem crossing to the guest triplet state or directly by Dexter transfer from the triplet of the host to that of the guest giving high device efficiencies as demonstrated by Baldo et al.^[5] Since phosphorescence arises from a spin-forbidden relaxation, organometallic complexes containing heavy metal atoms are often required to induce efficient intersystem crossing, such that the normally spin-forbidden singlet to triplet transitions become highly efficient. Additionally, these complexes possess substantially reduced triplet lifetimes due to the strong spin-orbital mixing induced by the heavy metal atom. Therefore, by using metal complexes the internal quantum efficiency of emission can, in principle, approach 100%.

1.3 Photoluminescence

Photoluminescence (PL) is the process whereby light is absorbed by the organic compound and then re-emitted, usually at a longer wavelength, known as a Stokes shift. ^[6] Absorbance of light by an organic molecule can promote an electron from the HOMO to the LUMO, to give rise to a π - π * transition, which is followed by a radiative decay to the ground state, figure 1.01.



Figure 1.02 Photoluminescence of Red, Green and Blue organic materials (0.1% Wt/Wt in DCM).

Photoluminescence has been observed as long ago as 1640 when the first monograph of phosphorescence was published by F. Liceti, entitled Litheosporus. Several centuries later Herschel^[7] in 1845 reported that a solution containing sulphate of quinine emitted a strong luminescence radiation when held in sunlight. The purpose of his report was to point out the difference between this type of radiation and ordinary scattered light.

1.4 Electroluminescence

Electroluminescence (EL) and photoluminescence (PL) are related physical phenomena. Since the discovery by Bernanose et al.^[8] that organic films subjected to an external

electric field can emit light, rapid development has led to high-brightness, thin film organic light-emitting diodes (OLEDs) converting electrical current to light, a phenomenon known as electroluminescence. Electroluminescence (EL) is the direct conversion of electrical energy into light. Light emitting diodes (LEDs) are flat-panel display devices, which emit light under the action of an electrical current passing through a thin layer of electroluminescent material, figure 1.03.



Figure 1.03 Green Organic Light-Emitting Diode.^[9]

Early attempts at electroluminescence devices were not particularly successful. However, later developments, such as the introduction of vapour deposited thin films, ^[10] made it possible for prototype devices to be made. Despite the fact that the EL efficiencies were still rather low, these devices demonstrated, in principle, the commercial potential of the fabrication of large-area light emitting devices. Major breakthroughs came in 1987 and 1989 when Tang and van Slyke ^[11, 12] constructed bilayer-Organic Light Emitting Diodes (OLEDs) and in 1990 when Friend et al. ^[13] observed that conjugated polymers could exhibit EL.

As discussed previously the phenomenon of phosphorescence can be utilised with EL for the fabrication of OLEDs. In 1985, King et al. ^[2] first synthesised triply coordinated neutral *fac*-Ir-(ppy)₃ (*fac*-tris[2-phenylpyridinato]Ir(III)) and investigated its photophysical and photochemical properties. Ir(ppy)₃ in degassed toluene shows very strong phosphorescence ($\lambda_{max} = 514$ nm, phosphorescence yield $\Phi_p = 0.4$) emitted from the predominantly metal-to-ligand charge transfer excited state at room temperature. In 1999, Baldo et al. ^[14] made an organic light-emitting diode with *fac*-Ir(ppy)₃ as a green phosphorescent dopant. The OLED device can utilise all of the electrogenerated singlet and triplet excitons, leading to ca. 100% internal quantum efficiency (η_{in}).

Altering the chemical structure can produce a red phosphorescent dopant, Adachi et al. ^[15] made a red phosphorescent OLED with the use of $(btpy)_2Ir(acac)$ (bis[2-(benzo[*b*]thiophen-2-yl)pyridinato]Ir(III)-(acetylacetonate)) as a dopant. The red OLED provided pure red electroluminescence [CIE coordinates (x, y) = (0.68, 0.32)] with an external quantum efficiency of $\eta_{ex} = 7\%$.

To fabricate highly efficient red-emissive OLEDs, it is necessary to search for redemissive metal complexes with large luminescence quantum yields. However, it is not easy to find such a red-emissive complex, since the luminescence quantum yields tend to decrease with an increase in the emission peak wavelength according to the energy gap law. ^[16]

1.5 Inorganic Semiconductors for Light-Emitting Diodes

Electroluminescence from a ZnS compound was discovered in 1936 by French physicist Destriau, ^[17] when a large electrical field was applied across a sample of ZnS. In the early 1960s the first LEDs emitting in the visible wavelength region were based on GaAsP compound semiconductors with external efficiencies of only 0.2%. In comparison today LEDs incorporating AlGaInP as a red emitter, have an external quantum efficiency exceeding 50%. Such LEDs can also emit orange, amber and yellow light. All colours of the visible spectrum are covered as AlGaInN compounds can emit efficiently in the UV, violet, blue, cyan and green areas of the electromagnetic spectrum. Figure 1.04 shows a typical LED device structure commonly used in modern LED devices.



Figure 1.04 Typical light-emitting diode device structure.^[18]

The first commercial thin-film EL products were introduced by Sharp^[19] in 1983. Since 1983 the commercial EL display industry has progressed from the technical novelty stage to its present status as one of the three major flat panel technologies with a broad user group in a wide range of applications. This has led to the fabrication of the first multicolour thin-film EL displays^[20] fulfilling customers requirements, figure 1.05.



Figure 1.05 Full colour inorganic LED display^[21].

However, inorganic LEDs are not within the scope of this thesis so will not be discussed further.

1.6 Organic Semiconductors

Metals are good conductors because they have their upper energy band partly filled with electrons. This band is called the valence band (VB). Because the VB is partly filled, electrons can flow and hence conduct electricity. However, insulators have their VB

filled so for the electrons to flow they must occupy the next available empty energy level. This is typically a few electron volts (eV) above the VB and is called the conduction band (CB). The energy gap between the VB and the CB is large and hence electrons cannot ordinarily occupy the CB. Therefore there is no electrical conduction. In semiconductors though the energy gap between the VB and the CB is smaller. This means that some electrons can get excited, thermally or through an applied field, from the VB to the CB and hence they can conduct electricity, figure 1.06.



Figure 1.06 Energy bands in an inorganic insulator, semiconductor and conductor

Organic molecules are known generally to be insulators but when a high degree of conjugation is present they may act as semiconductors. This is because in a carbon-carbon double bond the sp_z orbitals overlap to form a pair of π molecular orbitals. The lower energy level π orbital is the bonding MO and the higher energy π^* orbital is the anti-bonding MO. In semiconductor terms, the bonding and anti-bonding orbitals can be referred as the VB and CB respectively and there is therefore a bandgap between them. The essential property which comes out from conjugation is that the π electrons are much more mobile than the σ electrons, they can move from site to site between carbon atoms with a low potential energy barrier (delocalisation) compared to the ionisation potential.

The π electron system is responsible for all the essential electronic features of organic materials: light absorption and emission, charge generation and transport.

1.7 Organic Light-Emitting Diodes

In the past decade there has been a massive amount of research in academia and industry involving the synthesis of new organic semiconductors along with evaluation of their physical properties for optoelectronic and electronic applications.^[22] OLED is used as a general term for LEDs composed of organic materials containing organic semiconductors as the active charge-transporting and light-emitting components. However, they can be split into two general groups: the first is small-molecule OLEDs, ^[23, 24] the second are known as polymer-based LEDs or PLEDs. ^[13] Both types of device have gained serious industrial interest over the past ten years, with some displays appearing on the open market in recent years. However, these OLEDs have a relatively low information content and size compared to liquid crystal displays (LCDs) and plasma panel displays (PDPs). Problems with small-molecule OLEDs include processing costs and differential aging of the chromophores. Polymer OLEDs have poor multilayer capability due to interlayer mixing during solution processing. These problems are associated with the pixellation techniques (shadow masking and printing respectively) due to the type of material used in each display, vacuum deposition for small molecules and deposition from solution, eg, spin coating, doctor blade techniques or ink-jet printing.

A further problem of using organic materials for light-emitting devices is that the emission spectra of π -conjugated molecules are very broad, typically with a full width at half-maximum (FWHM) of 50 to 100 nm. This causes problems with colour purity, often resulting in molecules that will have mixed emission such as blue-green. This is caused by the vibrational and rotational motion of atoms inside the π -conjugated molecules. Despite this problem sharp red-green-blue emission has been demonstrated from OLEDs based on organometallic materials, such as europium chelates, aggregated structures such as cyanine dyes or layered inorganic-organic perovskite compounds. ^[25, 26] Unfortunately

the quantum efficiency of these materials is too low to make them suitable for device purposes.

1.7.1 OLED Device physics

The internal EL quantum efficiency, η_{int} , of an OLED, *i.e.* the ratio of the number of photons emitted per electrons injected and is given by

$$\eta_{int} = \gamma \eta_R \Phi_F$$

Equation 1.02

where γ is the ratio of exciton-forming events to the number of electrons flowing in the external circuit, Φ_F is the quantum efficiency of fluorescence and η_R is the efficiency of singlet formation.

$$\eta_{int} = 2n^2 \eta_{ext}$$

Equation 1.03

The quantity η_{ext} can be experimentally determined. However, the external efficiency ^[27-29] is much lower than the internal efficiency due to internal reflection, i.e., photons emitted cannot be detected because a large number of the photons emitted are lost within the device as heat. Therefore, the external efficiency, η_{ext} , is reduced by a factor $2n^2$, where n is the refractive index of the organic material. It is important to consider the ratio of output light of the device to input of the electric power. This ratio is called the power efficiency ^[30], η_{pow} . The power efficiency can be determined from η_{ext} using the known values of the applied voltage *U* and the average energy of the emitted photons *E*_p.

$$\eta_{\rm pow} = \eta_{\rm ext} E_{\rm p} U^1$$

Equation 1.04

However, the electroluminescence efficiency is clearly limited by the quantum efficiency of photoluminescence. If, however, the lowest energy excited states are strongly bound excitons (electron-hole pairs in singlet or triplet states), the theoretical limit for the quantum efficiency of electroluminescence is 25% of the corresponding quantum efficiency for photoluminescence: an electron in the π^* -band and a hole in the π -band can form a triplet with multiplicity of three or a singlet with multiplicity of one, but only the singlet can decay radiatively. However, if the cross section for an electron-hole pair to form a singlet bound state is significantly higher than the cross section to form a triplet bound state, the ratio of EL quantum efficiency to PL quantum efficiency would be correspondingly larger than that predicted by the simple statistical argument given above, therefore larger than 25%. If the electron-hole binding energy is sufficiently weak, the maximum quantum efficiencies can theoretically approach that of the PL. In the weak interaction limit, electron-hole pairs in a triplet configuration would simply scatter but not recombine. Eventually the spin-orbit interaction would cause a spin-flip after which singlet formation and radiative recombination could occur.

OLEDs have been demonstrated to exhibit a brightness in excess of 200 cd m⁻² at reasonably low voltages. Values of 1000 cd m⁻² have been reported ^[31] at much higher voltages. Figure 1.06 shows a schematic energy level diagram of a generalised single layer organic device.

1.7.2 Single layer OLEDs

The simplest OLED is composed of a single thin film of the active organic material (30 - 500 nm), which is sandwiched between a metallic cathode and transparent anode, figure 1.07.



Figure 1.07 A typical single layer device structure.

Electrons and holes, which are injected into the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) respectively, figure 1.08, drift through the organic film under the influence of the applied electric field. The coulombic attraction between an electron and hole at the same chromophore site results in the formation of an exciton, a bound electron-hole pair, which recombines to produce luminescence called recombination radiation.



Figure 1.08 Diagram depicting singlet and triplet excited states.

If however the charge carriers move through the organic layer, due to the applied electric field and reach the oppositely charged electrode, they are non-radiatively discharged. This process is summarized in figure 1.09.

(a) Hole injection and transport, electron injection and (b) transport, (c) electron leakage current, (d) hole leakage current, (e) hole-electron recombination to form singlet excitons, (f) recombination to form triplet excitons, (g) intersystem crossing from singlet to triplet manifold (h) triplet-triplet annihilation to form singlet states, (i) nonradiative decay of singlet states, (j) radiative singlet emission of light, (k) non-radiative decay of triplets to ground state.



Figure 1.09 Diagram depicting charge carrier pathways.



Vacuum Level

Figure 1.10 Energy barriers for charge injection for a single layer OLED ^[32]

The diagram shows the work functions of the anode and the cathode (Φ_{anode} and $\Phi_{cathode}$ respectively), which depends on the nature of the electrodes used, the electron affinity (EA) and the ionisation potential (IP) for an active organic material. The energy barriers for charge injection depend on the relative positions of the energy levels (EA, IP) of the active layer and the work functions (Φ_{anode} and $\Phi_{cathode}$) of the electrode materials used. For efficient charge injection the work function of the cathode must match the electron affinity of the organic material and the work function of the anode should match the ionisation potential of the organic material. Another problem that occurs in single layer devices is that most active organic materials conduct holes/electrons at different rates. For example PPV has higher mobility of holes than electrons. This results in an unbalanced charge injection and recombination will occur near the cathode, figure 1.11, where quenching occurs.^[33]



Figure 1.11 Formation of excitons near the cathode due to unbalanced charge injection and transport.

Additionally many holes pass directly through the organic material without recombining with any electrons, causing only heat to be generated. In order to overcome these problems, where the work function of the cathode and anode should match the HOMO and LUMO energy levels of the EL material for balanced charge injection two or more organic layers with specific functions can be used, see figure 1.12.

1.7.3 Bi-Layer OLEDs

A two layer device was first demonstrated by Friend et al. ^[34] using PPV as the holetransporting emissive material and an electron-transporting/hole-blocking layer of 2-(biphenyl-4-yl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD). This resulted in an eightfold increase in efficiency compared to a single layer PPV device. This results from an improvement in transport mobilities of the charge carriers, a lowering of the potential energy barrier for charge injection and importantly helps prevent charge recombination close to the electrode-emissive layer interface. A typical bi-layer device is shown in figure 1.12, in the device of Friend et al. the emissive layer was PPV and the electrontransport layer (ETL) was PBD, luminescence is shown by the blue arrow, which occurs once hole-electron recombination occurs.



Figure 1.12 A typical bi-layer device structure.

1.7.4 Tri-Layer OLEDs

A typical tri-layer OLED, figure 1.13, consists of a glass substrate with a transparent anode deposited on top, the anode is indium tin oxide, ITO, as it is one of the few transparent anodes. A hole-transporting layer (HTL) is then deposited on top followed by

the emissive layer this is where hole and electron recombination is required, ideally away from the HTL or ETL interfaces. The hole and electron recombination is depicted by the red circles, holes, and grey circles, electrons, the diagram shows the ones that recombine produce excitons which deactivate by emission of either fluorescence or phosphorescence, shown by the blue arrow. The next layer deposited is the electrontransport layer, ETL, this is often a material with a high electron affinity and high ionisation potential. The final layer is the cathode, which is an electropositive metal with a high-workfunction, this can be aluminium, calcium, silver or magnesium. Often a thin layer of lithium fluoride is deposited on top of the ETL to prevent recombination at the cathode.



Figure 1.13 A typical tri-layer device structure.

The presence of hole-transport and electron-transport layers reduces the energy barriers for the injection of charge carriers from electrodes, hence facilitating charge injection from the electrodes and leading to a better balance in the number of holes and electrons. At the same time both layers block charge carriers from escaping from the emitting layer, confining injected holes and electrons to it. The tri-layer device was first developed by Adachi et al. ^[35] The main advantage of a tri-layer device being that the emissive layer can be very thin allowing electrons and holes to be confined to a small area, therefore

improving brightness and efficiency. The latest development of a tri-layer device is now more likely to be a device containing seven or eight layers, including a hole-blocking layer (HBL) and electron-blocking layer (EBL).

1.8 Hybrid Organic-Inorganic Light-Emitting Diodes

Some inorganic nanocrystals emit visible light with sharp emission spectra that are less than 30 nm FWHM. These nanocrystals are in reality quantum dots and because they confine their charge well within their small volume, a high quantum efficiency of 50% is possible. It would therefore make sense to assume that quantum dots incorporated into organic material in an OLED would provide excellent emission. ^[36] Electroluminescence has been observed by simply mixing inorganic nanocrystals with π -conjugated polymers. However the emission efficiency was far lower than that of conventional polymer LEDs. ^[37]

A major advantage of using quantum dots in an LED device is the ability to incorporate a single layer of molecules, meaning electrons and holes may be transferred directly from the surfaces of the electron-transport layer and the hole-transport layer. This is seen when a three layered structure is used, encompassing a thin emissive layer sandwiched between a hole-transport layer and an electron-transport layer. A thin layer of emissive material is more suitable as a thick layer requires the injection and transport of both electrons and holes. This means that the material must be ambipolar, i.e., combine the capabilities of the electron-transport and hole-transport layers, which is difficult to achieve in one material. This thin layer of material is often known as a molecular-size layer. An example of an OLED using a molecular-size emissive layer is shown by Matsumura et al. where they used a rubrene dye layer sandwiched between a hole-transport and electron-transport layer, each of 50 nm thickness. ^[38] Coe et al. used this molecular-size theory to incorporate quantum dots as the emissive layer rather than rubrene, into a hybrid quantum-dot LED.^[39] The emissive layer in their device is only a few nanometres thick, made up of uniformly distributed single CdSe nanocrystals each around 3 nm in diameter. The quantum-dot layer was processed via spin-casting with a solution of nanocrystals in

an organic material. Spontaneous phase segregation leads to the formation of a thin layer of nanocrystals on top of the underlying organic layer. Statistical mechanics limit the number of electron-hole recombinations in organic material resulting in light emission to less than 25%. Low light emission, however is not a problem for inorganic nanocrystals as every hole-electron recombination can result in light emission making it a promising technology for achieving 100% efficiency.

A different approach to hybrid organic-inorganic light-emitting diodes is the use of solgel co-assembly with organic materials and tetraethyl orthosilicate. Yang et al. showed that blue luminescent fluorene based amphiphile/silica forms co-assembled nanocomposite films show enhanced emission, often as much as several times. ^[40]

1.9 Emissive Materials for Organic Light-emitting Diodes

There are two major classes of materials used in organic light-emitting diodes, firstly small-molecule materials and secondly conjugated mainchain polymeric materials (PMs), as discussed earlier. Small molecules are deposited by vacuum deposition at high vacuum (10⁻⁵ Torr), whereas PMs are deposited by spin-coating from solution of a soluble polymer or polymer precursor onto a glass substrate. However small-molecules have two advantages with respect to PMs in that they are more homogeneous and they have better colour purity. PMs are sometimes difficult to purify because they cannot be sublimed, distilled or recrystallised. An insufficient purity of polymers can be detrimental to the performance of an OLED.

Polymer electroluminescent devices have received a lot of attention using main chain conducting polymers such as poly(phenylenevinylene) (PPV), ^[41] poly(*p*-phenylene) (PPP), ^[42] poly(thiophene) ^[43] and poly(fluorene). ^[44] A further problem with conjugated polymers, especially poly(fluorene) as a blue emitter, is the tendency to generate long wavelength emission around 550 nm either during annealing or passage of current, turning the desired blue emission colour into a blue-green emission with a drop of electroluminescence quantum efficiency. ^[45-47] Strong low-energy emission can also

occur in conjugated polymers, usually caused by the formation of keto defect sites ^[48] or aggregates/excimers, ^[49] to solve this problem several successful approaches have been reported, including the use of bulky end groups ^[50] and the use of cross-linkable groups. ^[51] However this thesis is concerned only with small-molecule materials, their polymerisable equivalents (reactive mesogens) and polymer networks formed from them, so mainchain polymer materials will not be discussed in any further detail. Generally the following criteria are required if organic materials are to find application in OLEDs as emissive materials. They should.

- possess suitable ionisation potentials and electron affinities. This means they should have well-matched energy levels for the injection of charge carriers from the electrodes and adjacent organic layers.
- be capable of forming smooth, uniform thin-films without pinholes.
- be both morphologically and thermally stable.

They should also exhibit more specialised properties, such as having a specific band-gap to provide a range of coloured emitters. Red, green and blue are the three most important ones. They should also preferably possess both electron-accepting and electron-donating properties as they should transport both holes and electrons. This is known as ambipolar character.

Organic light-emitting compounds consist of chromophoric functional groups that consist of either heterocyclic or homocyclic aromatic rings with a high degree of conjugation. Some typical functional groups are shown in figure 1.14. The design of molecular compounds and the choice of functional groups depend on whether the target compound is desired to transport holes or electrons and/or to emit bright visible light.



Figure 1.14 Typical aromatic chromophores useful as emissive materials.

Tang and Van Slyke (1987) ^[11] demonstrated that Alq₃, a small-molecule material, exhibits good EL and electron-transport properties. Alq₃ and other small-molecules were originally commercialised by Kodak. This material can also be used in a polymer matrix such as polymethymethacrylate (PMMA) and used in association with other organic dopant molecules to improve transport and luminescent properties. Some typical light-emitting dopants are shown in figure 1.15.



Figure 1.15 Typical extended conjugated materials used as dopant materials.

Recently a red-green-blue pixellated OLED has been demonstrated based on main chain polyfluorenes with photocrosslinkable oxetane side chains and a photoacid as a cationic initiator. ^[52] There is interest in another more attractive approach using liquid crystalline polymer networks formed from polymerisable light-emitting liquid crystals, known as reactive mesogens, RMs. ^[53-57] This approach to OLEDs is discussed in more detail later.

1.9.1 Doping as a means of Light-Emitting Materials

Concentration quenching as a result of interaction among molecules at high concentration, is a common and serious problem for molecule-based emissive materials in OLEDs. ^[58] Red-emissive molecular materials are usually polar, such as electron donor-substituted pyran containing compounds, ^[59] or extensively π -conjugated compounds, such as porphyrins .

These red emitters have an inherent tendency to crystallise or agglomerate into molecular stacks and become either weakly emissive or not emissive at all in the solid state, with very few exceptions. ^[60] This means poor efficiency is a real problem, especially at high current densities due to emissive quenching by charged or triplet species that are electrogenerated in the OLED. ^[61] This can be overcome by using low concentration doping in a suitable host, as already discussed during the description of phosphorescence. Doping also has the added benefit of overcoming attack by charges on red-emissive materials because of their smaller band-gap.

1.10 Charge-transporting and Charge-blocking Molecular Materials

Most organic conducting materials can be described as p-type semiconductors, in which holes in the valence band are the majority charge carriers. They are simply cation (positive) and anion (negative) radicals.

In an OLED the imbalance in electron injection caused by the low electron affinity of organic materials can be overcome by the incorporation of electron-transporting and hole-blocking layers, ^[62-64] as seen in the multi-layer devices discussed earlier. Most conjugated organic materials are electron rich. Therefore it is not surprising that in many cases these materials transport holes (cationic radicals), rather than electrons (anionic radicals). Enhancing the electron affinity of a molecule can be achieved by incorporating electron-deficient atoms, e.g., nitrogen atoms in the molecular structure. This can be achieved by synthesising materials that include heterocyclic aromatic rings, such as oxadiazole, ^[65] triazole ^[65-67] and quinoxaline. ^[68] The incorporation of pyridine, pyrimidine, tetrazine, benzothiazoles and benzothia(oxa)diazoles also has a similar effect. ^[69] Materials having high electron affinities usually provide good electron-transporting materials by accepting negative charges and allowing them to move through the molecules. Conversley hole-blocking materials should possess electron-accepting properties with high ionisation potentials so that they accept electrons from the electrontransport layer and transport them to the emitting layer, but also block hole carriers from escaping from the emitting layer.

1.11 Amorphous Molecular Materials

Recent studies have revealed that like polymers, small organic molecules can also readily form stable amorphous glasses above room temperature under appropriate conditions. A number of reports have been published since the mid-1990s, and a new field of organic materials science that deals with amorphous molecular glasses as electroluminescent materials has opened up. ^[63, 70]

The presence of an amorphous glassy state can be confirmed by a combination of optical polarising microscopy, X-ray diffraction and differential scanning calorimetry. Amorphous molecular materials are characterised by well-defined glass-transitions, usually associated with polymers and ready formation of uniform amorphous thin films by vacuum deposition or deposition from solution, plate 1.01, e.g., by spin coating, doctor blade techniques and drop casting.



Plate 1.01 Room temperature amorphous glass phase of compound 30.

Small-molecular materials can be purified by column chromatography, followed by recrystallisation or vacuum sublimation.

1.12 Liquid Crystals

The photoluminescent properties of a limited number of different kinds of nematic polymer networks and gels have been reported. ^[71-75] These reports highlighted the possibility of using light-emitting liquid crystals as polymer networks, gels or elastomers for use in OLEDs especially with polarised emission.

The molecules in a crystalline solid have long-range positional and orientational order. When heated the molecular interactions between the molecules begin to break-down. If all the interactions breakdown simultaneously then an isotropic liquid is formed. However, if the interactions breakdown in stages (i.e. side-to-side, end-to-end) then intermediate phases between the solid and liquid states are formed. The compounds that exhibit mesophases are called liquid crystals, although not all mesophases are liquid crystalline. Mesophases are characterized by partial ordering of the molecules. Their molecular axes possess an orientational order whereas the molecules possess little or no positional order. There are two main categories of liquid crystals: thermotropic and the lyotropic, see figure 1.16. Thermotropic liquid crystals are formed by the addition of solvent. Lyotropic liquid crystals will not be further discussed in this thesis as they are not suitable for OLEDs or other electro-optic displays due to the presence of solvent molecules.



Figure 1.16 A general classification of liquid crystals

Calamitic liquid crystals usually consist of a relatively rigid "rod-like" molecular core often containing co-linear six-membered rings, either aromatic and/or alicyclic, lateral substituents and flexible or polar end groups. They can be subdivided mainly in two categories: nematics and smectics, figure 1.17. Both types have chiral versions and a range of variants of the smectic state has been reported.

In the nematic phase the long molecular axes of adjacent molecules are on average aligned parallel to each other and in a preferred local direction known as the director (n). The nematic phase has one degree of order. The nematic phase is the least ordered liquid crystal phase and as a consequence has a high degree of fluidity.

The smectic mesophase is more ordered than the nematic phase due to the presence of a layer structure. The smectic phase shows polymorphism, i.e., there are several different types of smectic phases. The main phases of interest during this thesis are the smectic A and smectic C mesophases. These are the least ordered of the smectic phases and possess no positional order within the layers. Only orientational order is present. The relatively viscous, but still fluid, nature of the smectic A and semctic C phases, allows them to be processed and aligned in thin solid films much more easily than more ordered smectic phases with positional order within the layers. The smectic A phase consists of long, thin molecules with their molecular long axes aligned orthogonal, on average, to the layer plane. The smectic C phase has a similar structure to the smectic A phase. However, the molecular axes are aligned at an angle to the layer normal within the layered structure. This tilt angle usually increases with decreasing temperature.



Figure 1.17 Mesomorphic properties of a typical calamitic liquid crystal. ^[76]

1.12.1 Mesophase identification

Combinations of the following analytical techniques may be used to identify the phases exhibited by liquid crystals:

1.12.2 Optical Polarising Microscopy

This is the most widely used technique to identify phase types, since each different liquid crystal phase has one or more distinctive and characteristic optical texture observed between crossed-polarisers. These textures are a result of the anisotropic molecular orientation of domains within the mesophase. A thin sample of the material is sandwiched between a microscope slide and a cover slip. The slide is placed in a hotstage on the microscope where the temperature can be accurately controlled. The hotstage is situated between crossed polarisers. With no sample, or with an isotropic liquid, or indeed appropriately aligned liquid crystal material in place, light is extinguished and the field of view is black. When an anisotropic, birefringent medium is present polarised light is separated into an ordinary and extraordinary ray. Light is not extinguished and an

optical texture appears due to interference colours. The observed textures give information relating to the arrangement of the molecules within the liquid crystalline sample. The arrangement of the molecules within the mesophase is reflected in the observed textures. The so-called Schlieren texture, plate 1.02, is charachteristic of a smectic C phase. It differs from that of the nematic phase due to the presence of only four-point brushes. The Schlieren texture of the nematic phase contains two and four point brushes.



Plate 1.02 Schlieren texture of a Smectic C phase of compound 47.

Another important difference between a nematic phase and a smectic phase C, as both exhibit a Schlieren texture, is observed on cooling a sample from the isotropic phase. When a nematic mesophase is formed on cooling from the isotropic liquid, droplets form which coalesce to form a Schlieren texture, plate 1.03. This behaviour is not seen when a smectic mesophase, including a smectic A or smectic C phase, forms on cooling from the isotropic liquid. Droplets are not observed in these cases. The smectic A phase, for example, forms batonnets, plate 1.04. The nematic and smectic A phases can also exhibit a homeotropic texture, which is not possible for the smectic C phase.



Plate 1.03 Nematic droplets of a nematic phase formed on cooling from an isotropic liquid.



Plate 1.04 Batonnets of a smectic A phase formed on cooling from an isotropic liquid.

1.12.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a method used to confirm the number and the transition temperature of the phases exhibited by liquid crystals. This technique involves measuring the enthalpy changes at liquid crystal transitions. Two micro-furnaces are linked together, each with a separate heater and temperature sensor. One of the furnaces contains a reference material, which has a known heat of fusion, such as Al₂O₃, or gold. The other contains the sample under investigation. Heat energy is supplied to both

samples and the heating rates of the samples are maintained at an identical rate. At the melting transition extra heat is supplied to the sample in order to restore the uniform heating rate. The extra energy input is measured by the instrument and converted to a value for the enthalpy change (Δ H). DSC is useful for identifying the presence of a phase transition, which can be assigned using optical microscopy, and for measuring glass transition temperatures. A typical DSC trace is shown in figure 1.18.





X-ray diffraction studies can be used to determine the phase structure in a mesophase and so identify the type of the phase. Aligned samples are necessary to distinguish and classify the smectic C phases or highly ordered soft crystals. However it is a technique that is used sparingly as a combination of DSC and optical microscopy often proves to be sufficient to identify a mesophase and x-rays of liquid crystals can be difficult to interpret, although for more ordered phases the technique proves very useful.

1.13 Liquid Crystals for OLEDs

The first OLEDs using liquid crystalline polymer networks formed from polymerisable light-emitting liquid crystals (reactive mesogens, RM) were reported recently. ^[77-79] These OLEDs have the potential to overcome some of the disadvantages of standard OLEDs. For this to happen the light-emitting liquid crystals for OLEDs are required to

exhibit a narrow range of low-temperature liquid crystal phases for room temperature processing and a spectrum of related physical properties. Such as molecular energy levels and band-gap for electron and hole injection, moderately high charge transport for efficient and high-intensity emission, good film forming properties from solution in organic solvents, chemical, photochemical and electrochemical stability, as well as tunable colour and colour purity for multicolour OLEDs.

Liquid crystalline materials can be macroscopically aligned in one of the more fluid mesophases, such as the nematic phase or the smectic A or C phase. Macroscopicallyoriented materials have numerous applications in OLEDs, for example: linearly polarised light emission, enhanced charge transport and circularly polarised light emission. Until recently smectic liquid crystals were seen as unsuitable for OLEDs because of the difficulty in processing the viscous materials and aligning them in OLED configurations. However, the magnitude of the charge-carrier mobility of the least-ordered smectic phases (smectic A and smectic C) may well be sufficient for OLEDs. ^[80] The reactive mesogens synthesized were specifically for OLEDs, with red, green or blue emission from either smectic A or smectic C phases. The layered structure of smectic liquid crystals is known to lead to high charge carrier mobility, ^[81-85] which should in turn lead to more efficient OLEDs.

1.13.1 Liquid crystalline polymer networks in OLEDs

Multilayer OLEDs are the most efficient ^[11] type of OLED, e.g. compared to monolayer OLEDs. The most common methods up to date to construct such devices are vacuum deposition and spin coating. By vacuum deposition, well-defined, thin layers can be produced, but it is a time consuming and an expensive method as it is a batch process and is not consistent with continuous production methods. Spin coating is a cheap deposition process and large areas can be coated effectively with a thin uniform layer of organic material. However, interlayer mixing can occur during the deposition of each subsequent layer. Interlayer mixing occurs when the material to be deposited is a solute in a common organic solvent. The solvent often solvates the organic material already deposited,
causing mixing of the two organic materials at the layer interface. Interlayer mixing represents a major problem in the fabrication of PLEDs.

In order to facilitate multilayer fabrication *via* spin coating the solubility of the layers of small-molecules or polymers could be reduced after deposition. A possible solution involves the polymerisation of small-molecule liquid crystals incorporating polymerisable groups, i.e., reactive mesogens. Different photoreactive groups have been incorporated, such as acrylates, ^[74] oxetanes, ^[86] and dienes. ^[79] The latter appear at the moment to be the most attractive from a process point of view for a number of reasons, e.g., they prevent degradation during photopolymerisation and promote liquid crystalline properties. ^[87] The semi-rigid cyclic structure of the polymers formed by cyclopolymerisation of non-conjugated dienes also appears to improve the performance of the resultant polymer network in LC-OLEDs. The significance of intramolecular cyclisation of unconjugated dienes was highlighted in the 1950s when Butler et al. ^[88, 89] discovered that free radical solution polymerisation of diallyl quaternary ammonium salts resulted in the formation of soluble, uncrosslinked polymers with only a very small amount of residual unsaturation. Butler et al. demonstrated that intramolecular cyclisation occurs during the polymerisation of unconjugated dienes, in general, to form linear polymer chains consisting of cyclic structures composed of either five- and/or sixmembered heterocyclic rings.

Acrylate, methacrylate and non-conjugated diene groups are preferred as photochemically-initiated polymerisable end groups, rather than vinyl ethers, epoxides or oxetanes, for example, which require ionic initiators or chemical crosslinking agents such as amines in the case of epoxides. These initiators remain as an impurity within the highly crosslinked polymer networks and are suspected of causing short device lifetimes. However cationic or anionic polymerisation may have processing advantages as radical polymerisation needs cleaner, drier conditions to prevent polymerisation termination. The first OLED incorporating a light-emitting liquid crystal as a crosslinked polymer network demonstrated in 2001. A liquid crystalline material incorporating a was photopolymerisable group, shown by GJR 130 in figure 1.19 was aligned and quenched to form a glassy state. As the glass transition temperature of this material is low (Tg = 45° C) it could be crosslinked just above room temperature to form an insoluble anisotropic polymer network. The resultant film gave polarised electroluminescence with a moderately high polarisation ratio (11:1). ^[90] Importantly many of the performance data were superior for the LC-OLED incorporating the highly cross-linked polymer network compared to those of the LC-OLED based on the glassy liquid crystal monomer.



Figure 1.19 A photopolymerisable liquid crystal, GJR130.

During previous research photopolymerisable diene end groups have been incorporated in the liquid crystal monomers in order to produce polymer networks via the action of radiation of UV light for use of charge-transport and/or emission in a multilayer OLED. It has been reported that the crosslinking of reactive mesogens can also result in an increase of the charge carrier mobility by a factor of two. ^[91] The possible reason is the mesophase order that is retained in the network, this monodomain is shown in figure 1.20.



Figure 1.20 Schematic representation of the polymer network.

The majority of reactive mesogens investigated so far have been fluorene derivatives, which exhibit a nematic phase. ^[53, 78, 79, 91-94] Steric effects exerted by the two alkyl chains at the 9-postion prevent formation of the layer structure of smectic phases. The lower viscosity of the nematic phase compared to that of the smectic phase allows them to be spontaneously aligned on a suitable surface for polarised emission. ^[79]

1.13.2 Liquid Crystalline Networks in OFETs

The development of organic field effect transistors (OFETs) has generated a great deal of interest in the availability of solution processable organic semiconductors, which can combine both oxidative stability and high charge transport mobility. ^[95-98] It has been shown that the charge carrier mobility of an organic semiconductor in an OFET is strongly dependent on its microscopic and macroscopic morphology and order. ^[99, 100] This flexibility in structure and properties is a significant advantage of organic materials over their inorganic counterparts. The classic example of electrical properties being dominated by molecular order in organic-semiconductors is that of OFETs based on oligomeric sexithiophene as demonstrated by Servet and Garnier. ^[101] It was shown that molecular design could be used to control the packing arrangement of molecules in thin

solid films of oligothiophenes. The field-effect mobility in the OFET test device was improved by a factor of 50 by controlling the molecular order in the evaporated film.

Liquid crystal semiconductors have been shown to exhibit excellent charge carrier mobility by time-of flight experiments, due to the high degree of orientational order in a monodomain of a suitable mesophase. Liquid crystals studied for use in OFETs include nematic liquid crystal polymers and nematic and smectic small-molecule. A small number of smectic RMs have also been prepared for use as organic semiconductors in organic field effect transistors (OFETs). ^[69, 102-105] The short and long range order present in the layered structure of highly ordered smectic phases, or 'plastic crystals', leads to high charge carrier mobility. Unfortunately these highly viscous phases are difficult to process and align uniformly in an OFET or OLED configurations. Dewetting of the substrate during the deposition process is a common problem encountered in the fabrication of OFETs and OLEDs using small-molecules, especially liquid crystals with terminal aliphatic chains, due to weak interactions with the substrate surface.

A further potentially-important development is the integration of an OLED and an OFET in one device. This device combines the electrical switching functionality of a field-effect transistor and the ability to produce light, of an OLED. This device is known as an organic light-emitting transistor, OLET, and could be used for the development of an all-organic, active-matrix flat-panel-display. ^[106] OLETs may be an important development in the future as they are seen as a way of improving the lifetime and efficiency of OLEDs due to the different driving conditions they use compared to standard OLEDs. These modified driving conditions result in optimised charge-carrier balances. OLETs combine electron and hole field-effect transport, light emission and electrical switching.

OLETs differ from OLEDs in structural properties as well. OLEDs have a well known vertical structure, which has been proved successful in the development of commercial devices. An OLET differs in that it has a planar device geometry, which allows charge transport to occur in the plane at the dielectric/organic interface, known as field-effect charge transport, rather than perpendicular to the organic layers, known as bulk charge

transport. This is important under typical biasing conditions as the mobility of electrons and holes can be about four orders of magnitude higher in OLETs than in OLEDs. This phenomenon can be improve device lifetime and result in higher exciton emission. There are disadvantages to the planar geometry of an OLET device, e.g., holes and electrons must travel much greater distances in an OLET, typically a few hundred nanometres. This imposes more stringent requirements on the charge-transport properties of the organic materials. But this problem is far outweighed by the improvement in electroluminescent efficiency achieved, mainly due to the decrease in the amount of exciton quenching that occurs with the externally applied electric field and metal contacts.

1.14 Linearly Polarised Electroluminescence

A source of linearly polarised light is of interest for many reasons, one of which is the use as a backlight in brighter, cheaper, more efficient liquid crystal displays. A source linearly-polarised light would allow the removal of the normal backlight and polarizer combination. As a result the power efficiency and the brightness of such a device will be enhanced as only one polariser is used. Polarisers are one of the most expensive components of LCDs. Polarised electroluminescence has been observed from aligned films of both low-molecular-mass liquid crystals and from LC polymers. ^{[107], [108]} One of the most attractive techniques of achieving alignment of the liquid crystalline chromophores is by using alignment layers, e.g., a layer of rubbed polyimide, ^[75] which introduce homogeneous alignment of the liquid crystalline mesophase, figure 1.21. A layer of rubbed polyimide can be used to achieve homogeneous alignment. However, the alignment layer for OLEDs needs to be charge transporting and unfortunately polyimide is an insulator. To overcome this problem polyimide is usually doped with a charge transport material such as TBD. ^[109]



Figure 1.21 Diagram depicting homogeneous alignment.

Thermotropic liquid crystal polymers can be aligned and annealed at high temperatures and then quenched into the glassy state. A typical example of such a main chain, conjugated liquid crystalline and electroluminescent polymer is poly(9,9-dioctylfluorene), ^{[110], [111]} figure 1.22. Grell et al. have shown that polarised electroluminescence can be obtained from aligned samples of such a polymer material.



Figure 1.22 A main chain polyfluorene.

Small-molecule liquid crystalline materials have also been used to generate polarised emission. The main problem is the fluidity of the liquid crystal phase. This can be eliminated if the LC phase can be quenched into the ordered glassy state. Glass transition temperatures for small-molecules are rarely reported and are usually low. This creates problems in the fabrication of multilayer devices due to interlayer mixing. Polymers have a greater tendency to form high temperature glassy states than small molecules due to their polydispersity, high molecular weight, conformational inhomogeneity and high viscosity.

1.16.1 Circularly Polarised Electroluminescence

When optically-active chiral centres are present in an organic electroluminescent material then circularly polarised emission can be produced. Circularly polarised emission does

not require macroscopic alignment of the chromophores as the intrinsic molecular chirality and the chiral aggregate formation is the cause for the polarization, e.g., a chiral derivative of PPV has been reported to emit circularly polarised light. However, the degree of polarisation was found to be very low. ^[112] Oda et al. ^[113] reported a high degree of polarisation from a chiral polyfluorene, figure 1.23, exhibiting a chiral nematic mesophase.



Figure 1.23 A main chain chiral nematic polymer.

It has been suggested that the circular polarised emission is due to the helical structure of the nematic phase. Circularly polarized light is emitted during the propagation through the chiral nematic film. ^[114] However, the layers in an OLED are too thin to act as a wave guide and therefore the circularly polarised light is probably due to the formation of chiral aggregates in the emitting liquid crystalline film.

1.15 Liquid Crystals as Charge-Carrier Transport Layers

Electronic charge transport in liquid crystals was first reported in 1994 by Haarer et al. using discotic liquid crystals. ^[115] This report was followed by the observation of electronic mobility, rather than ionic mobility, in calamitic smectic liquid crystals by Funahashi and Hanna. ^[116] Generally ionic impurities exert a strong influence as charge carriers on electrical conduction in materials, particularly in liquids because of their viscosity-dependent mobilities. Electronic conduction may be masked by ionic conduction, even if the organic materials only contain a small concentration of ionic impurities. Therefore, not only very pure materials, but also chemically-stable molecules are indispensable for the characterisation of electrical properties in organic semiconductors without degradation occurring to produce ionic impurities.

The performance of an OLED is strongly influenced by the charge carrier mobility of both electrons and holes. New materials with high charge-carrier mobilities may involve the exploitation of the self-organisation taking place in liquid crystals. Compounds in the liquid crystalline state can exhibit higher charge–carrier mobility than in the crystalline state or in the liquid state. This is because of the high degree of molecular order in the liquid crystalline state without grain-boundary defects and traps associated with polycrystalline compounds and amorphous solids. ^[54] Generally, the hole-transport material must have a low ionisation potential for its easy loss of an electron to produce a hole in the conduction process. On the other hand an electron transport material must have high electron affinity.

Since the discovery in 1977 by Chandrasekhar, ^[117] discotic mesogens have been of great interest to the liquid crystal community. The first discotic mesogen was a hexasubstituted benzene derivative ^[117] and now there is a wide range of discotic molecules, including for example, triphenylene, ^[118] phthalocyanine, ^[119] pyrene ^[120] and perylene, derivatives. Discotic molecules can form a variety of columnar mesophases. The leastordered phase is the nematic discotic phase (N_d), ^[121, 122] in which the molecules are aligned parallel to each other, but there is no layer or columnar structures nor positional order within a nematic discotic domain. The hexagonal columnar (Col_h), ^[123-125] rectangular columnar (Col_r) ^[126] and oblique columnar (Col_{ob}) ^[127] phases are moreordered phases with positional and orientational order of the columns within a discotic domain.

Discotic materials, which are able to form columns, have been found to display unusually large values of the charge-carrier mobility for holes and probably for electrons as well, along the columns. Furthermore, the absolute magnitude of the mobility depends strongly on the state of order within the columnar phases as apparent from time-of-flight studies. ^{[128], [129]} An example is the hexakis(*n*-alkoxy)triphenylenes, shown in figure 1.24, which was found to exhibit high hole mobility in the columnar phase close to that found for organic single crystals and semiconductors. ^[130-132]



Fig 1.24 A hexakis(*n*-alkoxy)triphenylene structure.

Due to the insulating nature of the aliphatic chains the charge travels through the aromatic columns with a high degree of delocalisation of the high electron density. However one of the main problems of these systems is the alignment of the columns perpendicular to the anode surface as they tend to align parallel to the substrate, ^[133] figure 1.25. In order to incorporate columnar liquid crystals in OLEDs perpendicular alignment to the anode surface is required as well as same way to stabilise the order within the columnar layer and support emission and electron-transport layers above them.



Figure 1.25 The different alignments in a columnar phase

1.16 Stability and Reliability of OLEDs

The lifetime of a display device is probably one of the most important issues in characterising its performance. An operating lifetime of 10,000 hours is required at least combined with 5 years storage lifetime. The lifetimes of current OLEDs remain inferior to those of comparable inorganic LEDs. The organic materials used in OLEDs are semiconductors and therefore thin films of material (~ 100 nm) are necessary for low

voltage operation and low power consumption. One of the most important factors, which affects device stability and reliability is material purity. It has been shown that ionic purities can have a dramatic effect on device lifetime. The ionic impurities are detrimental to device operation as they act as a trap for excitons formed during the recombination process, this inhibits quantum efficiency. The ionic impurities also promote electrochemical degradation of the electrodes via redox reactions. These ionic impurities seem to have more of an effect than organic impurities resulting from the organic synthesis. Column chromatography and HPLC go a long way to removing organic impurities, often resulting in purities above 99.9%. However, these chromatographic techniques often fail to remove ionic impurities that may be introduced by the organic solvents and during the synthetic procedures. ^[134] Techniques to remove these ionic impurities include using ion-exchange resins and metal trapping agents. Other factors that can affect device stability and reliability include:

- Photochemical degradation, often caused by photo-oxidation when the organic materials react with oxygen.
- Electrochemical degradation, often caused by ionic impurities or water, which can cause redox reactions at the electrodes.
- Structural degradation, often caused by molecular-reorganisation and relaxation or crystallisation of glass phases or mesophases. This is often attributed to the effect of a constant voltage bias.
- Electrode degradation, the electrodes can react with the materials. This has been regarded as a form of ITO diffusion into organic layers.
- Colour purity, often red and blue pixels are the first to fail, which leaves a predominantly green display.

All these problems mean the organic material has to be exceptionally pure, not just in terms of organic impurities but also with respect to ionic impurities as well. The device has to be fabricated in an atmosphere free of moisture and oxygen. The organic materials have to be carefully selected to ensure that crystallisation does not occur.

1.17 Organic Photovoltaics

The energy reaching the earth from the sun in one single day would supply the earth's total population with sufficient energy for the next two to three decades, if all of it could be collected, stored and then utilised effectively. Therefore efficient, workable photovoltaic devices could offer many solutions to the environmental issues, such as global warming, acid rain, and holes in the ozone layer, by converting a fraction of this free abundant solar power into electricity.

The fifty year anniversary of the first silicon solar cell passed in 2005. The prohibitive costs of the first silicon photovoltaics prevented them becoming an instant commercial success, but the first reports of a solar cell attracted a lot of public interest in 1955. The highest efficiency solar cells currently available are triple-junction cells consisting of GaInP, GaAs and Ge. They can produce efficiencies up to 27% and are vastly more complex than original solar cells. Now types of or variants of inorganic solar cells are common place, but as will be discussed in the coming pages, they have some intrinsic disadvantages compared to photovoltaic devices using organic materials.

The most well known and efficient organic photovoltaic is a plant cell carrying out photosynthesis. This, of course, is a biological process, in which the sun's energy is captured and stored by a series of events that convert the energy of light into the biochemical energy needed to power life. The production of electric energy from sunlight in an organic photovoltaic is the result of a chain process, figure 1.26. Sunlight photons are absorbed (A) inside the device, carriers are then generated (G) from exciton dissociation, carriers are collected (C) by the electrodes and driven into the external circuit, shown by the arrow of current flow, producing energy, in this case light (L). These are the productive events of the PhotoVoltaic (PV) process. However, some solar radiation is lost through reflection (R). However, it is not clear exactly how much and is device dependent. This is a simplistic view of a device structure, but is representative of how the first organic photovoltaic devices were constructed. The single organic layer

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sandwiched between the anode and cathode has been replaced with heterojunction designs.



Figure 1.26 Diagram depicting the Photovoltaic Process.

The general structure used for organic solar cells is similar to OLEDs. The devices are fabricated in a sandwich geometry. As substrates, transparent, conducting electrodes, e.g., glass covered with ITO, are used. Alternatives to the expensive ITO have been sought and nanotube network electrodes potentially work as well. ^[135] The ITO can be surface modified often with the use of a PEDOT:PSS layer, which can improve the surface quality of the ITO electrode as well as facilitating the hole injection/extraction. The active layers are coated using solution or vacuum deposition in much the same way as discussed earlier for OLED devices. Finally the top electrode is evaporated. Usually a lower work-function metal, compared to ITO, is used such as aluminium is used often with an ultrathin lithium fluoride underlayer. In photoelectron spectroscopy studies, it was shown that the metal work function can be considerably reduced by evaporation of LiF layers. ^[136]

Organic materials are attractive for photovoltaics, primarily because of the prospect of cheap high-throughput manufacture using reel-to-reel or spray deposition of large-area photovoltaic devices. Additional attractions are the possibilities for ultra thin, flexible devices, which may be integrated into appliances or building materials and tuning of absorption through chemical synthesis. It is possible to draw on the extensive OLED research ^[137] that has been carried out to date to help with the design and commercialisation of organic photovoltaic devices, as both technologies need similar technological progress and improvements to become competitive technologies in their respective fields.

It was twenty years ago when a 1% conversion yield was achieved for an organic solar cell. ^[138] This has steadily been improved on and now 5% efficiency has been achieved. ^[139] The aim is to reach 10% efficiency within the next 5 years, which may make the technology commercially viable. The vast majority of these advances have come from new multi-layered thin film structures and interpenetrating networks, ^[140] and unique methods such as nematic gel templates. ^[141] The use of liquid crystals in organic photovoltaics have similar advantages to those discussed previously for OLEDs. Improved fabrication methods and materials have the effect of enlarging the heterointerface area to maximise charge separation and efficient transport to the electrodes. ^[142-144]

There are several reasons for using organic semiconductors in photovoltaic devices. The most important advantages are.

- They can be processed easily using spin coating, wet processing or evaporation techniques.
- Only small quantities of organic material are required, typically 100 nm thick layers, which makes large scale processing easier.
- The band gap, valence and conduction energies, charge transport and other structural properties can be altered by chemically tuning materials.

• Organic materials have a vast variety of suitable structures, which allows the problem of certain materials being under patent protection to be overcome.

In general organic semiconductors can be regarded as intrinsic wide band-gap insulators, band-gaps above 1.4 eV, down to insulators, band-gaps above 3eV, with a negligibly low intrinsic charge carrier density at room temperature in the dark.

Organic photovoltaic materials differ from inorganic semiconductors in the following important respects.

- Photogenerated excitons are strongly bound and do not spontaneously dissociate into separate charges. Typically exciton charge-dissociation in organic media requires an energy input of 100 meV compared to a few meV for a crystalline semiconductor. This can mean light absorption does not always result in carrier generation.
- Charge transport proceeds via hopping between localised states, rather than transport within a conduction band, which results in low mobility values.
- The spectral range of optical absorption is relatively narrow compared to the solar spectrum.
- Absorption coefficients are high, typically 10⁵ cm⁻¹, so films less than 100 nm thick can be used to achieve high optical densities.
- Organic materials are unstable in the presence of oxygen and water, especially under a constant voltage bias.

1.17.1 Absorption of Photons

In most organic photovoltaic devices only a small portion of the incident light is absorbed because the bandgap is too high. A bandgap of 1.1 eV (1100 nm) is required to absorb 77% of the solar radiation on earth, whereas the majority of organic semi-conducting molecules have bandgaps higher than 2.0 eV (600 nm), which limits the possible absorption to about 30%. Low charge carrier and exciton mobilities require layer

thickness in the order of 100 nm. Fortunately the absorption coefficient of organic materials is generally much higher than that of doped silicon, so that only about 100 nm are necessary to absorb light with a wavelength of between 60 nm and 905 nm, if a reflective back contact is used.

1.17.2 Reflection

Reflection losses are probably significant, but this is a little investigated phenomenon in organic materials. Systematic measurements of photovoltaic materials are desired to provide knowledge of their impact on absorption losses. Anti-reflection coatings as used in inorganic devices may then prove useful once other losses such as recombination become less dominant.

1.17.3 Exciton Diffusion

Ideally, all photoexcited excitons should reach a dissociation site. Since such a site may be at the other end of the semiconductor, their diffusion length should be at least equal to the layer thickness (for sufficient absorption), otherwise they recombine and photons are wasted. Exciton diffusion ranges in small molecules are usually around 10 nm. This is why distributed, rather than planar, heterointerfaces have been used to maximise charge separation.

1.17.4 Charge Separation

Charge separation is known to occur at heterojunctions, e.g., at organic semiconductor/metal interfaces, around impurities such oxygen or at the interface between materials with significantly different electron affinities (EA) and ionisation potentials (IA). In the latter, one material can then act as electron acceptor, while the other retains the positive charge and represents an electron donor. ^[138, 145] If the difference in IA and EA is not large enough, the exciton may just transfer to the material with the lower bandgap without charge separation occurring. The exciton will then relax eventually without contributing to the generation of photocurrent.

1.17.5 Charge Transport

The transport of charges is affected by recombination during the journey to the electrodes, particularly if the same material serves as transport medium for both electrons and holes. Also, interaction with atoms or other charges may hinder charge-transport and thereby limit the magnitude of the photoinduced current.

1.17.6 Charge Collection

In order to enter an electrode material with a relatively low workfunction (Al or Ca) the charges often have to overcome the potential barrier of a thin oxide layer. In addition, the metal may have formed a blocking contact with the semiconductor so that they cannot immediately reach the metal.

1.17.7 Device Degradation

Many effects can cause photovoltaic device degradation, many of which cause OLED degradation in the same way. These degradation factors are slowly being overcome as it is important to expose the device to more than ten years of solar radiation to make them competitive compared to traditional silicon devices. Ten years of exposure equates to 87 600 hours and at the moment only 20 000 hours is obtainable under normal working conditions. Obviously this is a problem as the technology will never become competitive unless substantial improvements are made.

To overcome lifetime issues improvements have to be made in key areas.

• Organic materials that are intrinsically stable, they must be stable under storage, under sunlight, and under reduction or oxidation conditions. This requires greater material development using varying synthetic techniques.

- Purification methods have to be improved, using ion-exchange resins and high quality HPLC are helping to remove impurities.
- Amorphous glass transition temperatures or mesophase transitions have to be improved, a higher and more stable glass phase will improve device stability, this will only occur when a greater array of organic materials are developed.
- Water and oxygen content have to be reduced to almost non existent quantities, this is achieved by improving device fabrication conditions, better glove boxes and better encapsulation techniques are required.

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H_{2n+1}C_nO

Introduction

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Aims of Research

2. Aims of Research

The overall aim of this research was to synthesise and evaluate novel liquid crystalline materials, including reactive mesogens to be used as light-emitting, chargetransporting or charge-accepting materials for use in OLEDs and or photovoltaic devices. Such compounds with photopolymerisable end groups could be cross-linked to form an insoluble polymer network that allows the fabrication of multi-layer OLEDs or phase-separated photovoltaic devices. The majority of materials to be synthesised should be capable of being aligned in the liquid crystalline state. The use of liquid crystalline materials means the chromophores of the materials could be aligned to allow the generation of linearly or circularly polarised light. The materials were designed to exhibit either an amorphous glassy phase or liquid crystalline properties. Materials incorporating a chiral centre were to be synthesised with the aim of producing circularly polarised light.

Perylenes show promising charge-transport properties as well as having the ability to form liquid crystalline phases. Unfortunately these materials usually exhibit very high melting points. Therefore, it was intended to incorporate branched alkyl chains in a perylene tetraester material, figure 2.01 in order to lower the melting point and produce soluble materials for deposition by spin-coating. The materials to be synthesised should have low melting and clearing points and a columnar mesophase with good charge-transport properties.



Figure 2.01 Proposed structure of low temperature liquid crystalline perylene compound.

In order to produce liquid crystalline materials with electron-transport properties it was proposed to use perfluorinated alkyl chains to replace the octyl chains of a liquid crystalline fluorene as shown in figure 2.02. The aim was to alter the energy levels of the alkyl-substituted material to produce a perfluorinated analogue with improved charge-transport properties.



Figure 2.02 Proposed structure of a dialkylperfluorinated fluorene with non-conjugated diene.

The charge-transporting properties of benzothidiazoles are well known. Therefore the aim was to synthesise analogous materials incorporating the benzoxadiazole moiety with an oxygen atom in place of the sulphur atom in the heterocyclic ring as shown in figure 2.03. It was expected that the material would possess a smectic liquid crystal phase similar to the analogous benzothiadiazole. The synthesis of liquid crystalline charge-transporting materials with a smectic phase was a further aim, since there is good evidence to suggest that the higher degree of order present in smectic phases may lead to higher charge-transport than that in similar materials with a nematic phase instead of a smectic phase.



Figure 2.03 Proposed structure of a benzoxadiazole containing reactive mesogen.

Heterocyclic materials containing nitrogen atoms have been shown to be suitable for charge-transporting properties. Another aim of this research was to synthesise liquid crystalline materials incorporating nitrogen heterocyclic rings in order to study the effect of the presence of a number of nitrogen atoms on the liquid crystalline properties and the energy levels of the materials produced. Figure 2.04 shows the general structure of a tetrazine material to be synthesised as part of this study.



Figure 2.04 Proposed general structure of electron-deficient tetrazine moiety.

It was intended to synthesise a unique Siamese type structure in order to explore the liquid crystalline properties of these type of materials and their electron-transporting properties. A typical structure of the kind of nitrogen heterocycle to be prepared is shown in figure 2.05.



Figure 2.05 Proposed Siamese type structure of an expected charge-transport material.

Another aim of this thesis was to study the effects of incorporating methyl groups into a fluorene-containing molecular core on the liquid crystalline properties of these materials. The intention was to produce materials with a low degree of aggregation of neighbouring chromophores. This should in turn result in high PL and EL efficiency. Figure 2.06 shows the general structure of the planned materials. The effect of varying the position and number of the methyl groups on the liquid crystalline properties was to be studied. The nature of the alkoxy-chains attached in a terminal position to the aromatic core was varied in order to study its effect on glass formation and the liquid crystalline behaviour of these materials.



Figure 2.06 General structure of a methyl substituted reactive mesogen.

A further aim of the work for this thesis was the synthesis of new liquid crystals for circularly polarised emission, such as that shown in figure 2.07. It was decided to synthesise a trimeric liquid crystal, with a chiral part and an emissive part to aid glass formation. Another aim was to use this trimer as the emissive layer in an OLED device for the first time.



Figure 2.07 Proposed structure of a chiral trimeric liquid crystalline material.

A further aim of the work for this thesis was the synthesis electroluminescent liquid crystals to facilitate the fabrication of a full-colour LC-OLED. Examples of such materials are shown in figure 2.08. The compounds vary only in the nature of the central aromatic moiety. This structural change is sufficient to red-shift emission from blue to green to red. These structures were chosen because of the strong prospect of each compound to exhibit liquid crystalline phases and high glass transition temperatures.



Figure 2.08 Proposed structures of blue, green and red-emitting liquid crystalline materials.

The Organophotonics research group had previously synthesised reactive mesogens with methacrylate groups at the end of the terminal aliphatic chains attached to the aromatic core. Therefore, it was intended to incorporate this kind of reactive mesogen into an OLED as an intractable polymer network for the first time. The structure of a liquid crystalline reactive mesogen is shown in figure 2.09.



Figure 2.09 Proposed structure of a methacrylate reactive mesogen.

The use of perylene materials as liquid crystalline semiconductors has been reported but there is a limited number of reported low-temperature liquid crystalline perylene *bis*-imides. Therefore, an additional aim of this thesis was to synthesise perylene *bis*imides with a high aspect ratio using sterically hindered 2,7-disubstituted-9,9dialkylfluorene materials to achieve low temperature nematic phases. A typical structure of such a material is shown in figure 2.10. The material was to be synthesised as an electron-acceptor for use in organic photovoltaics because of its broad UV-vis absorption spectrum and also possibly as an electron-transport layer in OLEDs.



Figure 2.10 Proposed structure of a perylene liquid crystalline material.

3.1 Evaluation of the Materials

¹H Nuclear Magnetic Resonance (NMR) Spectrometry

The structures of intermediates and final products were confirmed by ¹H NMR spectroscopy using a JEOL Lambda 400 spectrometer. An internal standard of tetramethylsilane (TMS) was used. The following abbreviations are an example of those used to describe the splitting patterns:

S	-	singlet	d	-	doublet	t	-	triplet
quart	-	quartet	quint	-	quintet	sext	-	sextet
sept	-	septet	dd	-	double doublet	dt	-	double triplet

Infrared (IR) spectrometry

Infrared spectroscopy was particularly useful for the confirmation of certain functional groups. The analysis was carried-out using a Perkin-Elmer 1000 Fourier Transform (FT-IR) spectro-photometer.

Mass spectroscopy (MS)

A mass spectrum was recorded using a Gas Chromatography/Mass Spectrometer (GC/MS) QP5050A Schimadzu with Electron Impact (EI) at a source temperature of 200 $^{\circ}$ C. Compounds with a RMM >800 g mol⁻¹ were analysed using a Bruker, reflex IV, Matrix Assisted Laser Desorption/Ionisation (MALDI), Time of Flight (TOF) MS. A 384 well microlite plate format was used with a scout target. Samples were dissolved in DCM with HABA (2-(4-hydroxyphenylazo)benzoic acid) matrix (1:10, respectively). The mass ion of the material is identified as M⁺.

Chromatography

The progress of reactions was frequently monitored by thin layer chromatography (TLC) and capillary gas chromatography (GC). Aluminium backed TLC plates coated with silica gel (60 F_{254} Merck) were utilised. GC was carried out using a Varian CP3800 gas chromatogaph equipped with a 10 m CP-SIL 5CB column.

Purification of intermediates and final products was mainly accomplished by column chromatography, using silica gel 60 (230 - 400 mesh). Electroluminescent and charge transport final compound materials were further purified by passing through a column consisting of a layer of basic alumina using the appropriate eluent. This was followed by passing through a column of ion-exchange resin to remove any inorganic ions present then recrystallisation from a suitable solvent, glass transition temperature allowing. All glassware used was thoroughly cleaned by rinsing with chromic acid followed by distilled water and then drying in an oven at 100 °C for ~ 45 minutes. The purity of the final products was normally confirmed by elemental analysis using a Fisons EA 1108 CHN.

Melting Points and Transition Temperatures

The melting point and other transition temperatures were measured for each of the new compounds using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarising microscope. The melting point and transition temperatures of all the final materials were determined using a Perkin-Elmer DSC-7 in conjunction with a TAC 7/3 instrument controller.

Reagents and reaction solvents

Reagents that were purchased were used without further purification unless otherwise stated. Reaction solvents, such as diethyl ether and tetrahydrofuran, were dried and distilled over sodium wire and used immediately. Dimethylformamide was distilled and

dried over molecular sieves (4Å). Triethylamine was dried, distilled and subsequently stored over KOH. Other solvents were used as purchased. All reactions were performed under an atmosphere of dry nitrogen unless otherwise stated. Some abbreviations that are commonly known or have been used in this work are described below:

BHT	-	2,6-Di-tert-butyl-4-methylphenol
<i>n</i> -BuLi	-	<i>n</i> -Butyllithium
N^*	-	Chiral nematic phase
Cr	-	Crystal
CV	-	Cyclic voltammetry
DCC	-	N,N'-Dicyclohexylcarbodiimide
DCM	-	Dichloromethane
DHP	-	3,4-Dihydro-2 <i>H</i> -pyran
DMAP	-	4-(N,N'-Dimethylamino)pyridine
DME	-	1,2-Dimethoxyethane
DMF	-	Dimethyl formamide
DMSO	-	Dimethylsulphoxide
dppf	-	1,1'-bis(diphenylphosphino)ferrocene
EL	-	Electroluminescence
EtOH	-	Ethanol
FT-IR	-	Fourier transform-infrared
GC	-	Gas chromatography
Ι	-	Isotropic liquid
KF	-	Potassium Fluoride
Lit.	-	Literature
MS	-	Mass spectrometry
MeOH	-	Methanol
Ν	-	Nematic phase
NMR	-	Nuclear magnetic resonance
NBS	-	N-Bromosuccinimide
PL	-	Photoluminescence

RT	-	Room temperature
Sm	-	Smectic phase
THF	-	Tetrahydrofuran
TLC	-	Thin layer chromatography
TBAB	-	Tributylammonium bromide

3.2 Experimental discussion

The synthetic pathways to the intermediates and final products are shown in schemes 1 - 20. A brief discussion of the synthesis and some of the problems encountered are given below.

Scheme One

The starting materials perylene-3,4,9,10-tetracarboxylic dianhydride **1** and 1bromooctane are commercially available and are used without further purification. The tetraester **2**, which had been previously ^[1] synthesised, was obtained by the alkylation of the dianhydride, **1**, using 1-bromooctane as reagent and solvent in poor yield (11%). The product **2** was purified by column chromatography. The poor yield is due to a large amount of dialkylated product, which formed an insoluble red precipitate. A cyclo addition reaction of compound **2** with commercially available phenylurazole resulted in phenylurazole **3**, in poor yield (18%). The aim of this step was the addition of phenylurazole in both of the bays of the perylene **2** to try and induce columnar liquid crystalline properties. This proved unsuccessful probably due to the electron withdrawing effects of the four ester groups of perylene **2**, as a similar reaction has proved successful on perylene. ^[2] This effect probably also contributed to the low yield of compound **3**, along with the difficulty in separating compound **3** from the small amount of the desired product shown overleaf, compound A, which could not be isolated and characterised in a pure state.



Scheme Two

1-Bromo-3,7-dimethyloctane **5** was synthesized using a well known bromination procedure ^[3] from commercially available 3,7-dimethyl-1-octanol **4** using *N*bromosuccinimide and triphenyl phosphine in dichloromethane as solvent in excellent yield (81%). The alkyl bromide **5** was used both as a solvent and reagent in an esterification reaction to produce the tetraester **6** in a moderate yield (37%). The tetraester **6** was not recrystallised as the compound is liquid crystalline at room temperature and a suitable solvent could not be found. If the tetraester **6** was to be synthesised again a similar procedure has shown that a mixture of the 1-bromo-3,7-dimethyloctane **5** and 3,7dimethyl-1-octanol **4** using similar conditions maybe more successful. ^[1]

Scheme Three

The 9,9-disubstituted fluorene **9** with partially perfluorinated chains was synthesized in two steps from commercially available fluorene **7** using *n*-butyllithium at – 78 $^{\circ}$ C followed by quenching with 1H,1H,2H,2H-perfluorooctyl iodide to produce compound **8**. ^[4] A simple workup was then followed by repetition of the above procedure to produce compound **9**. The poor overall yield (26%) was probably due to the low solubility of

1H,1H,2H,2H-perfluorooctyl iodide in THF at – 78 °C, which resulted in the perfluorinated chain forming a suspension. A more simple and convenient procedure using sodium hydroxide ^[5] or potassium-*t*-butoxide ^[6] as base was attempted, but proved unsuccessful, possibly due to decomposition of the perfluorinated chain. Bromination of compound 9 was then carried out using bromine and DCM as solvent in a standard procedure in a moderate yield (58%) of compound **10**. ^[6] The electron-withdrawing effects of the perfluorinated chains meant the bromination was slow and had to be carried out under reflux. The biphenyl-boronic acid 13 was synthesised by a previously published procedure in two steps. The ether 12 was first prepared in good yield (70%) via a Williamson-ether synthesis.^[7] The second step was carried out by the lithiation of the phenyl bromide **12**, followed by quenching with trimethyl borate and acid hydrolysis ^[8] to yield the boronic acid 13 also in good yield (70%). The NMR spectra of compound 13 showed the presence of a significant amount of the boronic anhydride. However, this derivative of compound 13 also reacts in the following reaction and was not removed by a purification procedure. A palladium-catalysed Suzuki aryl-aryl cross-coupling reaction ^[9] of compounds **10** and **13** resulted in the formation of the hexaphenylene **14** in a moderate yield (46%).

Scheme Three a

The bisphenol **15** was obtained in high yield (82%) by dealkylation of **14** using boron tribromide. ^[10] Even though the alkyl chains at the 9-position of the fluorene **14** were partially perfluorinated compound **14** was still soluble in many common organic solvents, which allowed the dealkylation to be carried out in DCM. The diene ester **17** was synthesised from commercially available penta-1,4-dien-3-ol and bomoundecanoic acid **16** in a base-assisted esterification reaction using DCC and DMAP in good yield (65%). ^[11] A Williamson ether reaction was used to synthesise the diester **18** in moderate yield (45%). ^[7] The non-conjugated units do not polymerise under these reaction conditions so no radical inhibitor was required.

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Scheme Four

2-Bromo-7-iodofluorene 20 was synthesised by iodination of commercially available 2bromofluorene **19**^[12] in a standard procedure in good yield (69%) using a combination of iodine and periodic acid. This was followed by the di-alkylation in the 9-position of the fluorene 20 with 1-bromopropane in a standard procedure in a good yield (49%) to give the 9,9-dialkylfluorene **21**.^[5] The aryl-iodide **21** was converted selectively to the phenol 22 by a standard procedure, $^{[13]}$ in good yield (62%). The phenol was protected with commercially available 3,4-dihydropyran to give the THP-ether 23 in good yield (68%). This step was necessary to prevent the formation of a lithoxy salt during the next step. Lithiation of the aryl-bromide 23 with *n*-butyllithium at -78 °C, followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2 dioxaborolane to give the dioxaborolane 24 in an moderate yield (43%). The thiadiazole-dibromide 26 was synthesised in good yield (65%) using bromination of benzo[1,2,5]thiadiazole **25** in a standard procedure. ^[13] A palladium-catalysed Suzuki aryl-aryl coupling ^[9] of compounds 24 and 26 produced a compound that proved difficult to remove from a silica gel column using DCM as eluent. This was due to the acidic nature of silica gel, which had acted as a deprotecting reagent to remove the tetrahydropyran groups and thus form the bisphenol 27. This actually made the purification easier as flash chromatography was used to flush all starting materials and mono-addition products from the column before ethyl acetate:hexane (1:1) was used to remove the much more polar bisphenol 27. However the yield was poor (32%), which is probably due to the deprotection of the THP-protected ether formed during the arylaryl coupling reaction on the silica column.

Scheme Four a

The diene ester **29** was synthesised from the commercially available bromoalkanoyl chloride **28** and penta-1,4-dien-3-ol in good yield (76%) in a base-assisted esterification. ^[11] The bromide **29** was used in a Williamson ether synthesis to alkylate the bisphenol **27** to give the diether **30** in good yield (76%). The diether **30** could not be recrystallised as it formed a waxy solid over a number of days and no suitable solvent could be found once it had formed a solid.

Scheme Five

Protection of commercially available 4-bromophenol **31** with 3,4-dihydropyran resulted in the ether **32** in excellent yield (82%). The yield is high, which may be partially due to the ease of purification as a consequence of the great difference in polarity of the compounds **31** and **32**. The purification was carried out on a neutral alumina column to prevent the deprotection seen in scheme four. Lithiation of the aryl ether 32 with nbutyllithium at - 78 °C, followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2 dioxaborolane yielded the THP-protected dioxaborolane **33** in a good yield (75%). The THP-protected di-arylether 35 was synthesised using commercially available 2,5dibromopyridine **34** and compound **33** in a Suzuki aryl-aryl cross-coupling reaction catalysed by tetrakis(triphenylphosphine)palladium (0).^[9] This reaction resulted in a small quantity of the desired product 35, essentially as a minor side-product, but deprotection on the column again occurred to give the bisphenol 36 in excellent yield (83%). The bisphenol **36** is less soluble than other diphenols synthesised in this thesis due to the lack of alkyl chains in a lateral position, for example at the 9-position of a fluorene moiety. This means that NMR analysis had to be carried out in DMSO. The Williamson ether reaction between bromoalkane 29 and the diphenol 36 was carried out in DMF a very polar solvent. However, solubility problems may have contributed to the low yield (18%).

Scheme Five a

4,7-Dibromobenzo[1,2,5]oxadiazole **39** was synthesised in a similar bromination procedure to that used for 4,7-dibromo[1,2,5]thiadiazole **26** using the commercially available benzo[1,2,5]oxadiazole **38** in good yield (60%). A palladium-catalysed Suzuki aryl-aryl cross-coupling using the THP-protected dioxaborolane **33** and dibromooxadiazole **39** yielded the THP-protected diaryl ether **40** in high yield (71%). ^[9]
To prevent the THP deprotection of the bisphenol of the THP-protected diaryl ether **40**, purification was carried out using column chromatography and neutral alumina. THP-deprotection of the THP-protected diaryl ether **40** was carried out using *p*-TSA in a solvent combination of DCM/EtOH to help increase solubility of the mono deprotected byproduct. This reaction resulted in the bisphenol **41** in an excellent yield (86%). The Williamson ether reaction between the diene ester **29** and bisphenol **41** gave the diether **42** in good yield (55%).

Scheme Six

The dihydrotetrazine **44** was synthesised in an excellent yield (91%) according to a standard procedure, ^[14] which involved heating hydroxybenzonitrile **43** and hydrazine hydrate under reflux. The tetrazine **45** was synthesised by the oxidation of the dihydrotetrazine **44** using an aqueous solution of sodium nitrite in an ethanoic acid and water mixture. The yield (22%) was poor because of the lack of solubility of the dihydrotetrazine **44** in an ethanoic acid water mixture. The low solubility of the tetrazine allowed the crude product to be purified by trituration on a sinter with DCM, which removed the starting materials. The diether **46** and **47** final products were synthesised using a Williamson ether synthesis using the bisphenoltetrazine **45** and diene esters **17** and **29** to yield the diethers **46** and **47** respectively in good yields (71%, 45%). ^[7]

Scheme Six a

The diether **48**^[15] was synthesised in excellent yield (84%) using a Willliamson ether synthesis involving the bisphenol **45**. The diether **48** was then heated under reflux in toluene with 1,4-diethynylbenzene over four days to yield the dipyridizine **49** in a poor yield (22%). The low yield is likely due to the dipyridizine **49** being a bulky, sterically-hindered molecule preventing diethertetrazine **48** addition on both sides of 1,4-diethynylbenzene.

Scheme Seven

The dipyridinetetrazine **52** was synthesized from the reaction of 2-cyanopyridine **50** and hydrazine hydrate ^[16] to yield the dihydrotetrazine **51** in a moderate yield (32%), which was oxidized using sodium nitrite under aqueous and acidic conditions to give the dipyridinetetrazine **52** in poor yield (29%). The yield was poor due to the lack of solubility of compound **51** in an aqueous / acidic solvent mixture. The dipyridinetetrazine **52** was heated under reflux for six days with 1,4-diethynylbenzene in toluene. The isolated bisdipyridinepyridizine **53** was obtained in a very poor yield (8%) due to the steric bulk of the material limiting product formation as seen in scheme six a.

Scheme Eight

The bromoiodofluorene **20** was synthesised as shown in scheme four. The dialkylfluorene 54 was synthesised using a quicker and more efficient alkylation procedure than that used in scheme four, using potassium hydroxide, potassium iodide, 1-bromohexane and DMSO at RT, resulting in a good yield (78%).^[12] The next step involved the selective reaction of the iodo-fluorene 54 in a concentrated solution of copper cyanide and DMF to give the mono-cyanofluorene 55 in a good yield (67%). In an improved procedure compared to that used in previous schemes, the cyanofluorene 55 was reacted with hydrazine hydrate, EtOH and sublimed sulphur to yield the dihydrotetrazine. ^[14, 17] The oxidation was carried out without isolation and purification of the dihydrotetrazine using a solution of ethanoic acid and THF with aqueous sodium nitrite, which resulted in the difluorenetetrazine 56 in moderate yield (31%). The use of sulphur, which is thought to improve the yield ^[14] and the use of THF as solvent during the oxidation step, had the desired effect of improving the overall yield compared to that of the compounds synthesized in scheme six. The alkoxybromopyridine 58 was synthesised in good yield (63%) from the commercially available 2-hydroxy-5-bromopyridine 57 using a simple Williamson ether synthesis with DMF as solvent. The lithiation of the bromopyridine 58 at -78 °C followed by quenching with trimethyl borate, stirring overnight and acidification with hydrochloric acid (20%, v/v) resulted in purification of the pyridine-

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boronic acid **59** in moderate yield (48%). A Suzuki aryl-aryl cross-coupling reaction using $Pd(PPh_3)_4$ as a catalyst, DME as the solvent, sodium carbonate (20%, w/w) as the base and the bromo-tetrazine **56** and the pyridine-boronic acid **59** gave the difluorenetetrazine **60** in moderate yield (37%).

Scheme Nine

The synthesis of the difluorenetetrazine **56** has been described in scheme eight and the preparation of the phenyl-boronic acid **13** described in scheme three. These compounds were combined in a Suzuki aryl-aryl cross-coupling with $Pd(PPh_3)_4$ as catalyst, DME as solvent and sodium carbonate (20%, w/w) as base to give the difluorenetetrazine **61** in a good yield (69%). ^[9]

Scheme Ten

The synthesis of the tetrazine **56** has already been described in scheme eight. The phenylboronic acid **63** was synthesised from the alkylation of commercially available 4bromophenol, which gave the alkoxy bromobenzene **62** in good yield (68%). This was followed by the lithiation of the alkoxy bromobenzene **62** with *n*-BuLi in THF at -78 °C followed by quenching with trimethyl borate stirring overnight and acidification with hydrochloric acid (20%, v/v), which gave the phenyl-boronic acid **63** in a moderate yield (58%). The melting point is given for the phenyl-boronic acid **63** but it has a broad value probably due to the presence of some quantity of the anhydride, shown by NMR analysis, a possible reason why its melting point has not been reported previously. ^[18, 19] A Suzuki aryl-aryl cross-coupling was carried using difluorenetetrazine **56** and phenyl-boronic acid **63**, Pd(PPh₃)₄ as catalyst, DME as solvent and sodium carbonate (20%, w/w) as base to give the tetrazine **64** in a poor yield (26%). ^[9] The poor yield may be due to what appeared to be a high percentage of homo-coupled product of phenyl-boronic acid **63** to produce the biphenyl, compound B, shown overleaf.



Compound B.

Scheme Eleven

The synthesis of the 2-bromo-7-iodofluorene 20 and the corresponding dialkyl substituted fluorene 21 has been described in scheme four. The methoxyphenyl thiophene 66 was synthesised from commercially-available 1-bromo-4-methoxy-2-methylbenzene and tributyl(thiophen-2-yl)stannane in a Stille aryl-aryl cross-coupling ^[20] using Pd(PPh₃)₄ as catalyst and DMF as solvent in moderate yield (50%). The acidic hydrogen in the 2position of 2-(4-methoxy-2-methylphenyl)thiophene **66** was lithiated using *n*-BuLi in THF at -78 °C and quenched using tributyltin chloride, which gave the stannylthiophene **67**. ^[21] This Stille tin intermediate was not purified further as it has been shown that the acidic nature of silica gel can protonate the 2-position of tributyl[5-(4-methoxy-2methylphenyl)thiophen-2-yl]stannane and thereby remove the tributyltin moiety.^[22] GC analysis showed a purity of 79%, which was taken into consideration when calculating stoichiometric quantities for the next step. Using the dialkyl substituted flourene 21 and stannyl thiophene 67 in a Stille aryl-aryl cross-coupling using $Pd(PPh_3)_4$ as catalyst and DMF as solvent, gave the fluorene 68 with six aromatic rings in good yield (71%). Commercially available boron tribromide was used in concentrated form with DCM as solvent to remove the methoxy groups, to give the bisphenol 69 in good yield (72%). The diethers 70, 71 and 72 were prepared in a Williamson ether synthesis using the appropriate bromoalkanoates and potassium carbonate, potassium iodide and DMF in good yields (61, 51 and 72%). The diethers 70 and 71 were not recrystallised as a suitable solvent could not be found because the compounds formed waxy solids over a number of days.

Scheme Twelve

The synthesis of the 2-bromo-7-iodofluorene 20 and the corresponding dialkyl substituted fluorene 21 has been described in scheme four. The methoxyphenyl thiophene 74 was synthesised from commercially available 4-bromo-1-methoxy-2-methylbenzene and tributyl(thiophen-2-yl)stannane in a Stille aryl-aryl cross-coupling ^[20] using Pd(PPh₃)₄ as catalyst and DMF as solvent in a good yield (77%). The acidic hydrogen in the 2-position of 2-(4-methoxy-3-methylphenyl)thiophene 74 was lithiated using *n*-BuLi in THF at -78 ^oC and guenched using tributyltin chloride, which gave the stannyl thiophene **75**. The Stille tin intermediate was not purified further as it has been shown that the acidic nature of silica gel can protonate the 2-position of tributyl[5-(4-methoxy-3methylphenyl)thiophen-2-yl]stannane and thereby remove the tributyltin moiety.^[22] GC analysis showed a purity of 68%, which was taken into consideration when calculating stoichiometric quantities for the next step. Using the 9-disubstituted fluorene 21 and stannyl thiophene **75** in a Stille aryl-aryl cross-coupling using Pd(PPh₃)₄ as catalyst and DMF as solvent, gave the fluorene 76 with six aromatic rings in a good yield (67%). Commercially available boron tribromide was used in concentrated form in DCM to remove the methoxy groups, which gave the bisphenol 77 in good yield (85%). The diethers 78, 79 and 80 were prepared in a Williamson ether synthesis using the appropriate bromoalkanoates and potassium carbonate, potassium iodide and DMF or butanone in good yields (61, 64 and 64%) for compounds 78, 79 and 80 respectively. The diethers 78 and 79 were not recrystallised as a suitable solvent could not be found because the compounds formed waxy solids over a number of days.

Scheme Thirteen

The synthesis of the 2-bromo-7-iodofluorene **20** and the corresponding dialkyl substituted fluorene **21** has been described in scheme four. The methoxyphenyl thiophene **82** was synthesised from commercially-available 2-bromo-5-methoxy-1,3-dimethylbenzene and tributyl(thiophen-2-yl)stannane in a Stille aryl-aryl cross-coupling ^[20] using Pd(PPh₃)₄ as catalyst and DMF as solvent in a good yield (77%). The acidic hydrogen in the 2-position

of 2-(3,5-dimethyl-4-methoxyphenyl)thiophene, compound 82, was lithiated using n-BuLi in THF at -78 °C and quenched using tributyltin chloride, which gave the stannyl thiophene 83. The Stille tin intermediate was not purified further as it has been shown that the acidic nature of silica gel can protonate the 2-position of the stannyl thiopheneand thereby remove the tributyltin moiety.^[22] GC analysis showed a purity of 73%, which was taken into consideration when calculating stoichiometric quantities for the next step. Using the dialkylsubstituted fluorene 21 and stannyl thiophene 83 in a Stille aryl-aryl cross-coupling using $Pd(PPh_3)_4$ as catalyst and DMF as solvent, gave the fluorene 84 with six aromatic rings in excellent yield (84%). Commercially available boron tribromide was used in concentrated form in DCM to remove the methoxy groups to give the bisphenol 85 in excellent yield (81%). The diethers 86 and 87 were prepared in a Williamson ether synthesis using the appropriate bromoalkanoates and potassium carbonate, potassium iodide and DMF or butanone in good yields (61, 80%) respectively. The diethers 86 and 87 were not recrystallised as a suitable solvent could not be found because the compounds had very low nematic clearing point transition temperatures meaning they formed a waxy oil rather than a crystalline solid.

Scheme Fourteen

The synthesis of the bisphenol **77** has been discussed earlier during scheme twelve. This compound was reacted with the dihydrocholesterol bromoalkanoate **89** in a Williamson ether reaction, which resulted in the diether **90** in a good yield (72%). The dihydrocholesterol ester **89** was synthesised from commercially available 6-bromohexanoic acid and 3 β -cholestanol using DCM as solvent and DCC and DMAP as reagents in an excellent yield (81%).

Scheme Fifteen

The synthesis of the alkoxyphenyl **62** has been discussed earlier in scheme ten. Compound **62** was reacted with tributyl(thiophen-2-yl)stannane in a Stille aryl-aryl crosscoupling ^[20] using Pd(PPh₃)₄ as catalyst and DMF as solvent to give the 2-alkoxyphenyl-

substituted thiophene **91** in a good yield (66%). It is important to point out that during every Stille coupling carried out in the work of this thesis an aqueous workup was carried out after the reaction with a saturated potassium fluoride solution in order to try and polymerise the tributyltin chloride bi-product to aid purification. The alkoxyphenyl thiophene **91** was lithiated using *n*-BuLi in THF at -78 °C and quenched using tributyltin chloride resulting in the stannyl thiophene **92**. The compound was not purified further for reasons explained above. The dialkylsubstituted fluorene **94** was synthesised from commercially available bromofluorene, potassium hydroxide, potassium iodide and DMSO in a good yield (77%). A Stille aryl-aryl cross-coupling was carried out between the stannyl thiophene **92** and 9-dialkylsubstituted fluorene **94** using Pd(PPh₃)₄ as catalyst and DMF as solvent to give the dialkoxy-substituted fluorene **95**. This compound has been synthesised previously with similar yields (56% and 44% respectively) and identical liquid crystal transition temperatures. ^[11] Commercially available boron tribromide was used in concentrated form in DCM to remove the octyloxy groups to provide the bisphenol **96** in an excellent yield (86%).

Scheme Fifteen a

The methacrylic ester **99** was synthesised from commercially available methacrylic acid and 11-bromoundecan-1-ol in a base-assisted esterification reaction using DCC, DMAP and DCM as solvent in a good yield (59%). A Williamson ether reaction using the bisphenol **96**, methacrylic ester **99**, potassium carbonate, potassium iodide and DMF was carried out. However, the methacrylic ester **99** wasn't added until the potassium salt had formed overnight and after the methacrylic ester **99** had been added a small quantity of BHT was included to inhibit radical formation and polymerisation of the methacrylate. Compound **100** was isolated in moderate yield of (46%).

Scheme Sixteen

The synthesis of compounds **20**, **62** and **92** has already been discussed in previous schemes. The 9-dialkylsubstituted fluorenes **101** and **103** were synthesised in the same

way that compound **94** was prepared as shown in scheme fifteen in good yields of 71 and 63%, respectively. The 2-bromofluorene **102** was synthesised by a Stille aryl-aryl crosscoupling ^[20] using the stannyl thiophene **92**, 9-dialkylsubstituted fluorene **101**, Pd(PPh₃)₄ as catalyst and DMF as solvent in a good yield (81%). The 2,7-bisdioxaborolane **104** was synthesised by the lithiation of the 2,7-dibromo positions of the 2,7-dibromofluorene **103** followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane, using THF as solvent and *n*-BuLi as lithiating agent. Five molar equivalents of *n*-BuLi were used as the reaction provided a poor yield, if lesser quantities were used. An alternative to the use of a large excess of *n*-BuLi is to use diethyl ether as solvent and allow the reaction to warm to room temperature. A Suzuki aryl-aryl cross-coupling reaction was then carried out between the bromofluorene **102** and bisdioxaborolane ester **104** using Pd(PPh₃)₄ as catalyst, DMF as solvent and tripotassium phosphate as base. The trifluorene **105** product was isolated in good yield (62%).

Scheme Seventeen

The synthesis of compounds **20**, **62** and **92** has already been discussed in previous schemes and the 9-dialkylsubstituted fluorene **101** was synthesised in a similar manner to other compounds in this thesis in a good yield (71%). The 2,7-bis-substituted fluorene **106** was synthesised *via* a Stille aryl-aryl cross-coupling ^[20] in an excellent yield (81%).

Scheme Seventeen a

The 2,7-bis-substituted fluorene **106** was lithiated using *n*-BuLi in THF at -78 °C and quenched using tributyltin chloride to form the stannylthiophene **107**, which was used without further purification for reasons explained above. ^[22] It has previously been shown that Stille cross-coupling reactions in the presence of CuI can improve the yield and rate of a cross-coupling reaction. ^[23] This is thought to occur because metal ion exchange occurs were the more reactive copper reagent is formed from the tin reagent. Copper iodide was used in the reaction of **107** with itself to induce a homo-coupling reaction.

This reaction proved very successful with a good yield (71%) of the symmetrical compound **108** with ten aromatic rings in the molecular core.

Scheme Seventeen b

The bisphenylfumaronitrile **110** was synthesised using commercially available 4bromophenylacetonitrile, sodium methoxide, iodine, methanol and diethyl ether in an excellent yield (89%). ^[24] The stannylthiophene **107** was synthesised in large quantities in scheme seventeen a so that the excess could be used in the Stille aryl-aryl cross-coupling reaction with the bisphenylfumaronitrile **110**. The Stille coupling ^[20] of compound **107** with compound **110** was carried out with Pd(PPh₃)₄ as catalyst and DMF as solvent at a temperature of 90 °C to give the bisthienylphenylfumaronitrile **111** in an excellent yield (81%).

Scheme Eighteen and Eighteen a

The synthesis of compounds **20** and **92** has been discussed previously. These reaction intermediates were synthesised in large quantities as part of previous schemes to use in later schemes. The 9-dialkylsubstituted fluorene **112** was synthesised using 2-bromo-7-iodofluorene **20**, commercially available 2-ethylhexyl bromide, potassium hydroxide, potassium iodide and DMSO at room temperature in a good yield (59%). The stannylthiophene **92** and 9-dialkylsubstituted fluorene **112** were reacted in a selective Stille aryl-aryl cross-coupling with Pd(PPh₃)₄ as catalyst and DMF as solvent to form the bromofluorene **113** in a good yield (70%). A Grignard reaction was carried out using the bromofluorene **113** in a THF solution, which was added dropwise to a suspension of washed magnesium turnings and a trace amount of iodine. This gave the nitrophenyl fluorene **114** in moderate yield (43%). The fairly low yield is attributable to incomplete conversion of the bromofluorene **113** to the Grignard reagent. The amine **115** was synthesised by a simple reduction of the corresponding nitro-substituted compound. Although there are many known methods for this reduction, one of the simplest, cleanest and most efficient is the use of commercially available tin chloride hydrate, using EtOH

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as solvent while heating under reflux. ^[25] This method gave the amine **115** in an excellent yield (94%), which was used without further purification in order to avoid the possibility of decomposition of the primary amine. The crude product was used immediately for the final step of the reaction, which involved the formation of a perylene bisimide using commercially available perylene-3,4,9,10-tetracarboxylic dianhydride, zinc acetate dihydrate and imidazole. The imidazole acts as the solvent at temperatures above its melting point at 80 °C. This resulted in the bisimide **117** in moderate yield (58%). This seems to be a typical yield for the formation of a perylene bisimide, ^[26] the product yields a deep-red crystalline solid.

Scheme Nineteen

The synthesis of 9-dialkylsubstitutedfluorene **121** has been discussed previously. Compound 121 was synthesised in large quantities as it is a commonly-used reaction intermediate. The synthesis of 2-methoxyphenyl-substituted thiophene **119** was carried out using a Stille aryl-aryl cross-coupling reaction of compound **118** with tributyl stannyl thiophene, $Pd(PPh_3)_4$ as catalyst and DMF as solvent in an excellent yield (80%). The stannylthiophene 120 was synthesised by the lithiation of the 2-position of the thiophene of the mehoxyphenyl thiophene **119** at -78 °C, this was then quenched with tributyltin chloride, allowed to warm to room temperature overnight and the product isolated. Further purification of the crude product was not carried out for the reason already discussed. A selective Stille aryl-aryl cross-coupling of 9-dialkylsubstitutedfluorene 121 and stannylthiophene 120 was then carried out using $Pd(PPh_3)_4$ as catalyst and DMF as solvent, which gave the selectively coupled bromofluorene 122 in a good yield (61%). A Grignard reaction was carried out using the bromofluorene 122 to give the nitrothiophene **123** in moderate yield (39%). The fairly low yield is attributable to incomplete conversion of the bromofluorene **122** to the Grignard reagent as described previously. The aminothiophene **124** was synthesized in a quantitive yield by a simple nitro reduction using commercially available tin chloride hydrate and EtOH as solvent while heating under reflux.^[25] The crude amine was used immediately for the final step of the reaction in order to avoid oxidation. The final step of the reaction scheme involved the formation

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of a perylene bisimide **125** using commercially available perylene-3,4,9,10tetracarboxylic dianhydride, zinc acetate dihydrate and imidazole as the solvent above 80 °C in moderate yield (53%).

Scheme Twenty

This scheme involves two simple steps seen before in previous schemes. The aminofluorene **127** was synthesised *via* reaction of commercially-available 2-aminofluorene with 1-bromododecane, potassium hydroxide, potassium iodide and DMSO at room temperature and although the yield was low (39%), the removal of a reduction step of the nitrofluorene means the overall yield is comparable. The second step of the scheme involved the reaction of the commercially available perylene-3,4,9,10-tetracarboxylic dianhydride, zinc acetate dihydrate and imidazole to form the perylene bisimide **128** in a moderate yield (40%).





a: BrC₈H₁₇, K₂CO₃. b: Pb(OAc)₄, Phenyl urazole, DCM.



a: PPh₃, NBS, DCM. b: 1, K₂CO₃.

Scheme 3



a: i) *n*-BuLi, ii) $I(CH_2)_2(CF_2)_5CF_3$, THF. b: i) *n*-BuLi, ii) $I(CH_2)_2(CF_2)_5CF_3$, THF. c: Br₂, DCM. d: BrC₈H₁₇, K₂CO₃, Butanone. e: i) *n*-BuLi, B(OMe)₃ THF, ii) HCl (aq). f: Pd(PPh₃)₄, Na₂CO₃ (20% aq), DME.





g: BBr₃, DCM. h: DCC, DMAP, HOCH(CH=CH₂)₂, DCM. i: K₂CO₃, KI, DMF.



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₃H₇, TBAB, NaOH (aq), Toluene. c: i) *n*-BuLi, THF. ii) B(OMe)₃. iii) HCl (aq). iv) H₂O₂, Et₂O. d: DHP, *p*-TSA, DCM. e: i) *n*-BuLi, THF. ii) see scheme. f: Br₂, HBr (42% w/w). g: i) Pd(PPh₃)₄, K₃PO₄, DMF ii) *p*-TSA, DCM, EtOH.

Scheme 4a



h: Et₃N, HOCH(CH=CH₂)₂, DCM. i: K₂CO₃, DMF.





a: DHP, *p*-TSA, DCM. b: i) *n*-BuLi, THF. ii) see scheme. c: K₃PO₄, Pd(PPh₃)₄, DMF. d: *p*-TSA, DCM, EtOH. e: K₂CO₃, DMF.





a: DHP, *p*-TSA, DCM. b: i) *n*-BuLi, THF. ii) see scheme. f: Br₂, HBr. g: K₃PO₄, Pd(PPh₃)₄, DMF. h: *p*-TSA, DCM. I: **29**, K₂CO₃, KI, DMF.



Scheme 6

46: n = 5 **47**: n = 10

a: H₂NNH₂. b: NaNO₂, H₂O, AcOH. c: **29**, K₂CO₃, DMF.



d: BrC₈H₁₇, K₂CO₃, KI, DMF. e: Toluene.



Scheme 7

a: H₂NNH₂. b: NaNO₂, H₂O, AcOH. c: Toluene.

Scheme 8



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₆H₁₃, KOH, KI, DMSO. c: CuCN, DMF. d: i) H₂NNH₂, S, ii) THF, NaNO₂, H₂O, AcOH. e: BrC₈H₁₇, K₂CO₃, KI, DMF. f: *n*-BuLi, B(OMe)₃, THF. g: Pd(PPh₃)₄, Na₂CO₃, DME.

Scheme 9



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₆H₁₃, KOH, KI, DMSO. c: CuCN, DMF. d: i) H₂NNH₂, S, ii) THF, NaNO₂, H₂O, AcOH. e: BrC₈H₁₇, K₂CO₃, Butanone. f: *n*-BuLi, B(OMe)₃, THF. g: Pd(PPh₃)₄, Na₂CO₃, DME.

Scheme 10



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₆H₁₃, KOH, KI, DMSO. c: CuCN, DMF. d: i) H₂NNH₂, S, ii) THF, NaNO₂, H₂O, AcOH. e: BrC₈H₁₇, K₂CO₃, Butanone. f: *n*-BuLi, B(OMe)₃, THF. g: Pd(PPh₃)₄, Na₂CO₃, DME.



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₃H₇, TBAB, NaOH (aq), Toluene. c: Pd(PPh₃)₄, DMF. d: i) *n*-BuLi, THF ii) Sn(Bu)₃Cl, THF. e: Pd(PPh₃)₄, DMF. f: i) BBr₃, DCM, ii) H₂O. g: Br(CH₂)_nCO₂CH(CH=CH₂)₂ or BrC₈H₁₇, K₂CO₃, KI, DMF.



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₃H₇, TBAB, NaOH (aq), Toluene. c: Pd(PPh₃)₄, DMF. d: i) *n*-BuLi, THF ii) Sn(Bu)₃Cl, THF. e: Pd(PPh₃)₄, DMF. f: i) BBr₃, DCM, ii) H₂O. g: Br(CH₂)_nCO₂CH(CH=CH₂)₂ or BrC₈H₁₇, K₂CO₃, KI, DMF or Butanone.



a: I₂, H₅IO₆, H₂SO₄, AcOH. b: BrC₃H₇, TBAB, NaOH (aq), Toluene. c: Pd(PPh₃)₄, DMF. d: i) *n*-BuLi, THF ii) Sn(Bu)₃Cl, THF. e: Pd(PPh₃)₄, DMF. f: i) BBr₃, DCM, ii) H₂O. g: Br(CH₂)₅CO₂CH(CH=CH₂)₂ or BrC₈H₁₇, K₂CO₃, KI, DMF or Butanone.



a: DCC, DMAP, DCM. b: K₂CO₃, KI, DMF.





a: Pd(PPh₃)₄, DMF. b: i) *n*-BuLi, THF ii) Sn(Bu)₃Cl, THF. c: BrC₃H₇, KOH, KI, DMSO. d: Pd(PPh₃)₄, DMF. e: BBr₃, DCM. ii) H₂O





f: DCC, DMAP, DCM. g: K₂CO₃, KI, DMF.

Scheme 16



a: BrC_8H_{17} , K_2CO_3 , KI, Butanone. b: $Pd(PPh_3)_4$, DMF. c: i) *n*-BuLi, THF ii) $Sn(Bu)_3Cl$, THF. d: I₂, H₅IO₆, H₂SO₄, AcOH. e: BrC_5H_{11} , KOH, KI, DMSO. f: $Pd(PPh_3)_4$, DMF. g: BrC_8H_{17} , KOH, KI, DMSO. h: *n*-BuLi, THF. i: $Pd(PPh_3)_4$, K₃PO₄, DMF.



Scheme 17

a: BrC_8H_{17} , K_2CO_3 , Butanone. b: $Pd(PPh_3)_4$, DMF. c: i) *n*-BuLi, THF ii) $Sn(Bu)_3Cl$, THF, THF. d: I_2 , H_5IO_6 , H_2SO_4 , AcOH. e: BrC_5H_{11} , KOH, KI, DMSO. f: $Pd(PPh_3)_4$, DMF. G: $Pd(PPh_3)_4$, DMF.

Scheme 17a



h: i) *n*-BuLi, -78°C, ii) i) *n*-BuLi, THF ii) Sn(Bu)₃Cl, THF. i: Pd(PPh₃)₄, CuI, DMF.

Scheme 17b



j: I₂, NaOCH₃, CH₃OH, Et₂O. k: Pd(PPh₃)₄, DMF.



Scheme 18

a: BrC_8H_{17} , K_2CO_3 , Butanone. b: $Pd(PPh_3)_4$, DMF. c: i) *n*-BuLi, THF ii) $Sn(Bu)_3Cl$, THF. d: I_2 , H_5IO_6 , H_2SO_4 , AcOH. e: BrC_8H_{17} , KOH, KI, DMSO. f: $Pd(PPh_3)_4$, DMF. g: i) Mg, I_2 , THF, ii) $Pd(dppf)Cl_2$, THF. h: $SnCl_2.2H_2O$, EtOH.
Scheme 18a



i: Zn(OAc)₂.2H₂O, Imidazole.



a: Pd(PPh₃)₄, DMF. b: : i) *n*-BuLi, THF ii) Sn(Bu)₃Cl, THF. c: BrC₈H₁₇, KOH, KI, DMSO. d: Pd(PPh₃)₄, DMF. e: i) Mg, I₂, THF, ii) Pd(dppf)Cl₂, THF. f: SnCl₂.2H₂O, EtOH. g: Zn(OAc)₂.2H₂O, Imidazole.



a: $BrC_{12}H_{25}$, KOH, KI, DMSO. b: $Zn(OAc)_2.2H_2O$, EtOH.

3.4 Synthesis of the Materials

Perylene-3,4,9,10-tetracarboxylic acid tetraoctyl ester (2)



A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (1) (2.00 g, 0.0051 mol), 1bromooctane (50 cm³, 0.2900 mol) and potassium carbonate (10.00 g, 0.0724 mol) was heated under reflux for 4 days. The cooled reaction mixture was extracted with diethyl ether (200 cm³) and the resultant solution was then washed with brine (3 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure to give a pale orange solid. Purification was carried out via column chromatography [silica gel, ethyl acetate : DCM, 9 : 1] to yield an orange crystalline solid (0.47 g, 11%). Transition temp. /^OC: **Cr** 63 **Col**_{hex} 138 **I** (Lit. **Cr** 62 **Col**_{hex} 132 **I**). ^[1]

¹H NMR (CDCl₃) δ_{H} : 0.86 (12H, t), 1.28 – 1.49 (40H, m), 1.80 (8H, quint), 4.32 (8H, t), 7.85 (4H, d, J = 8.1 Hz), 7.95 (4H, d, J = 8.1 Hz).

IR v_{max}/cm^{-1} :	2953, 2926, 28	51, 1731,	1714, 1	700, 15	591, 1507,	1469,	1384,
	1307, 1274, 11	66, 1136,	1097, 8	343, 803	5, 747.		

MS *m*/*z* (EI): 877 (M⁺), 700, 636, 588, 432, 431, 352, 195, 85, 44 (M 100).

Combustion analysis:

Expected: C 76.68%, H 8.73%

Obtained: C 76.98%, H 9.00%





Perylene-3,4,9,10-tetracarboxylic acid tetraoctyl ester (**2**) (0.20 g, 0.0002 mol) was added to a solution of phenylurazole (0.16 g, 0.0009 mol) in DCM (75 cm³) at 0 °C. The reaction mixture was stirred for 20 min followed by the dropwise addition of cold (0 °C) lead tetraacetate (0.45 g, 0.0010 mol) in DCM (25 cm³) over a period of 1 h. The resulting red slurry was stirred for a further 2 h, poured into H₂O (200 cm³) and then extracted into DCM (3 x 200 cm³). The combined organic extracts were washed with brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : ethyl acetate, 97 : 3] and recrystallisation from EtOH to yield a blue crystalline solid (0.28 g, 18%). Melting Point /^OC: 140 – 142. ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.87 (12H, t), 1.28 – 1.43 (40H, m), 1.76 (8H, quint), 4.25

(8H, t), 7.51 (1H, m), 7.58 (2H, d, J = 8.3 Hz), 7.68 (2H, d, J = 8.7 Hz), 7.70 (2H, d, J = 7.9 Hz), 7.79 (2H, d, J = 8.1 Hz), 8.78 (2H, s).

IR v_{max} /cm⁻¹: 3245, 3217, 2943, 2930, 2851, 1730, 1717, 1698, 1536, 1507, 1468, 1387, 1309, 1270, 1166, 1146, 1090, 843, 805, 747, 678, 536.

MS *m*/*z* (HABA): 1073 (M 100), 1050 (M⁺), 816.

Combustion analysis:

Expected:	C 73.19%, H 7.58%, N 4.00%
Obtained:	C 72.26%, H 7.67%, N 4.03%

1-Bromo-3,7-dimethyloctane (5)



3,7-Dimethyl-1-octanol (4) (32.95 g, 0.2080 mol) was added to triphenyl phosphine (54.56 g, 0.2080 mol) in DCM at 0 °C. Once all the triphenyl phosphine had dissolved, NBS (37.20 g, 0.2080 mol) was added over a period of 2 h, while maintaining the temperature below 5 °C. The formation of an orange solution and a white precipitate indicated the presence of the crude product. The resulting mixture was concentrated under reduced pressure and the product extracted into diethyl ether $(2 \times 250 \text{ cm}^3)$. The combined organic layers were washed with aqueous sodium metabisulphite solution (5%, 100 cm³), water (2 x 250 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting orange liquid mixture was distilled under reduced pressure (46 – 50 °C, 0.1 mm Hg), to yield the alkyl bromide as a colourless liquid (46.01 g, 81%). Boiling Point /^OC: 46 – 50, 0.08 mm Hg (Lit. 71 – 73, 0.1 mmHg).^[27] Purity: >99% (GC). ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.81 – 0.95 (9H, m), 1.06 – 1.41 (6H, m), 1.44 – 1.74 (2H, m), 1.83 – 1.92 (2H, m), 3.46 (2H, t). IR v_{max}/cm^{-1} : 2955, 2928, 2869, 1464, 1380, 1366, 1261, 1217, 1170. MS *m/z* (EI): 167, 149, 140, 125, 97, 85, 70, 57 (M100).

Perylene-3,4,9,10-tetracarboxylic acid tetra(3,7-dimethyloctyl) ester (6)



A mixture of 1-bromo-3,7-dimethyloctane (5) (27 cm^3 , 0.1030 mol), perylene-3,4,9,10tetracarboxylic dianhydride (1) (1.00 g, 0.0026 mol) and potassium carbonate (5.00 g, 0.0360 mol) was heated under reflux for 5 days. The crude product was extracted into

diethyl ether $(3 \times 300 \text{ cm}^3)$. The combined ethereal layers were washed with brine $(2 \times 300 \text{ cm}^3)$. 300 cm³), water (300 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure to a pale red solid. Purification was carried out via column chromatography [silica gel, hexane : DCM, 1 : 1] to yield a red waxy solid (0.94 g, 37%). Transition temp. / $^{\circ}$ C: Cr < -30 Col_{hex} 154 I. ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.87 (24H, d), 0.99 (12H,d), 1.14 – 1.39 (24H, m), 1.48 – 1.66 (12H, m), 1.80 – 1.87 (4H, m), 4.35 (8H, t), 7.99 (4H, d, J = 8.2 Hz), 8.26 (4H, d, J = 8.2 Hz). IR v_{max}/cm^{-1} : 2954, 2927, 2869, 1724, 1591, 1465, 1384, 1272, 1161, 1130, 1097, 990, 840, 803, 746. MS m/z (HABA): 942, 816. Combustion analysis: Expected: C 77.70%, H 9.40%

Obtained:	C 77.56%, H 9.67%.

9,9-*bis*(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)fluorene (9)



A solution of *n*-BuLi in hexanes (5.30 cm³, 2.5M, 0.0130 mol) was added slowly to a cooled (-78 $^{\circ}$ C) solution of fluorene (7) (2.00 g, 0.0120 mol) in THF (50 cm³). After stirring for 1h at -78 $^{\circ}$ C, 1H,1H,2H,2H-perfluorooctyl iodide (6.83 g, 0.01400 mol) was added dropwise. The reaction mixture was allowed to reach RT, stirred overnight, concentrated under reduced pressure and then extracted into DCM (500 cm³). The organic layer was washed with brine, dried (MgSO₄), filtered, concentrated under reduced pressure and the above procedure repeated. Once the procedure was repeated the resultant white crystalline crude product was purified via column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from ethanol to yield a white crystalline solid (2.68 g, 26%).

Melting point $/^{O}$ C: 65 – 67.

Purity:	>99% (GC).
¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	1.26 (4H, t), 2.38 (4H, t), 7.39 – 7.44 (6H, m), 7.76
	(2H, d, J = 7.0 Hz).
IR v_{max}/cm^{-1} :	1461, 1452, 1239, 1190, 1144, 1121, 1083, 1010, 732.
MS <i>m</i> / <i>z</i> (HABA):	1464, 1081, 826, 816, (M 100), 667.
Combustion analysis:	
Expected:	C 40.60%, H 1.90%
Obtained:	С 40.87%, Н 1.63%.

2,7,-Dibromo-9,9-*bis*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (10)



Bromine (0.49 cm³, 0.0096 mol) was added to a stirred solution of 9,9-

bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**9**) (2.75 g, 0.0032 mol) in DCM (50 cm³) at RT, followed by heating under reflux for 48h. The cooled reaction mixture was concentrated under reduced pressure and extracted into hexane (4 x 100 cm³). The combined organic extracts were washed with aqueous sodium metabisulphite (5%, 100 cm³) and then with brine (3 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via recrystallisation from ethanol to yield a white crystalline solid (1.90 g, 58%).

Melting point $/^{O}$ C: 121 – 122.

Purity: >99% (GC).

 1 H NMR (CDCl₃) δ_{H} : 1.25 (4H, t), 2.35 (4H, t), 7.55 – 7.64 (6H, m).

IR v_{max} /cm⁻¹: 2979, 2934, 2866, 1600, 1452, 1420, 1367, 1320, 1274, 1238, 1188, 1146, 1130, 1124, 1112, 1070, 1064, 1018, 911, 884, 865, 809, 697, 662.

MS *m*/*z* (HABA): 1203, 1181, 1125, 926, 905, 884, 877, (M 100), 862, 846, 788, 323.

Combustion analysis:

Expected:	C 34.30%, H 1.40%
Obtained:	C 34.22%, H 1.22%

4-Bromo-4'-octyloxybiphenyl (12)



A mixture of 4-bromo-4'-hydroxybiphenyl (**11**) (30.00 g, 0.1250 mol), 1-bromooctane (34.70g, 0.1446 mol) and potassium carbonate (49.9 g, 0.3614 mol) in butanone (400 cm³) was heated under reflux overnight. The cooled reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude product was recrystallised from ethanol to yield a white powder (30.40 g, 70%). Melting point /^OC: 120 (Lit. 120). ^[28]

Purity: >99% (GC).

¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.88 (3H, t), 1.24 – 1.56 (10H, m), 1.79 (2H, quint), 3.90 (2H, t), 6.95 (2H, d, J = 8.1 Hz), 7.41 (2H, d, J = 8.1 Hz), 7.46 (2H, d, J = 8.1 Hz), 7.52 (2H, d, J = 8.1 Hz). IR v_{max}/cm⁻¹: 3040, 2960, 2927, 2860, 1608, 1524, 1481, 1290, 1259, 1199, 1133, 1030, 814. MS *m*/*z* (EI): 362 (M⁺), 360 (M⁺), 250, (M 100), 248, 221, 195, 152, 139, 115, 89, 69.

4'-Octyloxybiphenyl-4-ylboronic acid (13)



A solution of *n*-BuLi in hexanes (38.20 cm³, 2.5*M*, 0.0956 mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 4-bromo-4'-octyloxybiphenyl (**12**) (30.00 g, 0.0831 mol) in THF (400 cm³). The resultant solution was stirred at this temperature for 1 h, then

trimethyl borate (17.3	30 g, 0.1662 mol) added dropwise to the mixture. After complete
addition the reaction	mixture was allowed to warm to RT and then stirred overnight.
Aqueous hydrochlori	c acid (20%, 200 cm ³) was added and the resultant mixture was
stirred for 1 h and the	n extracted into diethyl ether $(2 \times 350 \text{ cm}^3)$. The combined ethereal
extracts were washed	with water (2 x 350 cm ³), dried (MgSO ₄), filtered and concentrated
under reduced pressu	re. Purification was carried out via stirring with hexane $(200 \text{ cm}^3, 5 \text{ cm}^3)$
min) and filtering to y	vield a white crystalline solid (19.00 g, 70%).
Melting point / ^O C:	135 – 136 (Lit. 134 – 136). ^[28]
¹ H NMR (CDCl ₃) δ_{H} :	0.85 (3H, t), 1.24 – 1.44 (10H, m), 1.74 (2H, quint), 3.99 (2H, t),
	7.00 (2H, d, J = 8.1 Hz), 7.55 (2H, d, J = 8.1 Hz), 7.59 (2H, d, J =
	8.1 Hz), 7.84 (2H, d, J = 8.1 Hz) 8.04 (2H, s).
IR v_{max}/cm^{-1} :	3100 – 3550, 3040, 2960, 2933, 2860, 1608, 1533, 1473, 1340,
	1286, 1258, 1183, 1129, 1029, 997, 818.
MS <i>m</i> / <i>z</i> (EI):	326 (M ⁺), 282, 248, 170 (M 100), 115, 89, 76, 69.
Combustion analysis:	
Expected:	С 73.63%, Н 8.34%

Obtained: C 73.39%, H 8.54%

2,7-*bis*(4'-Octyloxybiphenyl-4-yl)-9,9-*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**14**).



Tetrakis(triphenylphosphine)palladium(0) (0.10 g, 8.12×10^{-5} mol) was added to a stirred solution of 4'-octyloxybiphenyl-4-ylboronic acid (**13**), (1.32 g, 0.0041 mol), 2,7,dibromo-9,9-*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**10**) (1.65 g, 0.0016 mol) and a aqueous sodium carbonate solution (20%, 0.52 g, 0.0049 mol) in DME (80 cm³) at RT. The reaction mixture was heated under reflux for 24 h. The cooled reaction mixture was added to water (100 cm³) and the product extracted into DCM (2 x 100 cm³). The combined organic layers were washed with aqueous hydrochloric acid (10%, 50

cm³), water (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried via column chromatography [silica gel, DCM : hexane, 4 : 1] and recrystallisation from hexane to yield a white crystalline solid (1.06 g, 46%). Melting point /^OC: 146. ¹H NMR (CDCl₂) δ_{H} : 0 90 (6H, t), 1.27 – 1.50 (28H, m), 1.81 (4H, quint), 2.51 (4H

$\prod \min (CDCI3) \cup_{F}$	(1, 0.90) (011, $(1, 1.27)$ = 1.50 (2011, 11), 1.01 (411, quint), 2.51 (411, quint), 2.51 (411, quint))
	t), 4.02 (4H, t), 7.00 (4H, d, J = 6.8 Hz), 7.61 (4H, d, J =
	6.8 Hz), 7.69 – 7.77 (12H, m), 7.88 (2H, d, J = 7.8 Hz).
IR v_{max}/cm^{-1} :	3030, 2920, 2854, 2361, 2341, 1609, 1578, 1527, 1501, 1467,
	1437, 1394, 1367, 1293, 1281, 1247, 1208, 1140, 1120, 1081, 1065,
	1045, 998, 818, 808, 799, 707, 699.

MS *m*/*z* (HABA): 1419 (M⁺, M 100), 1418.

Combustion analysis:

Expected:	C 58.40%, H 4.60%
Obtained:	C 58.70%, H 4.58%

2,7-*bis*(4'-Hydroxybiphenyl-4-yl)-9,9-*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**15**).



Boron tribromide (0.40 g, 0.0016 mol) was added dropwise to a cooled solution (0 $^{\circ}$ C) of 2,7-*bis*(4'-octyloxybiphenyl-4-yl)-9,9-*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**14**) (0.50 g, 3.52 x 10⁻⁴ mol) in DCM (10 cm³). The solution was allowed to warm to RT and stirred overnight. The resulting green solution was poured into ice water (200 cm³) and stirred for 1 h. The crude product was extracted into ethyl acetate (4 x 100 cm³). The combined organic extracts were washed with brine (2 x 50 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, hexane : ethyl acetate, 2 : 1] to yield a white crystalline solid (0.35 g, 82%).

Melting point $/^{O}C$: 189 – 191.

¹H NMR (CDCl₃) $\delta_{\rm H}$: 1.33 (4H, t), 2.47 (4H, t), 4.82 (2H, s), 6.95 (4H, d, J = 8.7 Hz), 7.55 (4H, d, J =8.7 Hz), 7.63 (2H, d, J = 2 Hz), 7.66 – 7.75 (10H, m), 7.85 (2H, d, J = 8.7 Hz). IR $v_{\rm max}$ /cm⁻¹: 3410, 3031, 2936, 2361, 2350, 1610, 1593, 1503, 1466, 1365, 1240, 1205, 1144, 1119, 1027, 1005, 896, 816, 734, 708, 650, 578, 532. MS *m*/*z* (HABA): 1195 (M⁺, M 100), 1194, 848.

Penta-1,4-dien-3-yl 11-bromoundecanoate (17)



DCC (3.89g, 0.0189 mol) was added to a stirred solution of 11-bromoundecanoic acid (**16**) (5.00 g, 0.00189 mol), 1,4-pentadien-3-ol (1.66 g, 0.0189 mol) and DMAP (2.31 g, 0.0189 mol) in DCM (150 cm³) at RT. The reaction mixture was stirred overnight, then the by-product, dicyclohexylurea (DCU) filtered off. The resulting pale brown filtrate was concentrated under reduced pressure and purified via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a colourless oil (4.09 g, 65%).

Purity: >99% (GC).

¹ H NMR (CDCl ₃)	δ _H : 1.23 – 1.36 (10H, m), 1.42 (2H, quint), 1.64 (2H, quint),
	1.85 (2H, quint), 2.34 (2H, t), 3.40 (2H, t), 5.21 - 5.30 (4H, m),
	5.72 (1H, d), 5.84 (2H, dt).
IR v_{max}/cm^{-1} :	3088, 3040, 2930, 28853, 1740, 1641, 1466, 1249, 1166, 986, 931,
	723.
MS <i>m</i> / <i>z</i> (EI):	332, 330 (M ⁺), 301, 247, 149, 123, 107, 97, 83, 67 (M 100).

2,7-*bis*{4'-[10-(1-Vinylallyloxycarbonyl)decanyloxy]biphenyl-4-yl}-9,9*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**18**).



A mixture of 2,7-*bis*(4'-hydroxybiphenyl-4-yl)-9,9-*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene (**17**) (0.20 g, 1.67 x 10^{-4} mol) potassium carbonate (0.07 g, 5.02 x 10^{-4} mol) and DMF (5 cm³) was heated (90 °C) and stirred overnight. Penta-1,4-dien-3-yl 11-bromoundecanoate (0.14 g, 4.18 x 10^{-4} mol) was added to the mixture and the mixture stirred for a further 24 h. The cooled reaction mixture was poured into water (50 cm³) and then the crude product extracted into DCM (3 x 100 cm³). The combined organic extracts washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, hexane : ethyl acetate, 9 : 1] and recrystallisation from EtOH/DCM to yield a white crystalline solid (0.13 g, 45%).

¹H NMR (CDCl₃) $\delta_{\rm H}$: 1.24 – 1.39 (28H, m), 1.59 – 1.67 (4H, m), 1.82 (4H, qunit), 2.35 (4H, t), 2.47 (4H, t), 4.02 (4H, t), 5.21 – 5.33 (8H, m), 5.73 (2H, m), 5.80 – 5.88 (4H, m), 7.01 (4H, d, J = 8.7 Hz), 7.59 (4H, d, J = 9 Hz), 7.63 (2H, d, J = 1.1 Hz), 7.67 – 7.74 (10 H, m), 7.85 (2H, d, J = 7.9 Hz). IR ν_{max} /cm⁻¹: 3447, 2921, 2851, 2360, 2349, 2341, 1741, 1654, 1608, 1600, 1500, 1466, 1244, 1143, 802, 698, 668.

MS *m*/*z* (HABA): 1696, 1695 (M⁺, M 100), 1429, 1281.

Combustion analysis:

Expected:	C 60.21%, H 4.99%
Obtained:	C 60.03%, H 5.01%

2-Bromo-7-iodofluorene (20).



A solution of 2-brome	ofluorene (19) (25.00 g, 0.1000 mol), glacial ethanoic acid (250	
cm ³), concentrated sul	phuric acid (3 cm ³)and water (20 cm ³) was heated (75 ^o C) for 10	
min, dehydrated perio	dic acid (4.56 g, 0.0200 mol) and pulverised I_2 (10.20 g, 0.0400	
mol) were then added	After 2 h the deep purple reaction mixture became yellow in	
colour. Glacial ethano	ic acid (100 cm ³) was added to the cooled reaction mixture, which	
was further diluted wi	th aqueous sodium metabisulphite solution (5%, 20 cm^3). The	
resultant yellow precip	pitate was filtered off, washed with MeOH ($3 \times 250 \text{ cm}^3$), aqueous	
NaOH (5%, 3 x 250 c	m^3) and water (3 x 250 cm ³). The product was then purified <i>via</i>	
recrystallisation from	EtOH/DCM to yield a white crystalline solid (24.45 g, 69%).	
Melting point / ^O C:	184 – 186 (Lit. 177 – 178, from EtOH). ^[29]	
Purity:	>99% (GC).	
1 H NMR (CDCl ₃) δ_{H} :	7.48 – 7.51 (2H, m), 7.60 (1H, d, J = 8.2 Hz), 7.66 – 7.71 (2H, m),	
	7.87 (1H, s).	
IR v_{max}/cm^{-1} :	1734, 1718, 1635, 1616, 1559, 1539, 1506, 1455, 1436, 1419,	
	1395, 1050, 1004, 803, 668, 419.	
MS <i>m</i> / <i>z</i> (EI):	372 (M ⁺), 370 (M ⁺) 324, 291, 243, 186, 163, 146, 137, 122, 113,	
87, 82 (M 100), 63, 50.		
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Combustion analysis:

Expected:	C 42.08%, H 2.17%
Obtained:	C 42.38%, H 1.83%

2-Bromo-7-iodo-9,9-dipropylfluorene (21).



A mixture of NaOH (65.00 g), water (130 cm³), 2-bromo-7-iodofluorene (**20**) (20.00 g, 0.0540 mol), 1-bromopropane (19.94 g, 0.1620 mol), toluene (130 cm³) and TBAB (0.80 g) was heated under reflux with vigorous stirring overnight. The reaction was allowed to cool and the product extracted into diethyl ether (3 x 250 cm³). The combined ethereal layers were washed with aqueous hydrochloric acid (10%, 500 cm³), water (3 x 250 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, hexane] and recrystallisation from EtOH to yield a pale yellow crystalline solid (12.05 g, 49%).

Melting point $/^{O}$ C: 140 – 142 (Lit. 136 – 139, EtOH). ^[30]

Purity: >99% (GC).

¹H NMR (CDCl₃) δ_{H} : 0.65 (10H, m), 1.89 (4H, t), 7.40 – 7.51 (4H, m), 7.64

(2H, d, J = 7.4 Hz).

IR ν_{max} /cm⁻¹: 2946, 2925, 2866, 2839, 1884, 1734, 1593, 1569, 1454, 1445, 1413, 1394, 1377, 1270, 1239, 1131, 1108, 1050, 1003, 930, 874, 809, 754, 742, 668, 659, 494, 424.

MS *m*/*z* (EI): 456 (M⁺), 454 (M⁺, M 100), 413, 408, 371, 332, 317, 304, 284, 269, 256, 248, 228, 219, 205, 189, 176, 163, 150, 101, 88, 75, 57.

Combustion analysis:

Expected:	C 50.14%, H 4.43%
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Obtained: C 50.29%, H 4.42%

2-Bromo-7-hydroxy-9,9-dipropylfluorene (22).



A solution of *n*-BuLi in hexanes (12.02 cm³, 2.5*M*, 0.0030 mol) was added dropwise to a cooled (-78 O C) solution of 2-bromo-7-iodo-9,9-dipropylfluorene (**21**) (11.40 g, 0.0250 mol) in THF (150 cm³). The resulting yellow mixture was stirred for 1 h and then trimethyl borate (3.12 g, 0.0300 mol) was added dropwise. The reaction mixture was allowed to warm to RT and stirred overnight. Aqueous hydrochloric acid (20%, 200 cm³) was added and the reaction stirred for 1 h. The yellow product was extracted into diethyl ether (300 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was dissolved in diethyl ether (100 cm³), aqueous hydrogen peroxide (6%, 100 cm³) added and the reaction mixture heated under reflux for 3 h. The organic layer was separated off, washed with aqueous sodium metabisulphite (5%, 20 cm³), aqueous hydrochloric acid (20%, 200 cm³), water (200 cm³), dried (MgSO₄), filtered and concentrated under reflux for 3 h. The organic layer was generated off, washed with aqueous sodium metabisulphite (5%, 20 cm³), aqueous hydrochloric acid (20%, 200 cm³), water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a colourless oil (5.37 g, 62%), which subsequently crystallised to form a white crystalline solid.

Melting point $/^{O}C$: 12	28 – 131 (Lit. 131 – 131.5, cyclohexane)	[6]
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Purity: >99% (GC).

¹H NMR (CDCl₃) δ_{H} : 0.63 – 0.67 (10H, m), 1.87 (4H t), 5.70 (1H, s), 6.77 – 6.81 (2H, m), 7.39 – 7.45 (3H, m), 7.51 (1H, d, J = 8.7 Hz).

IR v_{max} /cm⁻¹: 3332, 2956, 2930, 2870, 2843, 1612, 1586, 1488, 1455, 1404, 1378, 1352, 1293, 1274, 1251, 1190, 1175, 1097, 1063, 1005, 950, 869, 811, 752.

MS *m*/*z* (EI): 346 (M⁺), 344 (M⁺), 301, 279, 261, 222, (M 100), 214, 207, 195, 181, 165, 149, 140, 115, 96, 83, 69, 55, 43.

Combustion analysis:

Expected:	С 66.09%, Н 6.13%
Obtained:	C 66.28%, H 6.41%

2-Bromo-7-(tetrahydropyranyl-2-oxy)-9,9-dipropylfluorene (23).



A mixture of 2-bromo-7-hydroxy-9,9-dipropylfluorene (**22**) (5.00 g, 0.0145 mol), 3,4dihydropyran (1.22 g, 0.0159 mol), *para*-toluene-sulfonic acid (trace amount) and DCM (150 cm³) was stirred at RT for 2 h. The reaction solution was washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification of the purple crude product was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a colourless waxy solid (6.22 g, 68%). Melting point /^OC: 47 – 49. Purity: >99% (GC). ¹H NMR (CDCl₃) δ_{H} : 0.63 – 0.67 (10H, m), 1.50 – 1.91 (10H, m), 3.93 – 3.99 (2H, m), 5.46 (1H, t), 6.77 – 6.81 (1H, m), 7.02 (1H, t, J = 8.7 Hz),

	7.39 – 7.44 (3H, m), 7.54 (1H, d, J = 8.2 Hz).
IR v_{max}/cm^{-1} :	2942, 1875, 1591, 1492, 1390, 1381 1374, 1353, 1326, 1310, 1233,
	1115, 1101 1071, 1056 1023, 955, 919, 823, 649, 500, 456.

MS *m*/*z* (EI): 430 (M⁺), 428 (M⁺), 344, 301, 279, 265, 245, 222 (M 100), 207, 194, 165, 126, 85, 68, 43.

2-[9,9-Dipropyl-7-(tetrahydropyran-2-yloxy)fluoren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**).



A solution of *n*-BuLi in hexanes (4.71 cm³, 2.5*M*, 0.0118 mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 2-bromo-7-(tetrahydropyranyl-2-oxy)-9,9-dipropylfluorene (23) (4.21 g, 0.0098 mol) in THF (150 cm³) and stirred for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.55 g, 0.0140 mol) was added dropwise to the yellow reaction mixture, allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 x 200 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 4 : 1] to yield a yellow crystalline solid (2.00 g, 43%).

Melting point $/^{O}$ C: 57 – 58.

Purity: >98% (GC).

¹ H NMR (CDCl ₃) a	$\delta_{\rm H}$: 0.63 – 0.67 (10H, m), 1.38 (12H, s), 1.85 – 1.97 (10H, m), 3.93 –
	3.99 , (2H, m), 4.77 (1H, d), 6.80 (2H, t, J = 8.6 Hz), 7.52 – 7.59,
	(2H, m), 7.70 (1H, s), 7.76 (1H, d, J = 7.6 Hz).
IR v_{max}/cm^{-1} :	2976, 2943, 2877, 2369, 2280, 1606, 1571, 1569 1513, 1401,
	1363, 1320, 1273, 1246, 1239, 1203, 1175, 1165, 1149, 1111,
	1098, 1024, 1021, 965, 921, 910, 873, 853, 836, 656, 649.
MS <i>m/z</i> (EI):	476 (M ⁺), 392 (M 100), 377, 349, 335, 307, 293, 267, 249, 223,
	205, 177, 149, 126, 101, 84, 72, 56, 41.

4,7-Dibromobenzo[1,2,5]thiadiazole (26).



Bromine (52.8 g, 0.3300 mol) was added to a solution of benzo[1,2,5]thiadiazole (**25**) (8.10 g, 0.0320 mol) in hydrobromic acid (48%, 100 cm³) and the resulting solution heated under reflux for 2.5 h. The cooled reaction mixture was filtered and the solid product washed with water (3 x 200 cm³) and dried on the sinter. Purification was carried via recrystallisation from EtOH to yield a yellow crystalline solid (21.00 g, 65%). Melting point /^OC: 183 – 185 (Lit. 184 – 185, EtOH). ^[31] Purity: >99% (GC). ¹H NMR (CDCl₃) δ_{H} : 7.73 (2H, s). IR ν_{max} /cm⁻¹: 3077, 1587, 1476, 1310, 1184, 936, 875, 825, 586. MS m/z (EI): 296 (M⁺), 294 (M⁺), 292 (M⁺), 213, 134, 83, 70.

4,7-bis[7-(2-Hydroxy-9,9-dipropylfluoren-7-yl)]benzo[1,2,5]thiadiazole (27).



A mixture of 2-[9,9-dipropyl-7-(tetrahydropyran-2-yloxy)fluoren-2-yl]-4,4,5,5tetramethyl-1,3,2-dioxaborolane (**24**) (2.00 g, 0.0084 mol), 4,7dibromobenzo[1,2,5]thiadiazole (**26**) (0.50 g, 0.0042 mol), potassium phosphate (1.08 g, 0.0051 mol), tetrakis(triphenylphosphine)palladium(0) (0.10 g, 8.12 x 10^{-5} mol) and DMF (50 cm³) was heated (100 °C) for 24 h. The crude product was extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with brine (2 x 300 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel DCM : ethyl acetate, 1 : 1] to yield the di-phenol, (**27**) as an orange crystalline solid (0.89 g, 32%).

Melting point / ^O C:	149 – 150.
1 H NMR (CDCl ₃) δ_{H}	_H : 0.69 – 0.88 (20H, m), 1.95 – 2.10 (8H, m),
	4.85 (2H, s), 6.85 (4H, t, J = 8.3 Hz), 7.62 (2H, d,
	J = 7.8 Hz), 7.76 (2H, s), 7.89 (4H, d, J = 14.6 Hz), 8.00 (2H, d,
	J = 1.4 Hz).
IR v_{max}/cm^{-1} :	3369, 2950, 2927, 2867, 2364, 1734, 1700, 1684, 1669, 1653,
	1647, 1616, 1576, 1569, 1559, 1507, 1465, 1457, 1437, 1419,
	1363, 1252, 1174, 891, 811, 754, 668.
MS <i>m</i> / <i>z</i> (EI):	665, 664 (M ⁺), 621, 549, 530, 507, 332, 282, 268, 254, 239, 210,
	149, 111, 97, 82, 69, 55, 40 (M 100).

Combustion analysis:

Expected:	C 79.48%, H 6.67%, N 4.21%, S 4.82%
Obtained:	C 79.79%, H 6.58%, N 4.26%, S 4.55%

Penta-1,4-dien-3-yl 6-bromohexanoate (29).



A solution of 6-brome	bhexanoyl chloride (28) (25.00 g, 0.1174 mol) in DCM (250 cm ³)
was carefully added to	a solution of 1,4-pentadien-3-ol (10.90 g, 0.1291 mol) and
triethylamine (16.30 c	cm^3 , 0.1174 mol) in DCM (150 cm ³) at 0 $^{\rm O}$ C. The reaction mixture
was stirred at 0 °C for	² h. The white precipitate, $[HN^+(CH_3CH_2)_3Cl^-]$, was filtered off
and the filtrate concer	trated under reduced pressure. Purification was carried out via
column chromatograp	hy [silica gel, DCM] to yield a colourless oil (23.00 g, 76%).
Purity:	>99% (GC).
¹ H NMR (CDCl ₃) δ_{H} :	1.49 (2H, quint), 1.68 (2H, quint), 1.88 (2H, quint), 2.37 (2H, t),
	3.41 (2H, t), 5.23 (2H, d), 5.30 (2H, dd), 5.72 (1H, d), 5.84
	(2H, dt).
IR v_{max}/cm^{-1} :	3100, 3040, 2946, 2886, 1741, 1647, 1465, 1251, 1181, 987, 933,
	725.

4,7-*bis*{7-[5-(1-Vinylallyloxycarbonyl)pentyloxy]-9,9-dipropylfluoren-2-yl}benzo[[1,2,5]thiadiazole (**30**).

$$N_{C_{3}H_{7}}^{S} N_{C_{3}H_{7}}^{C_{3}H_{7}} O_{H_{10}C-O}^{O}$$

A mixture of 4,7-*bis*[7-(2-hydroxy-9,9-dipropylfluoren-2-yl)]benzo[1,2,5]thiadiazole (**27**) (0.30 g, 0.0005 mol), penta-1,4-dien-3-yl 6-bromohexanoate (**29**) (0.35 g, 0.0014 mol), potassium carbonate (0.19 g, 0.0014 mol) and DMF (30 cm³) was heated (100 $^{\circ}$ C) for 24 h. The orange fluorescent crude product was extracted into diethyl ether (3 x 100 cm³). The combined ethereal extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield an orange waxy liquid, which crystallised to yield (0.35 g, 76%) an orange waxy solid.

Melting point $/^{O}C$: 77.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$: 0.66 – 0.88 (20H, m), 1.56 (8H, quint), 1.75 – 2.05 (12H, m), 2.42
	(4H, t), 4.05 (4H, t), 5.23 – 5.33 (8H, m), 5.74 (2H, d), 5.81 – 5.90
	(4H, m), 6.90 (4H, t, J = 8.3 Hz), 7.65 (2H, d, J = 8.4 Hz),
	7.76 (2H, s), 7.89 (4H, d, J = 14.3 Hz), 8.00 (2H, d, J = 7.9 Hz).
IR v_{max}/cm^{-1} :	3447, 2953, 2869, 2360, 2344, 1734, 1700, 1696, 1684, 1653,
	1617, 1609, 1576, 1559, 1507, 1464, 1437, 1419, 1340, 1254, 1163,
	1097, 986, 931, 809, 668.

MS *m*/*z* (MALDI): 1026, 1025, (M⁺, M 100), 932, 844, 816, 643.

Combustion analysis:

Expected:	C 77.31%, H 7.47%, N 2.73%, S 3.13%
Obtained:	C 77.22%, H 7.47%, N 2.65%, S 3.36%

2-(4-Bromophenoxy)tetrahydropyran (32).



A mixture of 4-bromophenol (**31**) (20.00 g, 0.1156 mol) 3,4-dihydropyran (10.70 g, 0.1272 mol), *para*-toluene-sulfonic acid (trace amount) and DCM (150 cm³) was stirred at RT for 2 h. The reaction mixture was concentrated under reduced pressure and purified via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a colourless oil (24.35 g, 82%), which crystallised to form a solid.

Melting point / ⁰ C:	56 - 57 (Lit. $55.5 - 56$, benzene/pentane). ^[32]
Purity:	>99% (GC).
1 H NMR (CDCl ₃) δ_{H}	: 1.56 – 1.73 (3H, m), 1.83 – 2.02 (3H, m), 3.57 – 3.62 (1H, m),
	3.83 – 3.89 (1H, m), 5.37 (1H, t), 6.93 (2H, d, J = 9.0 Hz),
	7.36 (2H, d, J = 9.0 Hz).
IR v_{max}/cm^{-1} :	2944, 1878, 1590, 1492, 1391, 1372, 1353, 1326, 1233, 1115,
	1071, 1020, 957, 919, 825, 649, 500.
MS <i>m</i> / <i>z</i> (EI):	258 (M ⁺), 256 (M ⁺), 174, 157, 145, 131, 119, 93, 85 (M 100), 67,
	57.

2-[4-(4,4,5,5-Tetramethyl[1,3,2]dioxaborolan-2-yl)phenoxy]tetrahydropyran (33).



A solution of *n*-BuLi in hexanes (28.00 cm³, 2.5*M*, 0.0700 mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 2-(4-bromophenoxy)tetrahydropyran (**32**) (15.00 g, 0.0583 mol) in THF (200 cm³). The reaction was stirred for 1 h and 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (13.02 g, 0.0700 mol) added dropwise to the reaction mixture. The reaction was allowed to warm to RT and stirred overnight. The product was extracted into diethyl ether (2 x 200 cm³) and the combined organic layers were washed with brine (3 x 300 cm³), dried (MgSO₄), filtered and concentrated under reduced

pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a light brown waxy solid (13.40 g, 75%).

Melting point / ^O C:	53 – 54.
1 H NMR (CDCl ₃) δ_{H}	: 1.33 (12H, s), 1.49 – 1.70 (4H, m), 1.81 – 2.05 (2H, m), 3.50 –
	3.62 (1H, m), 3.85 – 3.91 (1H, m), 5.49 (1h, t), 6.82 (2H, d, J =
	8.7 Hz), 7.75 (2H, d, J = 8.8 Hz).
IR v_{max}/cm^{-1} :	2978, 2944, 2877, 2362, 1606, 1571, 1514, 1399, 1362, 1320,
	1273, 1238, 1203, 1175, 1144, 1112, 1090, 1038, 1022, 965, 921,
	873, 860, 835, 656.
MS <i>m</i> / <i>z</i> (EI):	304 (M ⁺), 241, 220, 205, 177, 163, 147, 134, 121, 105, 91, 85.
Combustion analysis:	
Expected:	С 67.12%, Н 8.28%
Obtained:	C 66.82%, H 8.42%

2,5-*bis*[4-(Tetrahydropyran-2-yloxy)phenyl]pyridine (**35**).



A mixture of 2,5-dibromopyridine (**34**) (2.00 g, 0.0084 mol), 2-[4-(4,4,5,5tetramethyl[1,3,2]dioxaborolan-2-yl)phenoxy]tetrahydropyran (**33**) (6.42 g, 0.0210 mol), potassium phosphate (5.38 g, 0.0130 mol), tetrakis(triphenylphosphine)palladium(0) (0.24 g, 0.0002 mol) and DMF (35 cm³) was heated (100 ^oC) for 24 h. The reaction mixture was cooled to RT and the product extracted into DCM (2 x 100 cm³). The combined organic extracts were washed with brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 4 : 1] to yield 2,5-*bis*(4hydroxyphenyl)pyridine (**36**) as a yellow crystalline solid (1.52 g, 83%). Melting point /^OC: 285 – 290. ¹H NMR ((CD₃)₂SO) $\delta_{\rm H}$: 3.40 (2H, s), 6.83 (4H, d, J = 8.7 Hz), 7.55 (2H, dd, J =

	6.9, 2.1 Hz), 7.82 (1H, d, J = 8.4 Hz), 7.90 – 7.96 (3H, m),
	8.80 (1H, d, J = 2.5 Hz)
IR v_{max}/cm^{-1} :	3467, 1692, 1609, 1475, 1375, 155, 1178, 1038, 1011, 849, 820,
	605, 504.
MS <i>m/z</i> (EI):	264, 263 (M ⁺), 246, 234, 195, 182, 171, 157, 149, 129,
	111, 97, 83, 69, 55, 44 (M 100).

2,5-*bis*{4-[5-(1-Vinylallyloxycarbonyl)pentyloxy]phenyl}pyridine (**37**).



A mixture of 2,5-*bis*(4-hydroxyphenyl)pyridine (**39**) (0.30 g, 0.0011 mol), penta-1,4dien-3-yl 6-bromohexanoate (**29**) (0.89 g, 0.0034 ml), potassium carbonate (0.47 g, 0.0034 mol) and DMF (30 cm³) was heated (100 $^{\circ}$ C) for 24 h with vigorous stirring. The resultant mixture was allowed to cool to RT and the product extracted into ethyl acetate (3 x 200 cm³). The combined organic layers were washed with brine (3 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, hexane : ethyl acetate, 1 : 1] and recrystallisation from EtOH/DCM to yield a white crystalline solid (0.13 g, 18%).

Transition temp. /^OC: Cr 96 SmC 145 I.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	1.50 – 1.58 (4H, m), 1.71 – 1.87 (8H, m), 2.40 (4H, t), 4.02
	(4H, m), 5.22 – 5.33 (8H, m), 5.71 – 5.75 (2H, m), 5.80 – 5.89
	(4H, m), 7.00 (4H, d, J = 8.7, Hz), 7.54 (2H, dd, J = 6.8,
	2.0 Hz), 7.72 (1H, d, J = 8.4 Hz), 7.88 – 7.98 (3H, m),
	8.85 (1H, d, J = 2.0 Hz).
IR v_{max}/cm^{-1} :	3086, 3018, 2939, 2868, 1734, 1700, 1684, 1652, 1647, 1606,
	1576, 1521, 1468, 1437, 1419, 1374, 1276, 1249, 1175, 1111, 1070,
	986, 928, 824, 808, 765, 668, 563, 507.
MS <i>m/z</i> (EI):	624, 623 (M ⁺), 557, 540, 522, 474, 442, 376, 328, 288,
	262, (M 100), 234, 217, 141, 115, 97, 67, 41.

Combustion analysis:

Expected:	C 75.09%, H 7.27%, N 2.25%
Obtained:	C 75.18%, H 7.39%, N 2.37%

4,7-Dibromobenzo[1,2,5]oxadiazole (39)



Bromine (52.8 g, 0.3300 mol) was added to a solution of benzo[1,2,5]oxadiazole (**38**) (5.00 g, 0. 0416 mol) in hydrobromic acid (48%, 100 cm³) and the resulting solution heated under reflux for 2.5 h. The cooled reaction mixture was filtered and the solid product washed with water (3 x 200 cm³) and dried on the sinter. Purification was carried *via* recrystallisation from EtOH to yield a white crystalline solid (6.94 g, 60%). Melting point /^OC: 114 (Lit. 112 – 112.5, EtOH). ^[33] Purity: >99% (GC). ¹H NMR (CDCl₃) δ_H: 7.66 (2H, S). IR v_{max}/cm⁻¹: 3011, 1603, 1471, 1371, 1132, 924, 870, 814, 585. MS *m*/*z* (EI): 280 (M⁺), 278 (M⁺, M100), 276 (M⁺), 201, 200, 198, 171, 167, 149, 132, 120, 113, 90, 79, 63.

4,7-bis[4-(Tetrahydropyran-2-yloxy)phenyl]benzo[1,2,5]oxadiazole (40)



Tetrakis(triphenylphosphine)palladium(0) (0.21 g, 1.80×10^{-4} mol) was added to a degassed solution of 4,7-dibromobenzo[1,2,5]oxadiazole (**39**) (1.00 g, 0.0036 mol), 2[4-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)phenoxy]tetrahydropyran (**33**) (2.74 g, 0.0090 mol), potassium phosphate (2.29 g, 0.0108 mol) and DMF (20 cm³). The mixture

was heated (80 $^{\circ}$ C) overnight then allowed to cool and poured into water. The crude product was extracted into DCM (3 x 100 cm³) and the combined organic extracts were washed with brine (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from EtOH to yield an orange crystalline solid (1.21 g, 71%).

Melting point / ^O C:	124 – 125.
¹ H NMR (CDCl ₃) δ_{H} :	1.57 – 1.74 (8H, m), 1.88 – 1.94 (4H, m), 3.63 – 3.67 (2H, m),
	3.91 – 3.99 (2H, m), 5.53 (2H, t), 7.21 (4H, d, J = 9 Hz),
	7.59 (2H, s), 7.99 (4H, d, J = 9 Hz).
IR v_{max}/cm^{-1} :	2942, 2872, 2346, 1607, 1506, 1452, 1356, 1282, 1242, 1178,
	1114, 1036, 1020, 959, 918, 872, 829.
MS <i>m</i> / <i>z</i> (EI):	473, 472 (M ⁺), 449, 448, 421, 404, 336, 305, 304, 274, 197,
	138, 121, 85, 69.

Combustion analysis:

Expected:	C 71.17%, H 5.97%, N 5.93%
Obtained:	C 71.16%, H 6.06%, N 5.66%

4,7-*bis*(4-Hydroxyphenyl)benzo[1,2,5]oxadiazole (41)



para-Toluene-sulphonic acid monohydrate was added to a solution of 4,7-*bis*[4-(tetrahydropyran-2-yloxy)phenyl]benzo[1,2,5]oxadiazole (**40**) (1.00 g, 0.0021 mol) in DCM (20 cm³) at RT until TLC analysis showed the complete conversion of 4,7-*bis*[4-(tetrahydropyran-2-yloxy)phenyl]benzo[1,2,5]oxadiazole (**40**) to 4,7-*bis*(4hydroxyphenyl)benzo[1,2,5]oxadiazole (**41**). Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 3 : 2] to yield an orange crystalline solid (0.55 g, 86%).

Melting point $/^{O}$ C: 179 – 180.

¹H NMR (CDCl₃) δ_{H} : 7.00 (4H, d, J = 8.8 Hz), 7.58 (2H, s), 7.97 (4H, d, J = 8.2 Hz). IR v_{max} /cm⁻¹: 3594, 3315, 3080, 2956, 1596, 1494, 1456, 1284, 1255, 1106, 872, 818, 642, 582. MS *m*/*z* (EI): 304 (M⁺, M 100), 288, 287, 286, 275, 274, 273, 260, 259, 258, 248, 247, 246, 245, 227, 214, 201, 190, 189, 175, 174, 157, 156, 137, 118, 108, 94, 77, 59.

4,7-bis{4-[5-(1-Vinylallyloxycarbonyl)pentyloxy]phenyl}benzo[1,2,5]oxadiazole (42)



A mixture of 4,7-*bis*(4-hydroxyphenyl)benzo[c][1,2,5]oxadiazole (**41**) (0.45 g, 0.0015 mol), potassium carbonate (0.61 g, 0.0044 mol), potassium iodide (0.02 g, 1.48 x 10^{-4} mol) and DMF (20 cm³), was heated (80 ^oC) overnight. Penta-1,4-dien-3-yl 6-bromohexanoate (**29**) (0.85 g, 0.0033 mol) was added to the solution, which was heated at 80^oC for a further 12 h. The reaction mixture was allowed to cool to RT, poured into water (200 cm³) and the crude product extracted into diethyl ether (3 x 100 cm³). The combined organic extracts were washed with brine (2 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM:hexane, 2 : 1] and recrystallisation from DCM/EtOH to yield an orange crystalline solid (0.54 g, 55%).

Transition temp. $/^{O}C$: **Cr** 60 **SmA** 98 **I**.

¹H NMR (CDCl₃)
$$\delta_{\rm H}$$
: 1.51 (4H, quint), 1.75 (4H, quint), 1.86 (4H, quint), 2.41 (4H, t),
4.05 (4H, t), 5.22 – 5.34 (8H, m), 5.73 (2H, d), 5.81 – 5.89
(4H, m), 7.04 (4H, d, J = 9 Hz), 7.59 (2H, s), 7.99 (4H,
d, J = 8.7 Hz).
IR $v_{\rm max}/{\rm cm}^{-1}$: 3460, 2946, 1737, 1607, 1508, 1378, 1251, 1190, 1024, 830.
MS m/z (EI): 665, 664 (M⁺, M100), 643, 599, 551, 535, 523, 507, 456,
435, 428, 423.

Combustion analysis:

Expected:	C 72.27%, H 6.67%, N 4.21%
Obtained:	C 72.28%, H 6.90%, N 4.17%

3,6-bis(4-Hydroxyphenyl)-1,2-dihydro-1,2,4,5-tetrazine (44).



4-Hydroxybenzonitrile (43) (25.00 g, 0.2100 mol) was dissolved in hydrazine hydrate (50 cm³) and the resultant reaction mixture heated under reflux for 4 h. The reaction mixture was allowed to cool to RT and refrigerated (2 $^{\circ}$ C) overnight. The orange precipitate was filtered off, washed with water (6 x 150 cm³), ethyl acetate (3 x 150 cm³) and DCM (3 x 150 cm³) and dried on the sinter to yield a pale orange crystalline solid (25.72 g, 91%), which quickly formed a red solid in air.

Melting point $/^{O}$ C: 275 – 277 (Lit. 286 – 289 (dec), dioxane).

¹H NMR (CDCl₃) δ_{H} : 6.76 (4H, d, J = 6.8 Hz), 7.64 (4H, d, J = 6.8 Hz), 8.76 (2H, s). IR v_{max} /cm⁻¹: 3393, 3335, 3285, 2592, 1653, 1641, 1608, 1595, 1560, 1517,

 1452, 1413, 1344, 1276, 1240, 1170, 1117, 1062, 1010, 980, 968,

 876, 838, 826, 775, 732, 668, 661, 641, 636, 629.

 MS m/z (EI):
 268 (M⁺), 253, 239, 197, 163, 148, 134, 119, (M 100), 107,

 91, 73, 64, 52.

3,6-*bis*(4-Hydroxyphenyl)-1,2,4,5-tetrazine (45).



A mixture of 3,6-bis(4-hydroxyphenyl)-1,2-dihydro[1,2,4,5]tetrazine (**44**) (10.00 g, 0.0370 mol), glacial ethanoic acid (250 cm³) and water (100 cm³) was stirred at RT for 30 min. Sodium nitrite (12.86 g, 0.1860 mol) in water (50 cm³) was added to the reaction

mixture over a period of 10 min, followed by stirring for 2 h. The red precipitate was filtered off, washed with water ($4 \times 500 \text{ cm}^3$) and allowed to dry on the sinter. The product was dissolved in acetone and the resultant solution concentrated under reduced pressure. The residue was collected as a red crystalline solid (2.15 g, 22%), which was used without further purification.

 $\begin{array}{ll} \mbox{Melting point} \slashed{P}^{0}\mbox{C:} &> 300 \mbox{ (Lit. 301).} \slashed{I}^{[34]} \\ \slashed{I}^{1}\mbox{H NMR (CDCl}_{3}) \ \ensuremath{\delta_{H}$:} \ 7.02 \ (4\mbox{H}, d, J = 8.7 \mbox{ Hz}), \ 8.35 \ (4\mbox{H}, d, J = 9.0 \mbox{ Hz}). \\ \mbox{IR v_{max}/cm^{-1}:} & 3291, 1608, 1586, 1554, 1527, 1502, 1451, 1396, 1369, 1288, \\ & 1239, 1221, 1171, 1102, 1052, 927, 837, 808, 726, 655, 585. \\ \mbox{MS m/z (EI):} & 266 \ (\mbox{M}^{+}), 252, 237, 214, 186, 170, 152, 141, \\ & 119 \ (\mbox{M 100}), 102, 91, 75, 64, 52. \\ \end{array}$

3,6-*bis*{4-[5-(1-Vinylallyloxycarbonyl)pentyloxy]phenyl}-1,2,4,5-tetrazine (46).



A mixture of 3,6-*bis*(4-hydroxyphenyl)-1,2,4,5-tetrazine (**45**) (0.30 g, 0.0113 mol), potassium carbonate (0.47 g, 0.0338 mol), penta-1,4-dien-3-yl 6-bromohexanoate (**32**) (0.74 g, 0.0282 mol) and DMF (30 cm³) was heated (100 $^{\circ}$ C) for 24 h. The product was extracted into ethyl acetate (2 x 200 cm³). The combined organic extracts were washed with brine (3 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 3 : 2] and recrystallisation from EtOH to yield a red crystalline solid (0.71 g, 71%).

Transition temp. $/^{O}C$: **Cr** 109 **I**.

¹H NMR (CDCl₃)
$$\delta_{\rm H}$$
: 1.52 – 1.60 (4H, m), 1.72 – 1.91 (8H, m), 2.41 (4H, t), 4.08 (4H, t),
5.22 – 5.33 (8H, m), 5.71 – 5.75 (2H, m), 5.80 – 5.89 (4H, m), 7.08 (4H, d, J = 9.0 Hz), 8.56 (4H, d, J = 9.0 Hz).
IR $v_{\rm max}$ /cm⁻¹: 3446, 2942, 2871, 1734, 1700, 1653, 1604, 1576, 1517, 1419, 1394, 1305, 1256, 1235, 1173, 1113, 1050, 1005, 947, 917, 836,

	728, 674, 668, 588.
MS <i>m/z</i> (EI):	627, 626 (M ⁺ , M100).
Combustion analysis:	
Expected:	C 68.99%, H 6.75%, N 8.94%
Obtained:	C 68.70%, H 6.95%, N 8.89%

3,6-bis{4-[10-(1-Vinylallyloxycarbonyl)decanyloxy]phenyl}-1,2,4,5-tetrazine (47).



A mixture of 3,6-*bis*(4-hydroxyphenyl)-1,2,4,5-tetrazine (**45**) (0.20 g, 0.0075 mol), potassium carbonate (0.36 g, 0.0263 mol), penta-1,4-dien-3-yl 11-bromoundecanoate (**17**) (0.75 g, 0.0225 mol) and DMF (30 cm³) was heated (100 $^{\circ}$ C) for 24 h. The product was extracted into ethyl acetate (2 x 200 cm³). The combined organic extracts were washed with brine (3 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 3 : 1] and recrystallisation from DCM/EtOH to yield a red crystalline solid (0.58 g, 45%).

Transition temp. /^oC: Cr 80 Sm C 132 I.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	1.25 – 1.34 (20H, m), 1.49 (4H, quint), 1.64 (4H, quint), 1.84 (4H,
	quint), 2.34 (4H, t), 4.07 (4H, t), 5.21 – 5.43 (8H, m) 5.71 – 5.73
	(2H, m), 5.79 - 5.88 (4H, m), 7.08 (4H, d, J = 9.0 Hz), 8.56 (4H, d, d, d)
	J = 9.0 Hz).
IR v_{max}/cm^{-1} :	3312, 3264, 2837, 2602, 2556, 2327, 1918, 1776, 1670, 1531,
	1485, 1342, 1144, 932, 857, 796, 716.
MS <i>m/z</i> (HABA):	766 (M ⁺), 764, 747, 669, 594, 573, 505.
Combustion analysis:	

Expected:	C 72.03%, H 8.15%, N 7.30%
Obtained:	C 72.23%, H 8.01%, N 7.21%

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3,6-*bis*(4-Octyloxyphenyl)-1,2,4,5-tetrazine (48).



A mixture of 3,6-*bis*(4-hydroxyphenyl)-1,2,4,5-tetrazine (**45**) (0.50 g, 0.0019 mol), potassium carbonate (0.91 g, 0.0657 mol), potassium iodide (trace amount) and DMF (10 cm³) was heated (100 $^{\circ}$ C) overnight. 1-Bromooctane (0.80 g, 0.0413 mol) was added to the mixture and stirred for a further 24 h. The deep red reaction mixture was poured into water (100 cm³), the resultant red precipitate filtered off washed with water (3 x 200 cm³), EtOH (4 x 50 cm³), hexane (2 x 100 cm³) and hot EtOH (2 x 100 cm³). The product was dried on the sinter and purified *via* recrystallisation from DCM/EtOH to yield red needles (0.77 g, 84%).

Transition temp. /^OC: Cr 132 SmC 188 N 196 I.

¹ H NMR (CDCl ₃) δ	H: 0.90 (6H, t), 1.25 – 1.40 (16H, m), 1.49 (4H, quint), 1.84
	(4H, quint), 4.07 (4H, t), 7.08 (4H, d, J = 9.0 Hz), 8.56
	(4H, d, J = 9.0 Hz).
IR v_{max}/cm^{-1} :	2920, 2852, 1605, 1578, 1518, 1469, 1391, 1172, 1111, 1062,
	1050, 1012, 960, 918, 834, 808, 720, 674, 586.
MS <i>m/z</i> (EI):	490 (M ⁺), 379, 254, 232, 231, 120, 119, 102, 83, 71,
	57 (M 100).

Combustion analysis:

Expected:	C 73.43%, H 8.63%, N 11.42%
O(1) (1)	C 72 170/ H 0 010/ N 11 220/

Obtained: C 73.17%, H 8.91%, N 11.23%

1,4-*bis*{3,6-*bis*[4-(Octyloxy)phenyl]pyridazin-4-yl}benzene (**49**)



A mixture of 3,5-*bis*(4-octyloxyphenyl)-1,2,4,5-tetrazine (**48**) (0.62 g, 0.0013 mol), 1,4diethynylbenzene (0.06 g, 4.76 x 10^{-4} mol) and toluene (10 cm^3) was heated under reflux for four days. The cooled reaction mixture was diluted with toluene (200 cm^3) and the resultant organic layer washed with brine (100 cm^3), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, ethyl acetate : hexane, 3 : 2] and recrystallisation from EtOH to yield an off white crystalline solid (0.11 g, 22%).

Transition temp. / O C: Cr 64 SmX 168 I.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$: 0.89 (12H, t), 1.26 – 1.52 (40H, m), 1.77 – 1.85 (8H, m), 3.97
	(4H, t), 4.05 (4H, t), 6.84 (4H, d, J = 9.0 Hz), 7.05 (4H, d,
	J = 9.0 Hz), 7.30 (4H, s), 7.43 (4H, d, J = 9.0 Hz), 7.76
	(2H, s), 8.15 (4H, d, J = 9.0 Hz).
IR v_{max}/cm^{-1} :	3066, 2926, 2854, 1608, 1575, 1521, 1467, 1418, 1387, 1295,
	1250, 1175, 1114, 1016, 969, 907, 831, 723, 659, 590, 543.
MS <i>m</i> / <i>z</i> (MALDI):	1052, 1051 (M ⁺ , M100).
Combustion analysis	:

Expected: C 79.96%, H 8.63%, N 5.33%

Obtained: C 80.14%, H 8.93%, N 5.12%

3,6-*bis*(Pyridin-2-yl)-1,2-dihydro-1,2,4,5-tetrazine (**51**)

$$\begin{array}{c} & & & \\ &$$

A mixture of 2-cyanopyridine (**50**) (20.00 g, 0.1920 mol) and hydrazine hydrate (20 cm³) was heated under reflux for 5 h. The cooled reaction solution was added to water (100 cm³), the resultant precipitate was collected on a sinter and the orange solid washed with water (200 cm³). Purification was carried out *via* recrystallisation from DCM/hexane to yield pale orange needles (7.30 g, 32%).

Melting point /^OC: 196 – 199 (Lit. 188 – 190, EtOH).^[35]

 1 H NMR (CDCl₃) δ_{H} : 5.51 (2H, s), 7.33 – 7.37 (2H, m), 7.76 – 7.78 (2H, m), 8.06

(2H, d, J = 7.84 Hz), 8.59 (2H, t, J = 5.2 Hz).

IR v_{max} /cm⁻¹: 3467, 3342, 3297, 3057, 1656, 1611, 1588, 1563, 1469, 1446, 1386, 1288, 1250, 1154, 1116, 1077, 1040, 990, 980, 903, 885, 793, 745, 720, 677, 654, 622.

MS *m*/*z* (EI): 238 (M⁺, M 100), 171, 112, 108, 105, 96, 78, 51.

Combustion analysis:

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Expected:C 60.50%, H 4.23%, N 35.27%Obtained:C 60.58%, H 4.12%, N 35.32%
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3,6-*bis*(Pyridin-2-yl)-1,2,4,5-tetrazine (52)

$$\begin{array}{c} & \overset{\mathsf{N}}{\longrightarrow} & \overset{\mathsf{N}=\mathsf{N}}{\longrightarrow} & \overset{\mathsf{N}}{\longrightarrow} \\ & \overset{\mathsf{N}=\mathsf{N}}{\longrightarrow} & \overset{\mathsf{N}=\mathsf{N}}{\longrightarrow} \end{array}$$

A mixture of 3,6-*bis*(pyridine-2-yl)-1,2-dihydro-1,2,4,5-tetrazine (**51**) (3.50 g, 0.0150 mol), glacial ethanoic acid (300 cm³) and water (200 cm³) was stirred at RT for 20 min. An aqueous solution of sodium nitrite (11.00 g, 0.1594 mol, 50 cm³) was added over 10 min. The resulting mixture was stirred for 2 h, the crude product extracted into DCM (3 x 300 cm³) and the combined organic extracts washed with brine (4 x 300 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel,ethyl acetate] to yield a red crystalline solid (1.02 g, 29%).

Melting point / ^O C:	226 – 227 (Lit. 229 – 230, benzene). ^[36]
1 H NMR (CDCl ₃) δ_{H}	: 7.58 – 7.61 (2H, m), 8.03 (2H, dt, J = 7.8, 2.0 Hz), 8.77 (2H, d,
	J = 7.8 Hz), 9.0 (2H, dt, J = 4.8, 0.8 Hz).
IR v_{max}/cm^{-1} :	3050, 1656, 1609, 1576, 1563, 1468, 1445, 1381, 1290, 1254,
	1150, 1112, 1079, 1045, 999, 980, 908, 890, 793, 745, 720, 677,
MS <i>m</i> / <i>z</i> (EI):	654, 622.
	236 (M ⁺), 224, 209, 196, 181, 168, 154, 127, 104 (M 100), 96,
	77, 50.
Combustion analysis	
Expected:	C 61.01%, H 3.41%, N 35.58%
Obtained:	C 61.19%, H 3.32%, N 35.40%

1,4-bis[3,6-Di(pyridine-2-yl)pyridazin-4-yl]benzene (53)



A mixture of 3,6-*bis*(pyridine-2-yl)-1,2,4,5-tetrazine (**52**) (2.34 g, 0.0091 mol), 1,4diethynylbenzene (0.50g, 0.0037 mol) and toluene (45 cm³) was heated under reflux for 6 days. The cooled reaction mixture was concentrated under reduced pressure and purified *via* column chromatography [silica gel, ethyl acetate : EtOH, 9 : 1] and recrystallisation from EtOH to yield off white needles (0.18 g, 8%).

Melting point /^OC: 288.

$$\label{eq:homoson} \begin{tabular}{l} ^1\!H \ NMR \ (CDCl_3) \ \delta_H \!\!: 7.23 \ (4H, \, s), \ 7.28 - 7.31 \ (2H, \, m), \ 7.43 - 7.46 \ (2H, \, m), \ 7.83 \ (2H, \ dt, \, J = 7.7, \ 1.7 \ Hz), \ 7.94 \ (4H, \, dt, \, J = 7.8, \ 1.4 \ Hz), \ 8.49 \ (2H, \, d, \, J = 4.2 \ Hz), \ 8.66 \ (2H, \, s), \ 8.76 \ (2H, \, d, \, J = 4.2 \ Hz), \ 8.81 \ (2H, \, d, \, J = 8.1 \ Hz). \end{tabular}$$

IR v_{max}/cm^{-1} :	3400, 1698, 1654, 1576, 1509, 1475, 1428, 1408, 1390, 1253, 1098,
	991, 931, 839, 796, 763, 745, 730, 651, 621, 593.
MS <i>m/z</i> (EI):	542 (M ⁺), 271, 183, 145, 126, 114, 98, 85, 69, 55
	(M 100).

Combustion analysis:

Expected:	C 75.26%, H 4.09%, N 20.65%
Obtained:	C 75.48%, H 4.06%, N 20.70%

2-Bromo-7-iodo-9,9-dihexylfluorene (54).



Powdered KOH (10.93 g, 0.1947 mol) was added in small portions over 30 min to a mixture of 2-bromo-7-iododfluorene (**20**) (17.00 g, 0.0458 mol), 1-bromohexane (16.63 g, 0.1008 mol), potassium iodide (0.76 g, 0.0046 mol) and DMSO (100 cm³) at RT. The mixture was stirred for two hours then poured into water (300 cm³). The crude product was extracted into DCM ($3 \times 200 \text{ cm}^3$). The combined organic extracts washed with aqueous hydrochloric acid (10%, 200 cm³), brine ($2 \times 200 \text{ cm}^3$), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane] and recrystallisation from EtOH, to yield white needles (19.30 g, 78%).

Melting point $/^{\circ}$ C: 57 – 58.

Purity: >99% (GC).

 1 H NMR (CDCl₃) δ_{H} : 0.58 (4H, quint), 0.83, (6H, t), 1.0 – 1.2 (12H, m), 1.90 (4H, t),

7.39 - 7.52 (4H, m), 7.63 - 7.66 (2H, m).

IR v_{max} /cm⁻¹: 2920, 1596, 1564, 1446, 1413, 1253, 1110, 1057, 1002, 941, 874, 842, 803, 745, 722, 662, 520, 438.

MS m/z (EI): 540 (M⁺), 538 (M⁺, M 100).

7-Bromo-9,9-dihexylfluorene-2-carbonitrile (55).



A mixture of 2-bromo-7-iodo-9,9-dihexylfluorene (48) (15.60 g, 0.0289 mol), copper cyanide (2.59 g, 0.0289 mol) and DMF (75 cm³) was heated (100 ^OC) and stirred for 48 h. The cooled reaction mixture was poured into water (500 cm³) and extracted into DCM $(3 \times 150 \text{ cm}^3)$. The combined organic extracts were washed with brine $(3 \times 250 \text{ cm}^3)$. dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] and recreation from EtOH to yield a pale yellow crystalline solid (8.50 g, 67%). Melting point /^OC: 92 – 93. Purity: >99% (GC). ¹H NMR (CDCl₃) δ_{H} : 0.50 – 0.65 (4H, m), 0.75 (6H, t), 0.95 – 1.15 (12H, m), 1.97 (4H, t), 7.50 (2H, t, J = 8 Hz), 7.62 (3H, t, J = 11.4 Hz), 7.73 (1H, d, J = 6.9 Hz).IR v_{max}/cm^{-1} : 2920, 2852, 2222, 1604, 1452, 1402, 1370, 1232, 1108, 1056, 880, 811, 750. MS *m*/*z* (EI): 439 (M⁺), 437 (M⁺), 354, 353, 352, 298, 284, 283, 282, 268 (M 100), 267, 266, 253, 228, 216, 215, 214, 203, 202, 190, 189, 176, 167, 149.

Combustion analysis:

Expected:	C 71.22%, H	H 7.36%,	N 3.19%
Expected:	C/1.22%, F	1 /.30%,	IN 3.19%

Obtained: C 71.48%, H 7.27%, N 3.06%
3,6-bis(7-Bromo-9,9-dihexylfluoren-2-yl)-1,2,4,5-tetrazine (56).



A mixture of 7-bromo-9,9-dihexylfluorene-2-carbonitrile (55) (8.00 g, 0.0182 mol) hydrazine hydrate (20 cm³), EtOH (80 cm³) and sublimed sulphur (0.50 g) was heated under reflux overnight. The cooled reaction mixture was poured into water (200 cm³) and the resulting precipitate filtered, washed with water $(2 \times 300 \text{ cm}^3)$ and dried on the sinter. The crude product was reduced by adding to a mixture of water (200 cm^3) , glacial ethanoic acid (100 cm³) and THF (10 cm³) and stirred at RT for 30 min. An aqueous sodium nitrite solution (12.56 g, 0.182 mol, 60 cm³) was added in small portions over 30 min and stirred for a further 1 h. The crude product was extracted into ethyl acetate (3 x 150 cm^3), the combined extracts washed with brine (3 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 3 : 1] and recrystallisation from DCM/EtOH to yield an pale pink crystalline solid (5.11 g, 31%). Melting point /^OC: 172 – 173. ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.64 – 0.68 (8H, m), 0.75 (12H, t), 0.99 – 1.14 (24H, m), 2.04 (8H, t), 7.53 (4H, d, J = 7.3 Hz), 7.67 (2H, d, J = 8.7 Hz), 7.90 (2H, d, J = 7.9), 8.65 (2H, s), 8.69 (2H, d, J = 7.9 Hz). IR v_{max}/cm^{-1} : 2926, 2854, 2362, 1608, 1458, 1384, 1259, 1117, 1060, 1005, 922,

816.

MS *m*/*z* (MALDI): 906 (M⁺), 905 (M⁺), 904 (M⁺, M 100).

Expected:	C 69.02%, H 7.13%, N 6.19%
Obtained:	C 69.31%, H 7.03%, N 5.96%

5-Bromo-2-(octyloxy)pyridine (58)



A mixture of 2-hydroxy-5-bromopyridine (57) (10.00 g, 0.0575 mol), potassium carbonate (15.89 g, (0.0115 mol), potassium iodide (0.95 g, 0.0057 mol) and DMF (75 cm^{3}) was heated (100 ^{O}C) for 24 h. The cooled reaction mixture was poured into water (400 cm^3) and the crude product extracted into ethyl acetate (3 x 200 cm³). The combined organic extracts washed with brine (3 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM] and recrystallisation from EtOH, to yield a white crystalline solid (10.36 g, 63%). Melting point $/^{O}C$: 39 – 41. Purity: >98% (GC). ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.86 (3H, t), 1.27 – 1.30 (6H, m), 1.31 (2H, quint), 1.43 (2H, quint), 1.76 (2H, quint), 4.01 (2H, t), 6.99 (1H, d), 7.47 (1H, dd), 8.18 (1H, d). IR v_{max}/cm^{-1} : 3100, 3082, 3080, 2984, 2977, 2965, 2949, 2934, 2926, 2907, 1704, 1689, 1675, 1667, 1618, 1570, 1501, 1440, 1392, 1224, 1108,

MS *m*/*z* (EI): 287, 285 (M⁺, M100), 207.

1002, 581.

6-(Octyloxy)pyridine-3-ylboronic acid (59)

A solution of *n*-BuLi in hexanes $(11.53 \text{ cm}^3, 2.5M, 0.0288 \text{ mol})$ was added dropwise to a cooled (-78 $^{\text{O}}\text{C}$) solution of 5-bromo-2-(octyloxy)pyridine (**58**) (7.50 g, 0.0262 mol) in THF (75 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\text{O}}\text{C}$. Trimethyl borate (5.44 g, 0.0524 mol) was added dropwise to the reaction mixture, which

was then allowed to warm to RT and stirred overnight. Aqueous hydrochloric acid (20%, 200 cm^3) was added and the separated layers stirred vigorously for 1 h. The crude product was extracted into diethyl ether (3 x 250 cm³), the combined extracts washed with brine (2 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* stirring in hexane (200 cm³) filtering the white solid and washing with hexane (3 x 300 cm³), EtOH (100 cm³), water (3 x 200 cm³) and EtOH (50 cm³) to yield a white crystalline solid (3.18 g, 48%).

Melting point
$$/^{O}C$$
: 118 – 119.

¹H NMR (CDCl₃)
$$\delta_{\rm H}$$
: 0.87 (3H, t), 1.26 – 1.30 (6H, m), 1.32 (2H, quint), 1.43 (2H, quint), 1.77 (2H, quint), 4.02 (2H, t), 6.71 (1H, d), 7.71 (1H, dd), 8.24 (1H, d).
IR $v_{\rm max}/{\rm cm}^{-1}$: 3475, 2922, 1645, 1608, 1558, 1395, 1248, 1155, 1047, 909, 852, 722, 647, 602, 513, 466.
MS m/z (EI): 251, (M⁺, M 100), 250, 207.

3,6-bis{9,9-Dihexyl-7-[6-(octyloxy)pyridine-3-yl]fluoren-2-yl}-1,2,4,5-tetrazine (60)



Tetrakis(triphenylphosphine)palladium(0) (0.01 g, 8.2 x 10^{-6}) was added to a solution of 3,6-*bis*(7-bromo-9,9-dihexylfluoren-2-yl)-1,2,4,5-tetrazine (**51**) (0.15 g, 1.66 X 10^{-4} mol), 6-(octyloxy)pyridine-3-ylboronic acid (**59**) (0.10 g, 4.15 x 10^{-4}), aqueous sodium carbonate (20%, 0.05 g, 4.97 x 10^{-4} mol) and DME (5 cm³). The mixture was heated under reflux for 24 h. The cooled reaction mixture was poured into water (50 cm³) and the crude product extracted into DCM (3 x 100 cm^3). The combined extracts were washed with brine (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] and recrystallisation from DCM/EtOH to yield red needles (0.07 g, 37%). Transition temp. /^OC: **T**_g 20 **Cr** 97 **I**.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	0.74 (12H, t), 0.90 (6H, t), 1.01 – 1.12 (20H, m), 1.30 – 1.39
	(32H, m), 1.82 (4H, quint), 2.11 (8H, t), 4.36 (4H, t), 6.85 (2H, d,
	J=8.4~Hz), 7.54-7.59~(4H,m), 7.86-7.90~(4H,m), 7.95~(2H,d,
	J = 7.9 Hz), 8.48 (2H, d, $J = 2.6 Hz$), 8.68 – 8.72 (4H, m).
IR v_{max}/cm^{-1} :	2925, 2854, 1600, 1489, 1466, 1422, 1385, 1342, 1288, 1093, 821,
	700.
MS <i>m/z</i> (MALDI):	1158, 1157 (M ⁺ , M 100), 1077, 1076, 1052 1051,
	1030, 1008 1007, 1006, 945.
Combustion analysis	

Combustion analysis:

Expected:	C 80.92%, H 9.05%, N 7.26%
Obtained:	C 80.96%, H 9.35%, N 7.14%

3,6-bis{9,9-Dihexyl-7-[4'-(octyloxy)biphenyl-4-yl]fluoren-2-yl}-1,2,4,5-tetrazine (61)



Tetrakis(triphenylphosphine)palladium(0) (1.38×10^{-5}) was added to a solution of 3,6*bis*(7-bromo-9,9-dihexylfluoren-2-yl)-1,2,4,5-tetrazine (**56**) (0.25 g, 2.76 x 10⁻⁴ mol), 4'octyloxybiphenyl-4-ylboronic acid (**13**) (0.23 g, 6.91 x 10⁻⁴), aqueous sodium carbonate (20%, 0.09 g, 8.29 x 10⁻⁴ mol) and DME (5 cm³). The mixture was heated under reflux for 24 h. The cooled reaction mixture was poured into water (100 cm³) and the crude product extracted into DCM (2 x 100 cm³) The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH to yield orange needles (0.25g, 69%).

Transition temp. O C: Cr 208 N 235 I.

 $\label{eq:hardenergy} {}^{1}\text{H NMR (CDCl_3) } \delta_{\text{H}} : 0.75 \ (12\text{H}, \ t), \ 0.90 \ (6\text{H}, \ t), \ 1.01 - 1.11 \ (20\text{H}, \ m), \ 1.31 - 1.39 \ (32\text{H}, \ m), \ 1.81 \ (4\text{H}, \ quint), \ 2.12 \ (8\text{H}, \ t), \ 4.02 \ (4\text{H}, \ t), \ 7.00 \ (4\text{H}, \ d, \ J) \ (4\text{H}, \ d, \ J)$

	= 9 Hz), 7.60 (4H, d, J = 8.7 Hz) 7.63 – 7.70 (8H, m), 7.76 (4H, d,
	J = 8.7 Hz), 7.89 (2H, d, J = 7.9 Hz), 7.96 (2H, d, J = 7.8 Hz),
	8.69 – 8.72 (4H, m).
IR v_{max}/cm^{-1} :	2925, 2855, 2362, 1606, 1498, 1465, 1384, 1288, 1248, 1202,
	1178, 1047, 915, 816.
MS <i>m/z</i> (MALDI):	1308 (M ⁺), 1307, 816, 640, 552.
Combustion analysis	s:
Expected:	C 84.48%, H 8.79%, N 4.28%
Obtained:	C 83.78%, H 9.23%, N 4.07%

1-Bromo-4-octyloxybenzene (62)



A mixture of 4-bromophenol (25.00 g, 0.1445 mol), potassium carbonate (29.96 g, 0.2168 mol), 1-bromooctane (33.49 g, 0.1734 mol) and butanone (400 cm³) was heated under reflux overnight. The cooled reaction mixture was poured into water (200 cm³) and the crude product extracted into ethyl acetate (4 x 100 cm³). The combined organic extracts were washed with brine (200 cm³) dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane] to yield a colourless liquid (28.03 g, 68%).

Purity: >98% (GC).

¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.88 (3H, t), 1.27 – 1.46 (12H, m), 3.89 (2H, t),

6.75 (2H, d, J = 9 Hz), 7.34 (2H, d, J = 9 Hz).

IR v_{max}/cm^{-1} :	3040, 2960, 2927, 2860, 1608, 1524, 1481, 1290, 1259, 1199,
	1133, 1030, 814.

MS <i>m</i> / <i>z</i> (EI): 286, 284	(M ⁺), 187, 17	75, 174 (M 1	00), 172, 13	55, 153, 93.
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Expected:	С 58.95%, Н 7.42%
Obtained:	C 59.09%, H 7.69%

4-Octyloxyphenylboronic acid (63)

A solution of *n*-BuLi in hexanes (33.66 cm³, 2.5*M*, 0.0841 mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 1-bromo-4-octyloxybenzene (**62**) (20.00 g, 0.0701 mol) in THF (300 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\circ}$ C. Trimethyl borate (14.57 g, 0.1402 mol) was added dropwise to the mixture, which was then allowed to warm to RT and stirred overnight. Aqueous hydrochloric acid (20%, 200 cm³) was added and the separated layers stirred vigorously for 1 h. The crude product was extracted into diethyl ether (3 x 250 cm³), washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was purified by stirring in hexane (100 cm³) filtering and washing with hexane (3 x 100 cm³) whilst on the sinter to yield a white crystalline solid (10.17 g, 58%).

¹ H NMR (CDCl ₃) δ_{H} : 0.89 (3H, t), 1.25 – 1.56 (10H, m), 1.75 – 1.90 (2H, m), 4.01
	(2H, t), 6.98 (2H, d, J = 8.8 Hz), 8.14 (2H, d, J = 8.8 Hz).
IR v_{max}/cm^{-1} :	3608, 2932, 2890, 1916, 1601, 1565, 1511, 1466, 1404, 1350, 1248,
	1179, 1113, 1053, 1010, 995, 864, 831, 790, 742, 727, 651, 625,
	592, 533, 514.
MS <i>m/z</i> (EI):	250 (M ⁺).

3,6-bis{9,9-Dihexyl-7-[4-(octyloxy)phenyl]fluoren-2-yl}-1,2,4,5-tetrazine (64)



Tetrakis(triphenylphosphine)palladium(0) (0.01 g, 8.30 x 10⁻⁶ mol) was added to a solution of 3,6-*bis*(7-bromo-9,9-dihexylfluoren-2-yl)-1,2,4,5-tetrazine (**56**) (0.15 g, 1.66

x 10^{-4} mol), 4-octyloxyphenylboronic acid (**63**) (0.10 g, 4.20 x 10^{-4} mol), aqueous sodium carbonate (20%, 0.05 g, 4.97 x 10^{-4} mol) and DME (5 cm³). The mixture was heated under reflux for 24 h. The cooled reaction mixture was poured into water (100 cm³) and the crude product extracted into DCM (2 x 100 cm³). The combined extracts washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] to yield an orange waxy solid, which was recrystallised from DCM/EtOH to yield an orange crystalline solid (0.05 g, 26%).

Transition temp. / O C: **Cr** 136 **I**.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$: 0.67, (6H, t), 0.77 – 0.86 (12H, m), 0.91 – 0.99 (20H, m), 1.13 –
	1.32 (32H, m), 1.76 (4H, quint), 2.05 (8H, t), 3.96 (4H, t), 6.95
	(4H, d, J = 6.8 Hz), 7.50 (2H, d, J = 1.1 Hz), 7.52 (2H, d,
	J = 1.7 Hz), 7.55 (4H, d, J = 6.7 Hz), 7.77 (2H, d,
	J = 7.8 Hz), 7.87 (2H, d, J = 7.8 Hz) 8.60 (2H, d, J = 1.1 Hz), 8.63
	(2H, dd, J = 8 Hz, 1.7 Hz).
IR v_{max}/cm^{-1} :	2955, 2921, 2855, 2370, 1607, 1500, 1475, 1394, 1274, 1250,
	1178, 1138, 1034, 994, 825, 810, 758, 721, 595, 518.
MS <i>m/z</i> (MALDI):	1156, 1155 (M ⁺), 743, 715, 645, 575, 502, 451, 410, 255,
	237, 228 (M 100), 195, 124.

Combustion analysis:

Expected:	C 83.14%, H 9.24%, N 4.85%
Obtained:	C 83.31%, H 9.33%, N 4.66%

2-(4-Methoxy-2-methylphenyl)thiophene (66)

Tetrakis(triphenylphosphine)palladium(0) (1.44 g, 1.24×10^{-3} mol) was added to a heated (90 °C) solution of 1-bromo-4-methoxy-2-methylbenzene (**65**) (5.00 g, 0.0249 mol), tributyl(thiophen-2-yl)stannane (9.28 g, 0.0249 mol) and DMF (80 cm³). The mixture

was stirred overnight, allowed to cool, poured into water (200 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed saturated KF solution (200 cm³), brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from EtOH to yield a white crystalline solid (2.56 g, 50%).

¹ H NMR (CDCl ₃) $\delta_{\rm H}$	2.25 (3H, s), 3.85 (3H, s), 6.82 (1H, d, J = 8.2 Hz), 7.04 (1H, dd,
	J = 5.1, 3.6 Hz), 7.18 – 7.21 (2H, m), 7.39 (1H, s), 7.42 (1H, d,
	J = 2.6 Hz)
IR v_{max}/cm^{-1} :	2942, 1603, 1530, 1494, 1323, 1300, 1247, 1133, 1024, 880, 810,
	753, 695, 600, 508.
MS <i>m</i> / <i>z</i> (EI):	204 (M ⁺), 191, 190, 189 (M 100), 171, 161, 145, 134,
	129, 128, 127, 110, 102, 89.

Combustion analysis:

Expected:	C 70.55%, H 5.92%, S 15.70%
Obtained:	C 70.77%, H 6.15%, S 16.00%

Tributyl[5-(4-methoxy-2-methylphenyl)thiophen-2-yl]stannane (67)



A solution of *n*-BuLi in hexanes (6.11 cm³, 2.5*M*, mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 2-(4-methoxy-2-methylphenyl)thiophene (2.40 g, 0.0117 mol) in THF (50 ml). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\circ}$ C, followed by the dropwise addition of tributyl tin chloride (4.97 g, 0.0153 mol). The mixture was allowed to warm to RT and stirred overnight then the crude product was extracted into diethyl ether (2 x 100 cm³). The combined organic extracts were washed

with water (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out.

Purity: >79% (GC). MS *m*/*z* (EI): 494 M (100), 493 (M⁺), 492, 454, 446, 431, 357, 345, 298, 206, 151, 126.

2-Bromo-7-iodo-9,9-dipropylfluorene (21)



A mixture of NaOH (65.00 g), water (130 cm³), 2-bromo-7-iodofluorene (20) (20.00 g, 0.0540 mol), 1-bromopropane (19.94 g, 0.1620 mol), toluene (130 cm³) and TBAB (0.80 g) was heated under reflux with vigorous stirring overnight. The reaction was allowed to cool and the product extracted into diethyl ether $(3 \times 250 \text{ cm}^3)$. The combined ethereal extracts were washed with aqueous hydrochloric acid $(10\%, 500 \text{ cm}^3)$, water (3×250) cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane] and recrystallisation from EtOH to yield a pale yellow crystalline solid (12.05 g, 49%). Melting point /^OC: 137 – 139 (Lit. 136 – 139, EtOH).^[30] Purity: >98% (GC). ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.66 (6H, t), 0.74 – 0.81 (4H, m), 1.89 (6H, t), 7.38 – 7.52 (4H, m), 7.63 – 7.66 (2H, m). IR v_{max}/cm^{-1} : 2946, 2925, 2866, 2839, 1884, 1734, 1593, 1569, 1454, 1445, 1413, 1394, 1377, 1270, 1239, 1131, 1108, 1050, 1003, 930, 874, 809, 754, 742, 668, 659, 494, 424. 455 (M⁺), 454 (M 100), 453 (M⁺), 423, 397, 330, 329, 327, 326, MS m/z (EI): 251, 250.

Expected:	C 50.14%, H 4.43%
Obtained:	C 50.29%, H 4.42%

2,7-*bis*[5-(4-Methoxy-2-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (68)



Tetrakis(triphenylphosphine)palladium(0) (0.32 g, 2.74 x 10^{-4} mol) was added to a heated (90 °C) solution of 2-bromo-7-iodo-9,9-dipropylfluorene (**21**) (1.25 g, 0.0027), tributyl[5-(4-methoxy-2-methylphenyl)thiophen-2-yl]stannane (**67**) (4.05 g, 0.0082 mol) and DMF (50 cm³). The mixture was stirred overnight, allowed to cool, poured into water (300 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with brine (2 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from EtOH/DCM, to yield a pale yellow crystalline solid (1.28 g, 71%). Transition temp. /^OC: **T**_g 85 **Cr** 196 **N** 220 **I**.

¹H NMR (CDCl₃) δ_{H} : 0.71 – 0.80 (10H, m), 2.02 (4H, t), 2.28 (6H, s), 3.88 (6H, s), 6.85 (2H, d, J = 8.2 Hz), 7.20 (2H, d, J = 3.6 Hz), 7.34 (2H, d J = 2.8 Hz), 7.45 (2H, s), 7.48 (2H, d, J = 2.6 Hz), 7.60 (4H, dt, J = 16.3, 1.7 Hz), 7.67 (2H, d, J = 7.8 Hz) IR v_{max}/cm⁻¹: 2954, 2926, 1605, 1505, 1474, 1295, 1250, 1136, 1033, 880, 796, 754. MS *m*/*z* (EI): 654 (M⁺), 591, 567, 407, 406 (M 100), 392, 391, 376, 348, 327, 319, 160, 138, 121.

Expected:	C 78.86%, H 6.46%, S 9.79%
Obtained:	C 77.91%, H 6.48%, S 9.76%

2,7-bis[5-(4-Hydroxy-2-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (69)



Boron tribromide (1.81 g, 0.0072 mol) was added dropwise to a cooled (0 $^{\circ}$ C) solution of *bis*-2,7-[5-(4-methoxy-2-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**68**) (1.05 g, 0.0016 mol) in DCM (10 cm³). The reaction mixture was allowed to warm to RT and stirred overnight, poured into ice (300 cm³) and stirred for 1 h. The organic layer was separated and the aqueous layer washed with DCM (3 x 200 cm³). The combined organic layers were dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 2 : 1] to yield a pale yellow crystalline solid (0.72 g, 72%).

Melting point $/^{O}C$: 243.

¹H NMR (CDCl₃)
$$\delta_{\text{H}}$$
: 0.71 – 0.80 (10H, m), 2.02 (4H, t), 2.31 (6H, s), 4.87 (2H, s), 6.80
(2H, d, J = 8.1 Hz), 7.19 (2H, d, J = 3.9 Hz), 7.34 (2H, d, J = 3.9 Hz), 7.38 – 7.43 (4H, m), 7.59 (4H, t, 7.8 Hz), 7.67 (2H, d, J = 7.8 Hz).
IR ν_{max} /cm⁻¹: 3436, 2955, 2910, 1606, 1543, 1508, 1474, 1332, 1260, 1113, 879, 798.
MS *m*/*z* (EI): 627, 626 (M⁺, M 100).

2,7-*bis*(5-{2-Methyl-4-[5-(1-vinylallyloxycarbonyl)pentyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (**70**)



A mixture of *bis*-2,7-[5-(4-hydroxy-2-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**69**) (0.25 g, 3.99×10^{-4} mol), K₂CO₃ (0.17 g, 0.0012 mol), KI (trace amount) and DMF (5 cm³) was heated (90 ^oC) and stirred overnight. Penta-1,4-dien-3-yl 6-bromohexanoate (**29**) (0.23 g, 8.77 x 10⁻⁴ mol) and BHT (trace amount) were added to the reaction mixture and stirred for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] to yield a yellow liquid which formed a waxy solid after 2 days (0.24 g, 61%).

Transition temp. / $^{\circ}$ C: **Tg** 33 **Cr** 89 **I**.

¹ H NMR (CDCl ₃)) δ_{H} : 0.70 – 0.79 (10H, m), 1.31 – 1.35 (8H, m), 1.74 (4H, quint), 1.85
	(4H, quint), 2.02 (4H, t), 2.27 (6H, s), 2.41 (4H, t), 4.01 (4H, t),
	5.22 – 5.33 (8H, m), 5.73 – 5.75 (2H, m), 5.80 – 5.89 (4H, m),
	6.82 (2H, d, J = 9.3 Hz), 7.20 (2H, d, J = 3.7 Hz), 7.34 (2H, d, J =
	3.7 Hz), 7.42 – 7.44 (4H, m), 7.57 – 7.62 (4H, m),
	7.67 (2H, d, J = 7.8 hz).
IR v_{max}/cm^{-1} :	2929, 2875, 1736, 1604, 1505, 1468, 1293, 1250, 1158, 1134, 976,
	925, 795.

MS *m*/*z* (MALDI): 931, 926, 905, 883, 877, 861.

Expected:	C 76.64%, H 7.15%, S 6.50%
Obtained:	C 76.58%, H 7.38%, S 6.25%

2,7-*bis*(5-{2-Methyl-4-[10-(1-vinylallyloxycarbonyl)decanyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (**71**)



A mixture of *bis*-2,7-[5-(4-hydroxy-2-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**69**) (0.25 g, 3.99 x 10^{-4} mol), K₂CO₃ (0.17 g, 0.0012 mol), KI (trace amount) and DMF (5 cm³) was heated (90 ^oC) overnight. Penta-1,4-dien-3-yl 11-bromoundecanoate (**17**) (0.29 g, 8.77 x 10^{-4} mol) and BHT (trace amount) were added to the reaction mixture and stirred for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] to yield a yellow liquid which formed a waxy solid after 3 days (0.23 g, 51%).

Transition temp. / ^{O}C : **Cr** 105 **I**.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	0.68 – 0.76 (10H, m), 1.28 – 1.37 (20H, m), 1.45 – 1.52 (4H, m),
	1.64 (4H, quint), 1.82 (4H, quint), 2.02 (4H, t), 2.28 (6H, s),
	$2.35 \; (4H, t), 4.00 \; (4H, t), 5.21 - 5.33 \; (8H, m), 5.72 - 5.74 \; (2H, m),$
	5.80 – 5.88 (4H, m), 6.83 (2H, d, J = 9.3 Hz), 7.20 (2H, d, J =
	3.7 Hz), 7.34 (2H, d, J = 3.6 Hz), 7.43 – 7.45 (4H, m),
	7.57 – 7.62 (4H, m), 7.67 (2H, d, J = 7.2 Hz).
IR v_{max}/cm^{-1} :	2927, 2853, 2361, 1736, 1605, 1540, 1505, 1469, 1294, 1252,
	1135, 1101, 929, 883, 795.
MS <i>m</i> / <i>z</i> (MALDI):	1128 (M ⁺), 1127 (M 100).
Combustion analysis:	

Expected:C 77.75%, H 8.04%, S 5.69%Obtained:C 78.00%, H 8.30%, S 5.40%

2,7-*bis*(5-{2-Methyl-4-[octyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (72)



A mixture of *bis*-2,7-[5-(4-hydroxy-2-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**69**) (0.25 g, 3.99 x 10⁻⁴ mol), K₂CO₃ (0.17 g, 0.0012 mol), KI (trace amount) and DMF (5 cm³) was heated (90 ^oC) and stirred overnight. 1-Bromooctane (0.08 g, 8.77 x 10⁻⁴ mol) was added to the reaction mixture and stirred for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH, to yield a yellow crystalline solid (0.26 g, 76%). Transition temp. /^oC: **Tg** 35 **Cr** 121 **N** 137 **I**.

¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.70 – 0.78 (10H, m), 0.90 (6H, t), 1.30 – 1.39 (20H, m), 1.82 (4H, quint), 2.02 (4H, t), 2.28 (6H, s), 4.00 (4H, t), 6.83 (2H, d, J = 9 Hz), 7.20 (2H, d, J = 3.7 Hz), 7.34 (2H, d, J = 3.9 Hz), 7.42 – 7.45 (4H, m), 7.57 – 7.62 (4H, m), 7.67 (2H, d, J = 7.6 Hz). IR v_{max}/cm⁻¹: 2924, 2879, 1605, 1540, 1505, 1467, 1294, 1134, 1029, 877, 795, 664. MS *m*/*z* (MALDI): 851, 850 (M⁺, M 100).

Expected:	C 80.42%, H 8.29%, S 7.53%
Obtained:	C 80.46%, H 9.58%, S 7.68%

2-(4-Methoxy-3-methylphenyl)thiophene (74)



Tetrakis(triphenylphosphine)palladium(0) (2.88 g, 2.48×10^{-3} mol) was added to a heated (90 °C) solution of 4-bromo-1-methoxy-2-methylbenzene (**73**) (10.00 g, 0.0498 mol), tributyl(thiophen-2-yl)stannane (18.54 g, 0.0498 mol) and DMF (160 cm³). The mixture was stirred overnight, allowed to cool, poured into water (200 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with saturated KF solution (200 cm³), brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a colourless liquid (7.82 g, 77%), which was used without further purification.

Purity: >99% (GC).

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	2.41 (3H, s), 3.84 (3H, s), 6.78 (1H, dd, J = 8.4, 2.8 Hz), 6.83 (1H,
	d, J = 2.8 Hz), 7.01 (1H, dd, J = 3.5, 1.1 Hz), 7.08 (1H, dd, J = 5.2,
	3.4 Hz), 7.31 (1H, dd, J = 5, 1.1 Hz), 7.34 (1H, d, J = 8.4 Hz).
IR v_{max}/cm^{-1} :	3071, 2999, 2955, 2834, 1607, 1570, 1537, 1494, 1464, 1435,
	1414, 1379, 1350, 1295, 1259, 1239, 1163, 1123, 1045, 963, 847,
	809, 697, 580, 452.
MS <i>m</i> / <i>z</i> (EI):	204 (M ⁺), 189, 173, 167, 149 (M 100), 128, 104, 84, 57.
Combustion analysis:	
Expected:	C 70.55%, H 5.92%, S 15.70%

Obtained: C 70.33%, H 6.09%, S 15.53%

Tributyl[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]stannane (75)



A solution of *n*-BuLi in hexanes (11.84 cm³, 2.5*M*, mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 2-(4-methoxy-3-methylphenyl)thiophene (**74**) (5.04 g, 0.0247 mol) in THF (50 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\circ}$ C, followed by the dropwise addition of tributyltin chloride (11.24 g, 0.0345 mol). The mixture was allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 x 100 cm³). The combined organic extracts were washed with water (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out.

Purity: >68% (GC). MS *m*/*z* (EI): 493 (M⁺), 491, 437, 436, 435, 381, 379, 325, 324, 323, 217, 173, 158, 128, 57.

2,7-bis[5-(4-Methoxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (76)



Tetrakis(triphenylphosphine)palladium(0) (0.44 g, 3.81×10^{-4} mol) was added to a heated (90 °C) solution of 2-bromo-7-iodo-9,9-dipropylfluorene (**21**) (1.75 g, 0.0038 mol), tributyl[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]stannane (**75**) (7.59 g, 0.0154 mol) and DMF (50 cm³). The mixture was stirred overnight, allowed to cool, poured into water (300 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with saturated aqueous KF (200 cm³), brine (2 x 250 cm³),

dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid (1.68 g, 67%). Transition temp. /^OC: **Cr** 157 **N** (125) **I**.

¹H NMR (CDCl₃)
$$\delta_{\text{H}}$$
: 0.74 (6H, t), 0.81 – 0.88 (4H, m), 2.02 (4H, t), 2.49 (6H, s),
3.85 (6H, s), 6.78 – 6.84 (6H, m), 7.00 (2H, d, J = 4.5 Hz),
7.40 (2H, d, J = 8.4 Hz), 7.59 – 7.72 (4H, m).
IR v_{max} /cm⁻¹: 2955, 2834, 1604, 1566, 1492, 1467, 1294, 1242, 1160, 1121,
1049, 865, 802, 721, 582, 451.
MS m/z (EI): 654 (M⁺), 537, 536, 494, 407, 406, 391, 368, 298, 247,
203, 152, 115.

2,7-*bis*[5-(4-Hydroxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (77)



Boron tribromide (2.58 g, 0.0103 mol) was added dropwise to a cooled (0 $^{\circ}$ C) solution of *bis*-2,7-[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**76**) (1.50 g, 0.0023 mol) in DCM (10 cm³). The reaction mixture was allowed to warm to RT and stirred overnight, poured into ice (300 cm³) and stirred for 1 h. The organic layer was separated and the aqueous layer extracted with DCM (3 x 200 cm³). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 2 : 1] to yield a pale yellow crystalline solid (1.23 g, 85%). Melting point /^OC: 171.

¹H NMR (CDCl₃) δ_{H} : 0.69 – 0.75 (10H, m), 2.02 (4H, t), 2.46 (6H, s), 4.74 (2H, s), 6.71 – 6.78 (6H, m), 7.00 (2H, d, J = 3.7 Hz), 7.29 – 7.37 (4H, m), 7.58 – 7.69 (4H, m).

IR
$$v_{max}/cm^{-1}$$
: 3306, 2952, 1603, 1577, 1454, 1289, 1239, 1161, 1005, 966, 862,
802, 654, 577, 451.
MS m/z (EI): 626 (M⁺), 555, 554, 378, 357, 356, 313, 278, 277, 187,
186 (M 100).

2,7-*bis*(5-{3-Methyl-4-[5-(1-vinylallyloxycarbonyl)pentyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (**78**)



A mixture of *bis*-2,7-[5-(4-hydroxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (77) (0.20 g, 3.05 x 10^{-4} mol), K₂CO₃ (0.15 g, 1.07 x 10^{-4} mol) and DMF (20 cm³) was heated (90 °C) overnight. Penta-1,4-dien-3-yl 6-bromohexanoate (29) (0.24 g, 9.16 x 10^{-4} mol) and BHT (trace amount) were added to the reaction mixture and heated at 90 °C for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] to yield a yellow liquid which formed a glassy solid after 2 days (0.19 g, 61%).

Transition temp. ^{O}C : **Cr** 1 **N** 16 **I**.

¹H NMR (CDCl₃) δ_{H} : 0.69 – 0.88 (10H, m), 1.23 – 1.28 (8H, m), 1.74 (4H, quint), 1.83 (4H, quint), 2.02 (4H, t), 2.47 (6H, s), 3.99 (4H, t), 5.23 – 5.33 (8H, m), 5.71 – 5.75 (2H, m), 5.81 – 5.89 (4H, m), 6.74 – 6.85 (6H, m), 6.99 (2H, d, J = 3.4 Hz), 7.34 – 7.38 (4H, m), 7.55 – 7.71 (4H, m). IR ν_{max} /cm⁻¹: 2951, 2867, 1736, 1604, 1566, 1500, 1471, 1379, 1296, 1241, 1169, 983, 930, 875, 801, 453.

MS *m/z* (MALDI): 986 (M⁺), 923, 921. Combustion analysis: Expected: C 76.64%, H 7.15%, S 6.50% Obtained: C 76.48%, H 7.37%, S 6.76%

2,7-*bis*(5-{3-Methyl-4-[10-(1-vinylallyloxycarbonyl)decanyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (**79**)



A mixture of *bis*-2,7-[5-(4-hydroxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**77**) (0.20 g, 3.19×10^{-4} mol), K₂CO₃ (0.15 g, 0.0011 mol) and DMF (20 cm³) was heated (90 °C) and stirred overnight. Penta-1,4-dien-3-yl 11-bromoundecanoate (**17**) (0.32 g, 9.57 x 10⁻⁴ mol) and BHT (trace amount) were added to the reaction mixture and heated at 90 °C for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] to yield a yellow liquid which formed a glassy solid after a number of days (0.23 g, 64%).

Transition temp. O C: **Cr** -10 **N** 9 **I**.

¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.69 – 0.73 (10H, m), 1.27 – 1.34 (20H, m), 1.46 (4H, quint), 1.64 (4H, quint), 1.79 (4H, quint), 2.01 (4H, t), 2.35 (4H, t), 2.48 (6H, s), 3.99 (4H, t), 5.22 – 5.33 (8H, m), 5.69 – 5.75 (2H, m), 5.80 – 5.89 (4H, m), 6.75 – 6.83 (6H, m), 7.00 (2H, d, J = 3.7 Hz), 7.34 – 7.37 (4H, m), 7.57 – 7.69 (4H, m). IR v_{max} /cm⁻¹: 2953, 2868, 1734, 1604, 1561, 1501, 1473, 1375, 1293, 1241, 1170, 981, 939, 875, 806, 453. MS *m*/*z* (MALDI): 1128, 1127 (M⁺, M 100), 1034, 879, 621.

Combustion analysis:

Expected:	C 77.75%, H 8.04%, S 5.69%
Obtained:	C 77.37%, H 8.08%, S 4.66%

2,7-*bis*(5-{3-Methyl-4-[octyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (80)



A mixture of *bis*-2,7-[5-(4-hydroxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (77) (0.20 g, 3.19 x 10^{-4} mol), K₂CO₃ (0.15 g, 0.0011 mol) and butanone (20 cm³) was heated (90 °C) and stirred overnight. 1-Bromooctane (0.18 g, 9.57 x 10^{-4} mol) was added to the reaction mixture and heated at 90 °C for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH, to yield a yellow crystalline solid (0.22 g, 74%).

Transition temp. / $^{\circ}$ C: **Tg** 17 **Cr** 111 **N** (80) **I**.

1 H NMR (CDCl ₃) δ_{H}	₁: 0.69 – 0.88 (10H, m), 0.90 (6H, t), 1.30 – 1.36 (20H, m),
	1.44 – 1.49 (4H, m), 1.75 – 1.80 (4H, m), 2.02 (4H, m), 2.47
	(6H, m), 3.99 (4H, t), 6.74 – 6.86 (6H, m), 7.00 (2H, d,
	J = 3.4 Hz), 7.29 – 7.39 (4H, m), 7.58 – 7.71 (4H, m).
IR v_{max}/cm^{-1} :	2922, 2853, 2361, 1605, 1564, 1492, 1469, 1384, 1296, 1242,
	1173, 1123, 1049, 867, 804, 699, 447.
MS <i>m</i> / <i>z</i> (MALDI):	850 (M ⁺), 738, 670, 637, 636, 447, 412, 359, 331, 300,
	277, 207, 186, 150, 120, 92.

Combustion analysis:

Expected:	C 80.42%, H 8.29%, S 7.53%
Obtained:	C 80.46%, H 8.24%, S 7.75%

2-(3,5-Dimethyl-4-methoxyphenyl)thiophene (82)



Tetrakis(triphenylphosphine)palladium(0) (2.67 g, 0.0023 mol) was added to a heated (90 °C) solution of 5-bromo-2-methoxy-1,3-dimethylbenzene (81) (10.00 g, 0.0465 mol), tributyl(thiophen-2-yl)stannane (19.09 g, 0.0511 mol) and DMF (100 cm³). The mixture was heated at 90 $^{\circ}$ C overnight, allowed to cool, poured into water (200 cm³) and the crude product extracted into diethyl ether $(3 \times 200 \text{ cm}^3)$. The combined organic extracts were washed with saturated KF solution (200 cm³), brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] to yield a colourless liquid (7.14 g, 70%), which solidified to form a waxy solid over a number of days. 44 – 45 (Lit. 46 – 47, MeOH).^[37] Melting Point /^OC: Purity: >98% (GC). ¹H NMR (CDCl₃) $\delta_{\rm H}$: 2.38 (6H, s), 3.79 (3H, s), 7.10 (1H, dd, J = 4.7, 3.9 Hz), 7.27 (2H, dd, J = 2.5, 1.4 Hz), 7.33 (2H, s). IR v_{max}/cm^{-1} : 2944, 1479, 1280, 1210, 1006, 890, 876, 740, 510. MS *m*/*z* (EI): 218 (M⁺, M 100), 205, 204, 203, 187, 175, 160, 142,

141, 115, 109, 91, 86.

Tributyl[5-(3,5-dimethyl-4-methoxyphenyl)thiophen-2-yl]stannane (83)



A solution of *n*-BuLi in hexanes (6.93 cm³, 2.5*M*, 0.0173 mol) was added dropwise to a cooled (-78 O C) solution of 2-(3,5-dimethyl-4-methoxyphenyl)thiophene (**82**) (3.15 g, 0.0144 mol) in THF (30 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 O C, followed by the dropwise addition of tributyltin chloride (6.57 g, 0.0202 mol). The mixture was allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 x 100 cm³). The combined organic extracts were washed with water (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out.

Purity: = 73% (GC).

MS *m*/*z* (EI): 508 (M⁺), 506, 505, 452, 451, 449, 448, 395, 393, 392, 339, 337, 336, 335, 334, 274, 231, 203, 187, 186, 172, 169, 153, 141, 115.

2,7-*bis*[5-(3,5-Dimethyl-4-methoxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (84).



Tetrakis(triphenylphosphine)palladium(0) (0.28 g, 2.46 x 10^{-4} mol) was added to a heated (90 °C) solution of 2-bromo-7-iodo-9,9-dipropylfluorene (**21**) (1.12 g, 0.0025 mol), tributyl[5-(3,5-dimethyl-4-methoxyphenyl)thiophen-2-yl]stannane (**83**) (5.00 g, 0.0098 mol) and DMF (40 cm³). The mixture was heated at 90 °C overnight, allowed to cool, poured into water (300 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with saturated KF solution (200 cm³),

brine $(2 \times 250 \text{ cm}^3)$, dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid (1.43 g, 85%).

Transition temp. / ^O C	: Tg 88 Cr 159 N (111) I .
1 H NMR (CDCl ₃) δ_{H}	: 0.68 – 0.76 (4H, m), 0.92 (6H, t), 2.02 (4H, t), 2.33 (12H, s),
	3.75 (6H, s), 7.23 (2H, d, J = 3.9 Hz), 7.32 (4H, s), 7.35 (2H, d, J =
	3.9 Hz), 7.58 – 7.63 (4H, m), 7.68 (2H, d, J = 7.9 Hz).
IR v_{max}/cm^{-1} :	2925, 1472, 1230, 1180, 1065, 1013, 834, 796, 490.
MS m/z (MALDI):	682 (M ⁺), 435, 434, 420, 419, 405, 404, 331, 312, 311,
	259, 258, 257, 138, 122, 121, 93, 92.

Combustion analysis:

Expected:	C 78.86%, H 6.46%, S 9.79%
Obtained:	C 78.88%, H 6.32%, S 10.26%

2,7-*bis*[5-(3,5-Dimethyl-4-hydroxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (85)



Boron tribromide (2.05 g, 0.0082 mol) was added dropwise to a cooled (0 $^{\circ}$ C) solution of *bis*-2,7-[5-(3,5-dimethyl-4-methoxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**84**) (1.40 g, 0.0021 mol) in DCM (10 cm³). The reaction mixture was allowed to warm to RT and stirred overnight, poured into ice (300 cm³) and stirred for 1 h. The organic layer was separated off and the aqueous layer extracted with DCM (3 x 200 cm³). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 2 : 1] to yield a pale yellow crystalline solid (1.08 g, 81%). Melting point /^oC: 233.

 1 H NMR (CDCl₃) δ_{H} : 0.70 – 0.73 (4H, m), 0.88 (6H, t), 2.01 – 2.04 (4H, m),

2.32 (12H, s), 4.70 (2H, s), 7.18 (2H, d, J = 3.9 Hz), 7.30 (4H, s), 7.34 (2H, d, J = 3.9 Hz), 7.60 - 7.62 (4H, m), 7.67 (2H, d, J = 8 Hz).IR v_{max}/cm⁻¹: 3432, 2952, 1471, 1239, 1195, 1165, 1067, 872, 798. MS *m*/*z* (EI): 655, 654 (M⁺, M 100).

2,7-*bis*(5-{3,5-Dimethyl-4-[5-(1-vinylallyloxycarbonyl)pentyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (**86**)



A mixture of *bis*-2,7-[5-(3,5-dimethyl-4-hydroxyphenyl)thiophen-2-yl]-9,9dipropylfluorene (**85**) (0.20 g, $3.05 \times 10^{-4} \text{ mol}$), K₂CO₃ (0.15 g, 0.0011 mol) and DMF (20 cm³) was heated (90 °C) overnight. Penta-1,4-dien-3-yl 6-bromohexanoate (**29**) (0.24 g, 9.16 x 10⁻⁴ mol) and BHT (trace amount) were added to the reaction mixture and heated at 90 °C for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] to yield a yellow liquid which formed a glassy solid over 2 days (0.19 g, 61%).

Transition temp. $^{\circ}$ C: **Tg** 22 **Cr** < -40 **SmC** 30 **I**.

¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.70 – 0.75 (4H, m), 0.87 (6H, t), 1.54 – 1.60 (8H, m), 1.76 (4H, quint), 1.85 (4H, quint), 2.02 (4H, t), 2.32 (12H, s), 3.79 (4H, t), 5.23 – 5.34 (8H, m), 5.73 – 5.75 (2H, m), 5.81 – 5.89 (4H, m), 7.23 (2H, d, J = 3.9 Hz), 7.31 (4H, s), 7.34 (2H, d, J = 3.9 Hz), 7.57 – 7.62 (4H, m), 7.67 (2H, d, J = 7.9 Hz). IR $\nu_{\rm max}/{\rm cm}^{-1}$: 2954, 2868, 1736, 1600, 1549, 1498, 1478, 1374, 1299, 1242,

1158, 991, 929, 877, 808, 449.MS m/z (MALDI):1015, 1014 (M⁺), 991, 571.Combustion analysis:Expected:C 76.88%, H 7.35%, S 6.32%Obtained:C 76.89%, H 7.38%, S 6.54%

2,7-*bis*(5-{3,5-Dimethyl-4-[octyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (87)



A mixture of *bis*-2,7-[5-(3,5-dimethyl-4-hydroxyphenyl)thiophen-2-yl]-9,9dipropylfluorene (**85**) (0.15 g, 2.29 x 10^{-4} mol), K₂CO₃ (0.11 g, 8.02 x 10^{-4} mol) and butanone (15 cm³) was heated (90 °C) overnight. 1-Bromooctane (0.13 g, 6.87 x 10^{-4} mol) was added to the reaction mixture and heated at 90 °C for a further 24 h. The cooled reaction mixture was poured into water (250 cm³) and the crude product extracted into diethyl ether (3 x 150 cm³). The combined organic extracts were washed with water (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH, to yield a yellow crystalline solid (0.16 g, 80%). Transition temp. /^OC: **Tg** 26 **Cr** 120 **N** (95) **I**.

¹H NMR (CDCl₃) δ_{H} : 0.70 – 0.74 (4H, m), 0.90 (6H, t), 1.31 – 1.39 (24H, m),

1.82 (4H, quint), 2.01 (4H, t), 2.34 (12H, s), 3.79 (4H, t), 7.21 (2H, d, J = 3.9 Hz), 7.31 (4H, s), 7.36 (2H, d, J = 3.9 Hz), 7.52 – 7.58 (4H, m), 7.67 – 7.74 (2H, m).

IR v_{max}/cm^{-1} : 2926, 2852, 1608, 1469, 1377, 1249, 1226, 1168, 1083, 871, 801, 494.

MS *m*/*z* (MALDI): 880, 879 (M⁺).

Combustion analysis:

Expected:	C 80.59%, H 8.48%, S 7.29%
Obtained:	C 80.30%, H 8.63%, S 7.09%

Cholestan-3β-yl 6-bromohexanoate (89)



DCC (0.0142 mol) was added to a stirred solution of 6-bromohexanoic acid (**88**) (3.02 g, 0.0142 mol), 3 β -cholestanol (6.60 g, 0.0170 mol) and DMAP (0.0170 mol) in DCM (50 cm³) at RT. The reaction mixture was stirred overnight. The white precipitate, (DCU), was filtered off and the filtrate concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM] to yield a white crystalline solid (6.49 g, 81%), which was used without further purification.

Purity: >99%. (GC).

¹H NMR (CDCl₃) δ_{H} : 0.64 (3H, s), 0.82 – 0.91 (12H, m), 0.97 – 1.40 (20H, m), 1.97 (17H, m), 2.29 (2H, t), 3.41 (2H, t), 4.67 – 4.71 (1H, m). IR v_{max} /cm⁻¹: 2932, 2851, 1733, 1470, 1418, 1387, 1319, 1241, 1208, 1184, 1095, 800, 721, 653. MS *m*/*z* (EI): 564 (M⁺), 562 (M⁺), 481, 370, 215 (M 100), 201, 173, 147, 121, 107, 95, 81, 55, 43. 2,7-*bis*(5-{4-[5(Cholestan-3β-yl-oxycarbonyl)pentyloxy]3-methylphenyl}thien-2-yl)-9,9dipropylfluorene (**90**)



A mixture of *bis*-2,7-[5-(4-hydroxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**77**) (0.20 g, 3.05 x 10^{-4} mol), K₂CO₃ (0.15 g, 0.0011 mol), cholestan-3 β -yl 6-bromohexanoate (**89**) (0.40 g, 7.02 x 10^{-4} mol) and butanone (10 cm³) was heated under reflux overnight. The cooled reaction mixture was concentrated under reduced pressure and the crude product was purified *via* column chromatography [silica gel, hexane : ethyl acetate, 4 : 1] and recrystallisation from DCM/EtOH to yield a yellow crystalline solid (0.38 g, 72%).

Transition temp. / O C: **T**_g 60 **Cr** 124 **N**^{*} 160 **I**.

¹ H NMR (CDCl ₃) δ_1	H: 0.65 (6H, s), 0.70 – 0.74 (4H, m), 0.82 – 0.91 (30H, m), 0.97 –
	1.40 (40H, m), 1.97 (34H, m), 2.01 (4H, t), 2.27, (4H, m), 2.49
	(6H, s), 3.99 (4H, t), 4.66 – 4.74 (2H, m), 6.75 – 6.83 (6H, m),
	7.00 (2H, d, J = 3.7 Hz), 7.34 – 7.37 (4H, m), 7.57 – 7.69 (4H, m)
IR v_{max}/cm^{-1} :	2931, 1730, 1604, 1469, 1240, 1172, 1045, 796.
MS m/z (MALDI):	1596 (M ⁺ , M 100), 1574, 1472, 1408, 1407,
	1406, 1405, 1388, 1387, 1386, 1350, 1349, 1348, 1347, 1320,
	1319.

Expected:	C 80.50%, H 9.47%, S 4.02%
Obtained:	C 80.63%, H 9.64%, S 3.85%

2-[4-(Octyloxy)phenyl]thiophene (91)



Tetrakis(triphenylphosphine)palladium(0) (2.03 g, 0.0018 mol) was added to a heated (90 ^oC) solution of 1-bromo-4-octyloxybenzene (20.00 g, 0.0701 mol), tributyl(thiophen-2vl)stannane (26.17 g, 0.0701 mol) and DMF (75 cm³). The mixture was stirred for 24 h, allowed to cool and poured into saturated aqueous KF (150 cm³). The crude product was extracted into DCM (3 x 200 cm³). The combined organic extracts were washed with brine $(2 \times 100 \text{ cm}^3)$, dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from EtOH, to yield a white crystalline solid (13.42 g, 66%). 69 – 72 (Lit. 68 – 70, EtOH).^[30] Melting Point $/^{O}C$: ¹H NMR (CDCl₃) δ_H: 0.89 (3H, t), 1.23 – 1.36 (10H, m), 1.43 – 1.48 (2H, m), 1.79 (2H, quint), 3.98 (2H, t), 6.90 (2H, d, J = 8.7 Hz), 7.04 (1H, dd, J = 5, 3.6 Hz), 7.19 – 7.21 (2H, m), 7.53 (2H, d, J = 8.7 Hz). IR v_{max}/cm^{-1} : 2923, 1606, 1572, 1531, 1501, 1435, 1393, 1270, 1251, 1169, 1086, 1026, 814, 681, 537, 487. MS *m*/*z* (EI): 288 (M⁺), 279, 213, 210, 178, 177, 176 (M 100), 167,

149, 131, 115, 84.

Combustion analysis:

Expected:	C 74.95%, H 8.39%, S 11.12%
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Obtained: C 74.95%, H 8.61%, S 10.97%

Tributyl{5-[4-(octyloxy)phenyl]thiophen-2-yl}stannane (92)



A solution of *n*-BuLi in hexanes (16.64 cm³, 2.5*M*, 0.0416 mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 2-[4-(octyloxy)phenyl]thiophene (**91**) (10.00 g, 0.0347 mol) in THF (150 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\circ}$ C, followed by the dropwise addition of tributyltin chloride (13.54 g, 0.0416 mol). The mixture was allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 x 100 cm³), washed with water (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out. Purity: 79% (GC). MS *m*/*z* (EI): 576 (M⁺), 575.

2,7-Dibromo-9,9-dipropylfluorene (94)



Powdered potassium hydroxide (7.37 g, 0.1313 mol) was added in small portions to a solution of 2,7-dibromofluorene (10.00 g, 0.0309 mol), 1-bromooctane (0.15 g, 0.0679 mol), potassium iodide (0.51 g, 0.0031 mol) and DMSO (200 cm³) at RT. The deep purple mixture was stirred for 3 h then poured into water (200 cm³). The crude product extracted into hexane (4 x 50 cm³). The combined organic extracts were washed with brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane] and recrystallisation from EtOH to yield white needles (9.74 g, 77%). Melting Point /^OC: 136 – 138 (Lit. 137 – 137.5, Hexane). ^[6] Purity: >99% (GC). ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.66 (10H, m), 1.90 (4H, t), 7.45 (4H, m), 7.51 (2H, d, J = 1 Hz).

IR v_{max}/cm^{-1} :	2954, 1574, 1451, 1416, 1270, 1238, 1111, 1057, 1006, 931, 878,
	808, 749.
MS <i>m/z</i> (EI):	411 (M ⁺), 409 (M ⁺), 365, 336, 323, 284, 269, 256, 248, 202, 189,
	176, 163.

2,7-*bis*{5-[4-(Octyloxy)phenyl]thiophen-2-yl}-9,9-dipropylfluorene (95)



Tetrakis(triphenylphosphine)palladium(0) (0.18 g, 1.53×10^{-4} mol) was added to a heated (90 °C) solution of 2,7-dibromo-9,9-dipropylfluorene (94) (1.25 g, 0.0031 mol), tributyl{5-[4-(octyloxy)phenyl]thiophen-2-yl}stannane (92) (5.31 g, 0.0092 mol) and DMF (15 cm³). The mixture was stirred overnight, allowed to cool, poured into water (300 cm^3) and the crude product extracted into diethyl ether $(3 \times 200 \text{ cm}^3)$. The combined organic extracts were washed with saturated aqueous KF (200 cm^3), brine ($2 \times 250 \text{ cm}^3$), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid (1.40 g, 56%). Transition temp. /^OC: Cr 166 N 173 I (Lit. Cr 166 N 174 I). ^[11] ¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.89 (3H, t), 1.23 – 1.36 (10H, m), 1.43 – 1.48 (2H, m), 1.79 (2H, quint), 1.90 (4H, t), 3.99 (2H, t), 6.93 (4H, d, J = 9 Hz), 7.20 (2H, d, J = 4Hz), 7.33 (2H, d, J = 4Hz), 7.57 (2H, s), 7.57 (4H, d, J = 9 Hz), 7.60 (2H, dd, J = 8, 1 Hz), 7.67 (2H, d, J = 8 Hz). IR v_{max}/cm^{-1} : 2953, 2922, 2851, 2359, 2344, 1467, 1376, 1248, 1225, 1167, 1082, 956, 870, 800, 760. MS m/z (MALDI): 823, 822 (M⁺). Calculated : C 80.24%, H 8.08%, S 7.79%

Obtained : C 80.42%, H 8.18%, S 7.81%

2,7-*bis*[5-(4-Hydroxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (96)



Boron tribromide (1.51 g, 0.0060 mol) was added dropwise to a cooled (0 $^{\circ}$ C) solution of 2,7-*bis*(5-{4-[octyloxy]phenyl}thiophen-2-yl)-9,9-dipropylfluorene (**95**) (1.10 g, 0.0013 mol) in DCM (15 cm³), allowed to cool to RT, stirred overnight and poured into ice (300 cm³). The crude product was extracted into DCM (5 x 150 cm³). The combined organic layers were washed with aqueous hydrochloric acid (10%, 100 cm³), brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 3 : 2], to yield a yellow crystalline solid (0.69 g, 86%).

Transition temp. /⁰C: Cr 279 N (257) I (Lit. Cr 279 N (258) I). [11]

¹H NMR (CDCl₃) $\delta_{\rm H}$: 0.70 – 0.78 (10H, m), 2.00 – 2.05 (4H, m), 4.95 (2H, s), 6.87 (4H, d, J = 8.7 Hz), 7.20 (2H, d, J = 3.6 Hz), 7.33 (2H, d, J = 3.6 Hz), 7.55 (4H, d, J = 8.7 Hz), 7.57 (2H, d, J = 1.6 Hz), 7.60 (2H, dd, J = 7.9, 1.7 Hz), 7.68 (2H, d, J = 7.9 Hz). IR v_{max}/cm⁻¹: 3367, 2953, 2927, 2360, 1699, 1607, 1510, 1474, 1453, 1374, 1234, 1172, 1104, 831, 797. MS *m*/*z* (EI): 598 (M⁺), 526, 513, 299, 263 (M 100), 248, 171, 149, 122, 105, 97, 77, 71.

11-Bromoundecyl methacrylate (99)



A solution of 11-bromoundecan-1-ol (**97**) (5.00 g, 0.0199 mol), DCC (0.0239 mol), DMAP (0.0199 mol) methacrylic acid (**98**) (1.71 g, 0.0239 mol), BHT (trace amount) and DCM (50 cm³) was stirred at RT overnight. The white precipitate was filtered off, the filtrate concentrated under reduced pressure and the crude product purified *via* column chromatography [silica gel, hexane : DCM, 2 : 1] to yield a colourless liquid (3.74 g, 59%).

Purity: > 98% (GC). ¹H NMR (CDCl₃) δ_{H} : 1.28 – 1.47 (14H, m), 1.65 (2H, quint), 1.85 (2H, quint), 1.94 (2H, quint), 3.41 (2H, t), 4.14 (2H, t), 5.55 (1H, quint), 6.10 (1H, quint). IR v_{max} /cm⁻¹: 2954, 2868, 1732, 1640, 1499 1380, 1254, 1112. MS *m*/*z* (EI): 320, 318 (M⁺), 293, 277, 276, 232, 203, 164, 150, 148, 135, 123, 111, 87.

2,7-*bis*{5-[4-(11-Methacryloylundecyloxy)phenyl]thiophen-2-yl}-9,9-dipropylfluorene (100)



A mixture of 2,7-*bis*[5-(4-hydroxyphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**96**) (0.50 g, 8.35 x 10^{-4} mol), K₂CO₃ (0.35 g, 0.0025 mol), KI (0.01 g, 8.35 x 10^{-5} mol), 11bromoundecyl methacrylate (**99**) (0.67 g, 0.0021 mol), DMF (10 cm³) and BHT (trace amount) was heated (80 °C) overnight. The cooled reaction mixture was poured into

water (300 cm³) and the crude product extracted into DCM (3 x 100 cm³). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : ethyl acetate, 95 : 5] and recrystallisation from EtOH/DCM to yield yellow crystalline needles (0.41 g, 46%).

Transition temp. / O C: **T**_g 6 **Cr** 76 **N** 96 **I**.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$: 0.69 – 0.74 (4H, m), 1.25 (6H, t), 1.30 – 1.38 (24 H, m), 1.67
	(4H, quint), 1.80 (4H, quint), 1.95 (6H, t), 2.02 (4H, m), 4.00
	(4H, t), 4.14 (4H, t), 5.55 (2H, quint), 6.10 (2H, quart), 6.93 (4H,
	d, J = 9 Hz), 7.20 (2H, d, J = 3.6 Hz), 7.34 (2H, d, J = 3.6 Hz),
	7.56 – 7.69 (10H, m).
IR v_{max}/cm^{-1} :	2918, 2850, 1716, 1604, 1508, 1471, 1288, 1252, 1178, 1158,
	1031, 828, 801, 492.
MS <i>m</i> / <i>z</i> (MALDI):	1075 (M ⁺ , M 100), 815, 551.
Combustion analysis	:
Expected:	C 77.05%, H 8.06%, S 5.96%

C 77.30%, H 8.36%, S 6.06%

2-Bromo-7-iodo-9,9-dipentylfluorene (101)



Powdered potassium hydroxide (6.43 g, 0.1146 mol) was added in small portions to a solution of 2-bromo-7-iodofluorene (10.00 g, 0.0270 mol), 1-bromopentane (8.96 g, 0.0593 mol), potassium iodide (0.45 g, 0.0027 mol) and DMSO (200 cm³) at RT. The deep purple mixture was stirred for 3 h then poured into water (200 cm³) and the crude product extracted into hexane (4 x 50 cm³). The combined organic extracts were washed with brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane] and recrystallisation from EtOH to yield white needles (9.74 g, 71%).

Obtained:

Melting Point / ^O C:	64 – 66.
¹ H NMR (CDCl ₃) δ_{H}	: 0.66 (6H, t), 0.74-0.81 (12H, m), 1.89 (4H, t), 7.38-7.52 (4H, m),
	7.63-7.66 (2H, m)
IR v_{max}/cm^{-1} :	2945, 2920, 2863, 2832, 1890, 1734, 1592, 1570, 1451, 1448, 1429,
	1399, 1368, 1245, 1208, 1144, 1097, 1050, 1006, 939,870, 809,
	750, 741, 669, 667, 494, 423.
MS <i>m/z</i> (EI):	512 (M ⁺), 510 (M ⁺), 329, 327, 326, 251, 250.
Combustion analysis	::
Expected:	C 54.03%, H 5.52%
Obtained:	C 54.30%, H 5.70%

2-(7-Bromo-9,9-dipentylfluoren-2-yl)-5-[4-(octyloxy)phenyl]thiophene (102)



Tetrakis(triphenylphosphine)palladium(0) (0.57 g, 4.9×10^{-4} mol) was added to a heated (90 $^{\circ}$ C) solution of 2-bromo-7-iodo-9,9-dipentylfluorene (**101**) (5.00 g, 0.0098 mol), tributyl{5-[4-(octyloxy)phenyl]thiophen-2-yl}stannane (**92**) (16.94 g, 0.0293 mol) and DMF (100 cm³). The mixture was heated at 90 $^{\circ}$ C overnight, allowed to cool, poured into a saturated KF solution (300 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with brine (2 x 250 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid (5.34 g, 81%).

Melting Point / $^{\mathrm{O}}\mathrm{C}$: 128 – 129.

¹H NMR (CDCl₃)
$$\delta_{\text{H}}$$
: 0.58 – 0.72 (11H, m), 0.84 – 0.89 (22H, M), 1.06 (2H, quint),
1.84 (2H, quint), 1.94 – 1.98 (4H, m), 6.92 (2H, d, J = 9 Hz),
7.19 (1H, d, J = 3.6 Hz), 7.32 (1H, d, J = 3.7 Hz),
7.52 – 7.65 (8H, m).
IR $v_{\text{max}}/\text{cm}^{-1}$: 2926, 2854, 1605, 1543, 1510, 1460, 1404, 1287, 1249, 1178,

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	1128, 1042, 998, 879, 828, 795, 726, 662, 498.
MS <i>m/z</i> (EI):	$672,670 ({ m M}^{\scriptscriptstyle +}),596,595,593,559,557,542,521,453,451,$
	430, 417, 408, 400, 386, 372, 365, 352, 351, 337, 321, 306, 287,
	214, 195, 138, 121.

Combustion analysis:

Expected:	C 73.30%, H 7.65%, S 4.77%
Obtained:	C 73.58%, H 7.92%, S 4.50%

2,7-Dibromo-9,9-dioctylfluorene (103)



Powdered potassium	hydroxide (7.36 g, 0.1312 mol) was added in small portions to a
solution of 2,7-dibro	mofluorene (10.00 g, 0.0309 mol), 1-bromooctane (13.10 g, 0.0679
mol), potassium iodi	de $(0.51 \text{ g}, 0.0031 \text{ mol})$ and DMSO (200 cm^3) at RT. The deep
purple mixture was s	stirred for 3 h then poured into water (200 cm ³) and the crude product
extracted into hexand	$(4 \times 50 \text{ cm}^3)$. The combined organic extracts were washed with
brine (200 cm ³), drie	ed (MgSO ₄), filtered and concentrated under reduced pressure.
Purification was carr	ied out via column chromatography [silica gel, hexane] and
recrystallisation fron	n EtOH to yield white needles (10.66 g, 63%).
Melting Point / ^O C:	48 – 49 (Lit. 46 – 47, EtOH). ^[38]
Purity:	>98% (GC).
¹ H NMR (CDCl ₃) $\delta_{\rm H}$	1: 0.64 – 0.70 (10H, m), 1.43 – 1.47 (20H, m), 1.92 (4H, t),
	7.45 (4H, m), 7.51 (2H, d, J = 1 Hz).
IR v_{max}/cm^{-1} :	2926, 1568, 1464, 1448, 1394, 1253, 1132, 1053, 1001, 881, 810,
	750, 722, 658, 510, 417.
MS <i>m/z</i> (EI):	$548 (M^{+}), 546 (M^{+}), 544 (M^{+}), 365, 336, 323, 284, 248, 202, 175,$
	163.

2,7-*bis*(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**104**)



A solution of *n*-BuLi in hexanes (18.23 cm³, 2.5*M*, 0.0456 mol) was added dropwise to a cooled (-78 $^{\text{O}}$ C) solution of 2-bromo-7-iodo-9,9-dioctylfluorene (**103**) (5.00 g, 0.0091 mol) in THF (50 cm³). The mixture was maintained at - 78 $^{\text{O}}$ C for 1 h then a solution of 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (3.73 g, 0.0201 mol) in THF (10 cm³) added dropwise and the solution allowed to warm to RT and stirred overnight. The reaction mixture was poured into water (200 cm³) and the crude product extracted into diethyl ether (3 x 100 cm³). The combined organic extracts were washed with brine (200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was purified *via* recrystallisation from DCM/MeOH to yield white crystalline needles (2.42 g, 41%).

Melting Point /^OC: 129 – 130 (Lit. 128 – 130, THF/MeOH). ^[39]

¹ H NMR (CDCl ₃) $\delta_{\rm H}$	_I : 0.54 (4H, quint), 0.80 (6H, t), 1.10 (24H, m), 1.39 (24H, s), 1.99
	(4H, quint), 7.71 – 7.74 (4H, m), 7.80 (2H, dd, J = 7.4, 0.8 Hz).
IR v_{max}/cm^{-1} :	2977, 2952, 2927, 2855, 1609, 1578, 1476, 1427, 1350, 1311,
	1256, 1143, 1118, 1080, 963, 862, 827, 700, 634, 416.
MS <i>m/z</i> (EI):	642 (M ⁺), 531, 530, 529 (M 100), 471, 429, 417, 416,
	359, 331, 303, 249, 231, 230, 205, 204, 179, 121.

Expected:	C 76.64%, H 10.04%
Obtained:	C 76.38%, H 10.33%
2,7-*bis*{7-[5-(4-(Octyloxy)phenyl]thiophen-2-yl}-9,9-dipentylfluoren-2-yl)-9,9-dioctylfluorene (**105**)



Tetrakis(triphenylphosphine)palladium(0) (0.09 g, 7.78 x 10^{-5} mol) was added to a heated (90 °C) solution of 2,7-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9dioctylfluorene (**104**) (1.00 g, 0.0016 mol), 2-(7-bromo-9,9-dipentylfluoren-2-yl)-5-[4-(octyloxy)phenyl]thiophene (**102**) (2.61 g, 0.0039 mol) potassium phosphate (0.99 g, 0.0047 mol) and DMF (40 ml). The mixture was stirred overnight, allowed to cool, poured into water (300 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with brine (2 x 250 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid (1.53 g, 62%).

Transition temp. / ^{O}C : T_g 41 Cr 131 N 166 I.

 1 H NMR (CDCl₃) δ_{H} : 0.66 (6H, t), 0.73 (12H, t), 0.83 (6H, t), 0.98 – 1.40 (48H, m),

	1.24 - 1.33 (24H, m), 1.75 (4H, quint), 1.96 - 2.07 (12H, m), 3.95
	(4H, t), 6.86 (4H, d, J = 8.7 Hz), 7.15 (2H, d, J = 3.4 Hz), 7.28 (2H,
	d, J = 3.4 Hz), 7.50 – 7.62 (16H, m), 7.66 – 7.78 (6H, m).
IR v_{max}/cm^{-1} :	2926, 2855, 1599, 1515, 1468, 1278, 1245, 1178, 1033, 889, 838,
	791, 758, 491.
MS <i>m/z</i> (MALDI):	1572 (M ⁺ , M100), 1571, 771, 233, 120.

Combustion analysis:

Expected:	C 84.78%, H 9.10%, S 4.08%
Obtained:	C 84.89%, H 9.00%, S 3.74%

2-[9,9-Dipentyl-7-(thiophen-2-yl)fluoren-2-yl)-5-[4-(octyloxy)phenyl]thiophene (106)



Tetrakis(triphenylphosphine)palladium(0) (0.23 g, 1.95×10^{-4} mol) was added to a heated (90 °C) solution of 2-(7-bromo-9,9-dipentylfluoren-2-yl)-5-[4-

(octyloxy)phenyl]thiophene (**102**) (2.60 g, 0.0039 mol), tributyl(thiophen-2-yl)stannane (1.59 g, 0.0043 mol) and DMF (20 cm³). The mixture was stirred overnight, allowed to cool, poured into a saturated KF solution (300 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with brine (2 x 250 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 2 : 1] and recrystallisation from DCM/EtOH to yield a yellow crystalline solid (2.30 g, 88%). Melting Point /^OC: 138 – 140.

¹H NMR (CDCl₃)
$$\delta_{\rm H}$$
: 0.71 (3H, t), 0.90 (6H, t), 1.04 – 1.11 (12H, m), 1.27 – 1.33
(10H, M), 1.81 (2H, quint), 2.00 – 2.04 (4H, m), 4.00 (2H, t), 6.93
(2H, d, J = 8.7 Hz), 7.11 (1H, dd, J = 5, 3.7 Hz), 7.21 (1H, d,
J = 3.6 Hz), 7.30 (1H, d, J = 5, 1.1 Hz), 7.34 (1H, d, J = 4 Hz), 7.38
(1Hz, dd, J = 3.6, 1.1 Hz), 7.56 – 7.62 (6H, m), 7.68 (2H, d,
J = 7.9 Hz).
IR v_{max}/cm⁻¹: 2890, 2728, 1634, 1510, 1474, 1391, 1298, 1136, 1101, 1044,1021,
999, 850, 757, 664, 465.
MS *m*/*z* (EI): 674 (M⁺, M100), 603, 562, 561, 435, 434, 433, 421,
281, 211, 112.

Tributyl[5-(7-{5-(4-(octyloxy)phenyl]thiophen-2-yl}-9,9-dipentylfluoren-2-yl)thiophen-2-yl]stannane (**107**)



A solution of *n*-BuLi in hexanes (1.35 cm³, 2.5*M*, 0.0034 mol) was added dropwise to a cooled (-78 $^{\text{O}}$ C) solution of 2-[9,9-dipentyl-7-(thiophen-2-yl)fluoren-2-yl)-5-[4- (octyloxy)phenyl]thiophene (**106**) (2.25 g, 0.0033 mol) in THF (150 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\text{O}}$ C, followed by the dropwise addition of tributyltin chloride (1.19 g, 0.0037 mol). The mixture was allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 x 100 cm³). The combined organic extracts were washed with water (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out. MS *m*/*z* (MALDI): 964 (M⁺), 963, 962, 950, 948, 946, 924, 922, 916, 914, 908, 906, 740 (M 100), 675.

5,5'-*bis*{7-[5-(4-(Octyloxy)phenyl]thiophen-2-yl}-9,9-dipentylfluoren-2-yl)-2,2'bithiophene (**108**)



Tetrakis(triphenylphosphine)palladium(0) (0.06 g, 5.19×10^{-5} mol) was added to a heated (90 ^oC) solution of tributyl[5-(7-{5-(4-(octyloxy)phenyl]thiophen-2-yl}-9,9-dipentylfluoren-2-yl)thiophen-2-yl]stannane (**107**) (1.00 g, 0.0010 mol), copper iodide (0.02 g, 1.04×10^{-4} mol) and DMF (20 cm³). The mixture was stirred overnight, allowed to cool, poured into a saturated KF solution (100 cm³) and the crude product extracted into diethyl ether (3 x 200 cm³). The combined organic extracts were washed with brine (2 x 250 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure.

Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 3 : 1] and recrystallisation from DCM/EtOH to yield a yellow crystalline solid (0.42 g, 61%). Transition temp. O C: **T**_g 54 **Cr** 206 **N** 214 **I**.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$	_H : 0.70 – 0.74 (8H, m), 0.87 (12H, t), 0.91 (6H, t), 1.24 – 1.33
	(36H, m), 1.81 (4H, quint), 2.01 – 2.06 (8H, m), 4.00 (4H, t),
	6.93 (4H, d, J = 9 Hz), 7.21 (2H, d, J = 3.6 Hz), 7.24 (2H, d, J =
	3.6 Hz), 7.34 (4H, t, J = 3.6 Hz), 7.56 – 7.63 (12H, m),
	7.70 (4H, dd, J = 7.9, 2 Hz).
IR v_{max}/cm^{-1} :	2925, 2855, 1606, 1510, 1469, 1278, 1249, 1177, 1029, 881, 828,
	791, 752, 490.
MS m/z (MALDI):	1348 (M ⁺ , M100), 1347, 1239, 1075, 876.
Combustion analysis	5:
Expected:	C 80.19%, H 7.93%, S 9.51%
Obtained:	C 80.04%, H 8.22%, S 9.39%

2,3-*bis*(4-Bromophenyl)fumaronitrile (**110**)



A cooled (-78 °C) solution of sodium methoxide (5.79 g, 0.1070 mol) in methanol (40 cm³) was added dropwise over 30 min to a cooled (-78 °C) solution of iodine (12.95 g, 0.0510 mol), 4-bromophenylacetonitrile (10.00 g, 0.0510 mol) and diethyl ether (200 cm³). The mixture was allowed to warm to 0 °C and stirred for 4 h maintaining the temperature at 0 °C. The mixture was acidified by the addition of aqueous hydrochloric acid (3%, v/v, 150 cm³) and the resulting precipitate filtered off on a sinter. The crude product was washed on the sinter with water (3 x 200 cm³), aqueous sodium metabisulphite (5%, 3 x 200 cm³), water (4 x 300 cm³) and EtOH (2 x 100 cm³). Purification was carried out by recrystallisation from EtOH to yield a pale yellow crystalline solid (8.79 g, 89%).

Purity: >99% (GC)

Melting Point / ^O C:	214 – 215 (Lit. 213, benzene). ^[40]
¹ H NMR (CDCl ₃) δ_{H} :	7.70 (8H, d, $J = 2Hz$).
IR v_{max}/cm^{-1} :	2883, 2538, 2479, 2391, 2234, 2097, 2038, 1960, 1882, 1798,
	1671, 1636, 1582, 1440, 1396, 1303, 1249, 1165, 1121, 999, 920,
	856, 817, 665.
MS <i>m</i> / <i>z</i> (EI):	390, 388 (M ⁺), 308, 307, 230, 229, 228 (M 100), 201,
	200, 175, 114.
Combustion englassion	

Combustion analysis:

Expected:	C 49.52%, H 2.08%, N 7.22%
Obtained:	C 50.22%, H 1.85%, N 7.11%

2,3-*bis*{4-[5-(7-{5-[4-(Octyloxy)phenyl]thiophen-2-yl}-9,9-dipentylfluoren-2-yl)thiophen-2-yl]phenyl}fumaronitrile (**111**)



Tetrakis(triphenylphosphine)palladium(0) (0.02 g, 1.73×10^{-5} mol) was added to a heated (90 $^{\circ}$ C) solution of tributyl[5-(7-{5-(4-(octyloxy)phenyl]thiophen-2-yl}-9,9-dipentylfluoren-2-yl)thiophen-2-yl]stannane (**107**) (2.45 g, 0.0026 mol) 2,3-bis(4-bromophenyl)fumaronitrile (**110**) (0.20 g, 0.0005 mol) and DMF (30 cm³). The mixture was heated at 90 $^{\circ}$ C overnight, allowed to cool, poured into a saturated KF solution (100 cm³) and the crude product extracted into DCM (3 x 200 cm³). The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 4 : 1] and recrystallisation from DCM/EtOH to yield a red crystalline solid (0.38 g, 81%).

Transition temp. / $^{\circ}$ C: T_g 77 Cr 180 N 246 I.

¹H NMR (CDCl₃) δ_{H} : 0.70 (12H, t), 0.88 (6H, t), 1.05 – 1.08 (12H, m), 1.24 – 1.35 (14H, m), 1.79 (4H, quint), 2.00 – 2.05 (8H, m), 4.00 (4H, t), 6.90

	– 6.98 (6H, m), 7.38 – 7.42 (2H, m), 7.46 – 7.70 (20H, m),
	7.80 (4H, d, J = 9 Hz), 7.92 (4H, d, J = 8.6 Hz).
IR v_{max}/cm^{-1} :	2924, 2853, 1601, 1542, 1509, 1469, 1449, 1280, 1248, 1176,
	1027, 883, 829, 797.
MS <i>m</i> / <i>z</i> (MALDI):	1576 (M ⁺), 1575, 1574, 816.
Combustion analysis:	
Expected:	C 80.77%, H 7.29%, N 1.78%, S 8.14%
Obtained:	C 80.66%, H 7.58%, N 1.91%, S 7.96%

2-Bromo-7-iodo-9,9-*di*(2-ethylhexyl)fluorene (**112**)



Powdered KOH (9.64 g, 0.1718 mol) was added in small portions over 30 min to a stirred solution of 2-bromo-7-iodofluorene (15.00 g, 0.0404 mol), 1-bromo-2-ethylhexane (17.18 g, 0.0889 mol), potassium iodide (0.67 g, 0.0014 mol) and DMSO (150 cm³) at RT. The mixture was stirred at RT for 2 h, then poured into water and the crude product extracted into hexane ($3 \times 250 \text{ cm}^3$). The combined organic extracts were washed with brine ($2 \times 200 \text{ cm}^3$), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane] to yield a colourless waxy oil (14.32 g, 59%).

Purity: >97% (GC).

¹ H NMR (CDCl ₃) $\delta_{\rm H}$: 0.46 – 0.56 (16H, m), 0.70 – 0.92 (14H, m), 1.90 – 1.96 (4H, m),
	7.38 – 7.45 (3H, m), 7.51 (1H, d, J = 8.7 Hz), 7.63 – 7.65 (2H, m).
IR v_{max}/cm^{-1} :	2926, 1568, 1464, 1448, 1394, 1253, 1132, 1053, 1001, 881, 810,
	750, 722, 658, 510, 417.
MS <i>m</i> / <i>z</i> (EI):	596, 595, 594 (M ⁺ , M100), 436, 371, 339, 323, 256, 243,
	215, 202, 176, 113.

2-[7-Bromo-9,9-di(2-ethylhexyl)fluoren-2-yl]-5-[4-(octyloxy)phenyl]thiophene (113)



Tetrakis(triphenylphosphine)palladium(0) (0.49 g, 4.20 x 10^{-4} mol) was added to a heated (90 °C) solution of 2-bromo-7-iodo-9,9-*di*(2-ethylhexyl)fluorene (**112**) (5.00 g, 0.0084 mol), tributyl{5-[4-(octyloxy)phenyl]thiophen-2-yl}stannane (**92**) (7.28 g, 0.0126 mol) and DMF (50 cm³). The mixture was stirred for 24 h, allowed to cool, poured into saturated aqueous KF (200 cm³) and the crude product extracted into diethyl ethyl acetate (3 x 100 cm³). The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid (4.31 g, 70%). Melting Point /^oC: 31 – 33.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$	2 0.52 (12H, t), 0.63 – 0.91 (26H, m), 1.30 – 1.35 (6H, m), 1.42 –
	1.51 (4H, m), 1.80 (2H, quint), 2.02 (4H, t), 3.99 (2H, t), 6.92 (2H,
	d, J = 8.7 Hz), 7.19 (1H, d, J = 3.9 Hz), 7.26 – 7.31 (4H, m), 7.58
	(4H, t, J = 8.4, 8.1 Hz), 7.68 (2H, d, J = 8.4 Hz).
IR v_{max}/cm^{-1} :	2921, 2844, 1601, 1559, 1510, 1439, 1403, 1291, 1234, 1177,
	1136, 1040, 998, 877, 828, 790, 723, 662, 497.
MS <i>m</i> / <i>z</i> (EI):	756 (M ⁺), 754 (M ⁺), 679, 678, 677, 676 (M 100), 564, 563,
	466, 465, 464, 451, 417, 365, 354, 353, 352, 351, 323.

2-[9,9-*di*(2-Ethylhexyl)-7-(4-nitrophenyl)fluoren-2-yl]-5-[4-(octyloxy)phenyl]thiophene (**114**)



A solution of 2-[7-bromo-9,9-di(2-ethylhexyl)fluoren-2-yl]-5-[4-

(octyloxy)phenyl]thiophene (**113**) (4.00 g, 0.0054 mol) in THF (40 cm³) was slowly added dropwise to a mixture of Mg (0.14 g 0.0060 mol, I₂ (trace amount) and THF (10 cm³). Once added the mixture was slowly brought to reflux and heated under reflux for a further 3 h until no Mg metal was present. The prepared Grignard reagent was transferred dropwise to a mixture of 1-bromo-4-nitrobenzene (1.20 g, 0.0060 mol) P(ddppf)Cl₂ (0.12 g, 1.63 x 10⁻⁴ mol) and THF (10 cm³). The mixture was heated under reflux overnight, allowed to cool poured into water (200 cm³) and extracted into DCM (3 x 100 cm³). The combined organic extracts were washed with aqueous hydrochloric acid (10%, 100 cm³), brine (2 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM] and recrystallisation from EtOH to yield orange needles (1.84 g, 43%).

Melting Point $/^{\circ}$ C: 160 – 163.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	0.53 - 0.64 (30H, m), 0.77 - 0.91 (10H, m), 1.48 (2H, quint),
	1.81 (2H, m), 2.09 (4H, m), 4.00 (2H, m), 6.94 (2H, d, J = 8.7 Hz),
	7.21 (1H, d, J = 3.9 Hz), 7.32 (1H, d, J = 3.4 Hz), 7.56 – 7.65
	(6H, m), 7.73 – 7.80 (4H, m), 8.32 (2H, d, J = 8.4 Hz).
IR v_{max}/cm^{-1} :	3435, 2925, 2856, 2361, 1594, 152, 1464, 1337, 1248, 1175, 1107,
	824.
MS <i>m</i> / <i>z</i> (EI):	798 (M ⁺ , M 100), 797, 770, 684, 597, 586, 585, 572, 474,
	473, 472, 460, 459, 458, 214, 202, 174, 135, 121.
Combustion analysis:	
Expected:	C 79.75%, H 8.46%, N 1.75%, S 4.02%

Obtained: C 79.62%, H 8.49%, N 1.91%, S 3.77%

4-[9,9-*di*(2-Ethylhexyl)-7-{5-[4-(octyloxy)phenyl]thiophen-2-yl}fluoren-2-yl]aniline (115)



A mixture of 2-[9,9-di(2-ethylhexyl)-7-(4-nitrophenyl)fluoren-2-yl]-5-[4-(octyloxy)phenyl]thiophene (**114**) (1.50 g, 0.0019 mol), tin chloride hydrate (2.17 g, 0.0096 mol) and EtOH (100 cm³) was heated under reflux for 1 h. The cooled mixture was poured into water (600 cm³), the suspension pH altered to 8 *via* the addition of aqueous NaHCO₃ (20%) and the crude product extracted into ethyl acetate (6 x 100 cm³). The combined organic extracts were washed with brine (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was used without further purification in the next step.

MS *m*/*z* (EI): 768 (M⁺), 767 (M 100), 656, 655, 654, 544, 543, 542, 468, 444, 443, 442, 430, 328, 222, 121.

2,9-*bis*[4-(7-{5-[4-(Octyloxy)phenyl]thiophen-2-yl}-9,9-*di*(2-ethylhexyl)fluoren-2-yl)phenyl]-perylene diimide (**117**)



A mixture of 4-[9,9-*bis*(2-ethylhexyl)-7-{5-[4-(octyloxy)phenyl]thiophen-2-yl}fluoren-2yl]aniline (**115**) (0.88 g, 0.0012 mol), perylene-3,4,9,10-tetracarboxylic dianhydride (**1**) $(0.09 \text{ g}, 2.29 \text{ x} 10^{-4} \text{ mol})$, imidazole (5.00 g) and zinc acetate dihydrate (g, 1.15 x 10⁻⁴ mol) was heated (160 °C) for 24 h. The reaction mixture was allowed to cool, water (200 cm³) added and the crude product extracted into DCM (4 x 150 cm³). The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM] and recrystallisation from EtOH/DCM to yield a red crystalline solid (0.28 g, 58%).

Transition temp. / $^{\circ}$ C: **Cr** 178 **N** 226 **I**.

¹H NMR (CDCl₃) δ_{H} : 0.57 (12H, t), 0.67 (12H, t), 0.81 – 0.92 (24H, m), 1.20 – 1.32 (36H, m), 1.81 (4H, quint), 2.09 (8H, d), 4.00 (4H, t), 6.94 (4H, dd, J = 6.7 Hz, 2.0 Hz), 7.22 (2H, d, J = 5 Hz), 7.31 (2H, d, J = 8.4 Hz), 7.47 (4H, d, J = 8.4 Hz), 7.58 (4H, dd, J = 6.7 Hz, 2.0 Hz), 7.62 – 7.67 (8H, m), 7.74 (2H, d, J = 8.1 Hz), 7.79 (2H, d, J = 7.9 Hz), 7.82 – 7.85 (4H, m), 8.76 (4H, d, J = 8.4 Hz), 8.83 (4H, d, J = 7.8 Hz). IR ν_{max} /cm⁻¹: 3430, 2921, 2853, 1707, 1699, 1593, 1510, 1466, 1402, 1350, 1248, 1176, 795, 746, 498. MS *m*/*z* (MALDI): 1893, 1892 (M⁺, M 100), 1891, 1713, 1502, 1200, 810, 753.

Combustion analysis:

Expected:	C 82.50%, H 7.56%, N 1.48%, S 3.39%
Obtained:	C 82.75%, H 7.94%, N 1.30%, S 3.09%

2-(4-Methoxyphenyl)thiophene (119)

,o-(_____s

Tetrakis(triphenylphosphine)palladium(0) (2.50 g, 0.0022 mol) was added to a heated (90 $^{\circ}$ C) solution of 4-bromoanisole (**118**) (28.77 g, 0.1538 mol), tributyl(thiophen-2-yl)stannane, (57.40 g, 0.1538 mol) and DMF (200 cm³). The mixture was heated at 90 $^{\circ}$ C for 24 h, allowed to cool and poured into saturated aqueous KF (150 cm³). The crude product was extracted into DCM (3 x 200 cm³). The combined organic extracts were

washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 1 : 1] and recrystallisation from DCM/EtOH, to yield a white crystalline solid (23.40 g, 80%).

Purity:	>99% (GC).
Melting point / ^O C:	105 – 107 (Lit. 106 – 107). ^[41]
1 H NMR (CDCl ₃) δ_{H} :	3.83 (3H, s), 6.91 (2H, d, J = 8.7 Hz), 7.05 (1H, dd, J = 5.2,
	3.6 Hz), 7.19 – 7.22 (2H, m), 7.54 (2H, d, J = 8.7 Hz).
IR v_{max}/cm^{-1} :	2960, 2915, 2834, 1605, 1570, 1531, 1500, 1464, 1428, 1292,
	1246, 1182, 1112, 1031, 851, 824, 810, 698, 662, 576, 534, 489.
MS <i>m</i> / <i>z</i> (EI):	190 (M ⁺ , M100), 177, 176, 175, 158, 149, 148, 147, 115,
	102, 89, 77, 62.

Combustion analysis:

Expected:	C 69.44%, H 5.30%, S 16.85%
Obtained:	C 69.62%, H 5.57%, S 16.61%

Tributyl-[5-(4-methoxyphenyl)thiophen-2-yl]stannane (120)



A solution of *n*-BuLi in hexanes (29.52 cm³, 2.5*M*, 0.0738 mol) was added dropwise to a cooled (-78 $^{\circ}$ C) solution of 2-(4-methoxyphenyl)thiophene (**119**) (11.70 g, 0.0615 mol) in THF (150 cm³). The mixture was stirred for 1 h, maintaining the temperature at -78 $^{\circ}$ C, followed by the dropwise addition of tributyltin chloride (21.02 g, 0.0646 mol). The mixture was allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 x 100 cm³), washed with water (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out. Purity: >87% (GC). ¹H NMR (CDCl₃) δ_{H} : 0.91 (9H, t), 1.11 (6H, quint), 1.35 (6H, quint), 1.57 (6H, t),

2-Bromo-7-iodo-9,9-dioctylfluorene (121)



Powdered KOH (10.93 g, 0.1947 mol) was added in small portions over 30 min to a stirred solution of 2-bromo-7-iodofluorene (20) (17.00 g, 0.0458 mol), 1-bromooctane (17.70 g, 0.0916 mol), potassium iodide (0.76 g, 4.58 x 10⁻³ mol) and DMSO (150 cm³) at RT. The mixture was stirred at RT for 2 h, then poured into water and the product extracted into hexane $(3 \times 250 \text{ cm}^3)$. The combined organic extracts were washed with brine $(2 \times 200 \text{ cm}^3)$, dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out via recrystallisation from EtOH, to yield white needles (27.28 g, 77%). Melting point /^oC: 51 – 53. Purity: >97% (GC). 1 H NMR (CDCl₃) δ_{H} : 0.55 – 0.61 (4H, m), 0.83 (6H, t), 1.05 – 1.26 (20H, m), 1.87 – 1.92 (4H, m), 7.39 – 7.46 (3H, m), 7.52 (1H, dd, J = 7.9, 0.8 Hz), 7.64 – 7.66 (2H, m). IR v_{max}/cm^{-1} : 2926, 1568, 1447, 1400, 1253, 1132, 1053, 1001, 881, 810, 750, 722, 658, 510, 417. 596 (M⁺), 594 (M⁺, M 100), 483, 402, 371, 370, 356, 355, 276, MS *m*/*z* (EI):

245, 176, 71.

2-(7-Bromo-9,9-dioctylfluoren-2-yl)-5-(4-methoxyphenyl)thiophene (122)



Tetrakis(triphenylphosphine)palladium(0) (1.75 g, 1.51×10^{-3} mol) was added to a heated (90 ^oC) solution of 2-bromo-7-iodo-9,9-dioctylfluorene (**121**) (18.00 g, 0.0302 mol), tributyl-[5-(4-methoxyphenyl)thiophen-2-yl]stannane (**120**) (28.98 g, 0.0605 mol) and DMF (100 cm³). The mixture was stirred for 16 h, allowed to cool, poured into aqueous KF (20%, 200 cm³) and the crude product extracted into diethyl ether (4 x 100 cm³). The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, hexane : DCM, 3 : 2] and recrystallisation from EtOH/DCM, to yield an off white crystalline solid (12.20 g, 61%).

Transition temp. / O C: T_{g} 10 Cr 86 N 98 I.

¹ H NMR (CDCl ₃) $\delta_{\rm H}$:	0.64 (4H, quint), 0.81 (6H, t), 1.06 – 1.22 (20H, m), 1.93 – 2.01
	(4H, m), 3.86 (3H, s), 6.94 (2H, d, J = 9Hz), 7.21 (1H, d,
	J = 3.6 Hz), 7.34 (1H, d, $J = 3.9 Hz$), 7.44 – 7.47 (2H, m), 7.53 –
	7.66 (6H, m).
IR v_{max}/cm^{-1} :	2952, 2924, 2851, 1605, 1510, 1484, 1462, 1290, 1251, 1177,
	1033, 879, 827, 797, 752, 722, 654, 590, 502.
MS <i>m</i> / <i>z</i> (EI):	658 (M ⁺), 656 (M ⁺ , M 100), 465, 464, 446, 432, 431, 351,
	321, 216, 215, 71.
Combustion analysis:	

Combustion analysis:

Expected:	C 73.04%, H 7.51%, S 4.87%
Obtained:	C 72.85%, H 7.74%, S 4.65%

2-(4-Methoxyphenyl)-5-[7-(5-nitrothiophen-2-yl)-9,9-dioctylfluoren-2-yl]thiophene (123)



A solution of 2-(7-bromo-9,9-dioctylfluoren-2-yl)-5-(4-methoxyphenyl)thiophene (**122**) (5.00 g, 0.0076 mol) in THF (50 cm³) was slowly added dropwise to a mixture of Mg (0.20 g, 0.0084 mol), I₂ (trace amount) and THF (10 cm³). Once added the mixture was slowly brought to reflux and heated under reflux for a further 3 h, until no Mg metal was present. The prepared Grignard reagent was transferred dropwise to a mixture of 2-bromo-5-nitrothiophene (1.74 g, 0.0084 mol) Pd(dppf)Cl₂ (0.17 g, 2.28 x 10^{-4} mol) and THF (10 cm³). The mixture was heated under reflux overnight, allowed to cool poured into water (200 cm³) and the crude product extracted into DCM (3 x 100 cm³). The combined organic extracts were washed with aqueous hydrochloric acid (10%, 100 cm³), brine (2 x 200 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 3 : 1] and recrystallisation from EtOH to yield an orange crystalline solid (2.07 g, 39%). Transition temp. /^OC: **Cr** 69 **N** 121 **I**.

¹H NMR (CDCl₃) δ_{H} : 0.61 – 0.72 (4H, m), 1.1 – 1.2 (20H, m), 2.15 (4H, t), 3.86 (3H, s), 6.95 (2H, d, J = 8.8 Hz), 7.22 (1H, d, J = 3.8 Hz), 7.32 (1H, d, J = 4.2 Hz), 7.36 (1H, d, J = 3.8 Hz), 7.56 – 7.60 (4H, m), 7.64 – 7.66 (2H, m), 7.73 (2H, t, J = 8.8 Hz), 7.95 (1H, d, J = 4.4 Hz). IR v_{max}/cm⁻¹: 2923, 2852, 1604, 1510, 1424, 1337, 1332, 1291, 1252, 1177, 1038, 827, 797, 733. MS *m*/*z* (EI): 705 (M⁺, M 100), 689, 591, 493, 480, 478, 461, 403,

353, 289, 240, 210, 121.

Combustion analysis:

Expected:	C 74.85%, H 7.28%, N 1.98%, S 9.08%
Obtained:	C 73.99%, H 7.34%, N 1.81%, S 8.65%

2-Amino-5-{7-[5-(4-methoxyphenyl)thiophen-2-yl]-9,9-dioctylfluoren-2-yl}thiophene (124)



A mixture of 2-(4-methoxyphenyl)-5-[7-(5-nitrothiophen-2-yl)-9,9-dioctylfluoren-2-yl]thiophene (**123**) (1.85 g, 0.0026 mol), tin chloride hydrate (2.96 g, 0.0131 mol) and EtOH (120 cm³) was heated under reflux for 2 h. The cooled mixture was poured into water (600 cm³), the suspension pH altered to 8 via the addition of aqueous NaHCO₃ (20%) and the crude product extracted into ethyl acetate (5 x 100 cm³). The combined organic extracts were washed with brine (100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. No further purification was carried out, the crude product was immediately used in the next step.

MS m/z (EI): 675 (M⁺)

2,9-*bis*[5-(7-{5-[4-(Methoxy)phenyl]thiophen-2-yl}-9,9-dioctylylfluoren-2-yl)thiophen-2-yl]-perylene diimide (**125**)



A mixture of 5-{7-[5-(4-methoxyphenyl)thiophen-2-yl]-9,9-dioctylfluoren-2yl}thiophen-2-amine (**124**) (1.25 g, 0.0018 mol), perylene-3,4,9,10-tetracarboxylic dianhydride (**116**) (0.24 g, 6.16 x 10^{-4} mol), imidazole (8.00 g) and zinc acetate dihydrate (0.07 g, 3.08 x 10^{-4} mol) was heated (160 ^oC) for 24 h. The cooled reaction mixture was

allowed to cool, poured into water (300 cm³) and the crude product extracted into DCM (4 x 100 cm³). The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 3 : 1] and recrystallisation from EtOH/DCM, to yield a red crystalline solid (0.56 g, 53%). Transition temp. /^OC: **T**_g 137 **Cr** 244 **I**.

1 H NMR (CDCl ₃) δ_{H}	: 0.70 (8H, quint), 0.80 (12H, t), 1.07 – 1.21 (40H, m), 2.03 (8H, t),
	3.86 (6H, s), 6.94 (4H, d, J = 8.7 Hz), 7.17 (2H, d,
	J = 4.0 Hz), 7.20 (2H, d, J = 3.6 Hz), 7.34 (2H, d, J = 3.6 Hz), 7.42
	(2H, d, J = 4.0 Hz), 7.58 – 7.72 (16H, m), 8.69 (4H, d, J = 8.4 Hz),
	8.80 (4H, d, J = 8.1 Hz).
IR v_{max}/cm^{-1} :	2924, 2877, 1716, 1683, 1594, 1542, 1508, 1458, 1326, 1249, 795.
MS <i>m/z</i> (MALDI):	1708 (M ⁺ , M100), 1707, 1529, 1270, 1201, 892, 877.
Combustion analysis	:
Expected:	C 78.74%, H 6.49%, N 1.64%, S 7.51%
Obtained:	C 78.44%, H 6.71%, N 1.84%, S 7.43%

2-Amino-9,9-didodecylfluorene (127)



Powdered KOH (3.29 g, 0.0586 mol) was added in small portions over 30 min to a stirred solution of 2-aminofluorene (**126**) (2.50 g, 0.0138 mol), 1-bromododecane (7.56 g, 0.0303 mol), potassium iodide (0.23 g, 0.0014 mol) and DMSO (25 cm³) at RT. The mixture was stirred at RT for 2 h, then poured into water and the crude product extracted into diethyl ether (3 x 300 cm³). The combined organic extracts were washed with brine (2 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM : hexane, 9 : 1] to yield a pale brown crystalline solid (2.79 g, 39%). Melting Point $/^{O}$ C: 64 – 66.

Purity:	>98% (GC).
1 H NMR (CDCl ₃) δ_{H}	: 0.61 (4H, quint), 0.81 (6H, t, J = 7.3 Hz), 1.03 – 1.20 (36H, m),
	1.89 (4H, m), 6.77 (2H, d, J = 7.8 Hz), 7.19 – 7.28 (3H, m),
	7.50 (1H, dd, J = 7.6, 0.8 Hz), 7.55 (1H, d, J = 8.4 Hz).
IR v_{max}/cm^{-1} :	3453, 3366, 3004, 2954, 2924, 2848, 1622, 1582, 1494, 1454,
	1352, 1327, 1275, 1256, 1211, 1134, 1024, 864, 820, 773, 738,
	588, 562.
MS <i>m</i> / <i>z</i> (EI):	517 (M ⁺).

2,9-bis(9,9-Didodecylfluoren-2-yl)-perylene diimide (128)



A mixture of 2-amino-9,9-didodecylfluorene (**127**) (2.40 g, 0.0046 mol), perylene-3,4,9,10-tetracarboxylic dianhydride (0.73 g, 0.0019 mol), zinc acetate dihydrate (0.41 g, 0.0019 mol) and imidazole (12 g, 0.1763 mol) was heated (160 $^{\rm O}$ C) for 24 h. The cooled reaction mixture was poured into water (200 cm³) and the crude product extracted into DCM (3 x 100 cm³). The combined organic extracts were washed with brine (4 x 100 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, DCM] and recrystallisation from DCM/EtOH to yield a red crystalline solid (1.03 g, 40%).

Melting point /^OC: 201.

¹H NMR (CDCl₃)
$$\delta_{\rm H}$$
: 0.86 (12H, t), 1.10 – 1.27 (80H, m), 1.99 (8H, t), 7.31 – 7.39
(10H, m), 7.76 (2H, dd, J = 7.6, 0.8 Hz), 7.88 (2H, d, 8.1 Hz),
8.70 (4H, d, J = 8.4 Hz), 8.79 (4H, d, J = 8.1 Hz).
IR $v_{\rm max}$ /cm⁻¹: 3427, 2923, 2850, 2364, 1703, 1664, 1592, 1452, 1430, 1403,
1356, 1253, 1176, 1122, 1122, 967, 806, 801, 737.

MS *m*/*z* (MALDI): 1392 (M⁺), 1390.

Combustion analysis:

Expected:	C 84.56%, H 8.83%, N 2.01%
Obtained:	C 84.54%, H 9.04%, N 1.74%

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4. Results and Discussion

The materials synthesised during this thesis serve two purposes: the first is for use in Organic Light-Emitting Diodes, including White-Light Organic Light-Emitting Diodes (WOLEDs), featured in schemes 1 – 17 and the second as materials for organic photovoltaics, schemes 18 – 20. All electroluminescence (EL), photoluminescence (PL) and cyclic voltammetry (CV) measurements were carried out by the physics group of the organophotonics group.

4.1 Scheme 1 and 2.

An OLED containing the tetraethyl perylene-3,4,9,10-tetracarboxylate, figure 4.01, has a maximum wavelength of EL of 615 nm with a fwhm of 77 nm and maximum EL brightness of 45 cd/m² at 28 V. ^[1] Although this OLED performance is poor, it shows that perylenes can be used as electroluminescent materials. The perylene core is light and chemically stable, cheap and readily available as perylene-3,4,9,10-tetracarboxylic dianhydride, which reacts with bromo alkyl chains to form perylenes like **2** and **6**. This makes these perylene materials good candidates for red-emitters in OLEDs as some possess columnar mesophases and form amorphous glassy phases. Therefore their ordered properties can be exploited at room temperature in the liquid crystalline glassy state.



Figure 4.01 Chemical structure of tetraethyl perylene-3,4,9,10-tetracarboxylate.

Compound **2** has been reported previously. ^[1] However, it was synthesised in this thesis as a pre-cursor to compound **3**. The melting point of compound **2** compares favorably with the previously reported value, 63 °C compared to 62 °C. This melting point is seen as a first-order transition and a large peak in the DSC thermograph, figure 4.02. The columnar mesophase is enantiotropic with a clearing point of 138 °C, which is a small

first-order transition. On the cooling cycle the columnar mesophase forms at a temperature of 133 °C and the material remains in the columnar phase until crystallisation occurs at 34 °C, plate 4.01. Once crystallisation has occurred paramorphism is observed as the material has crystallised in platelets, adopting the morphology of the hexagonal columnar phase present before crystallisation occurred. Microcrystalline morphology is important in producing a highly ordered solid with surprisingly high hole-mobilities within localised domains. ^[2]



 Table 4.01 Molecular structure and transition temperatures of compounds 2 and 6.





Plate 4.01 Room Temperature crystal phase of compound 2.

Compound $\mathbf{6}$ was synthesised in an attempt to try to produce an analogue of compound $\mathbf{2}$, but with lower clearing and melting points for the hexagonal columnar mesophase of compound 2. This would make device processing easier and make compound 6 more suitable for devices than compound 2, since compound 2 has no room temperature mesophase or amorphous glassy phase. It was hoped that the presence of the branched methyl groups in the 3 and 7 positions of the octyl chain would lower the van der Waals forces of attraction between neighbouring pervlene cores due to the steric effects of the methyl groups and thus lower the melting point of the mesophase. This modification of structure proved successful as the melting point was lowered from 63 °C, to less than -20 $^{\circ}$ C, figure 4.03. Not only was the melting point lowered but the clearing point was increased, from 138 to 156 °C, therefore increasing the columnar mesophase range considerably giving material properties that are much more favourable for device processing, as the material can be processed in a device at room temperature. This increase in the columnar mesophase is not fully understood but may be due to the branched chains filling space in the periphery of the disc, enhancing intermolecular attraction in the columnar phase. The DSC thermograph of compound 6 shows one firstorder transition at 156 °C, which is the columnar to isotropic liquid transition. The material is enantiotropic with a supercooled isotropic to columnar phase transition at 128 ^oC. Further confirmation of the presence of a hexagonal columnar phase was seen on

slow cooling at a rate of 0.1 °C, in the form of a star-like texture at the isotropic to columnar transition. No crystal to columnar phase transition is seen on heating or cooling, suggesting that the material is in the columnar phase during the whole temperature range. This means the crystal to columnar transition is below -20 °C. This is confirmed by optical-polarising microscopy, plate 4.02 shows the columnar mesophase present at 81 °C and plate 4.03 shows the phase is still present at room temperature, 22 °C, after seven days of standing at room temperature.







Plate 4.02 Columnar phase of compound 6 at 81 °C.



Plate 4.03 Room Temperature Columnar phase of compound 6 after seven days.

The synthesis of compound **3** was intended to produce a compound with a phenyl urazole group on both sides of the perylene core to maintain the columnar mesophase, but produce a different spectrum of physical properties. This aim proved difficult to achieve as many variations of the synthesis were tried but each method only yielded small quantities, < 2%, of the required product. The main product was the mono-addition product, compound **3**. The reason for the very low yield is probably due to the electron withdrawing effect of the four octyloxy carbonyl chains, preventing addition to both bay positions of the perylene moiety. However, compound **3** did show interesting results. As expected the columnar mesophase was lost, but a dramatic change in the electron affinity was observed. While the ionisation potential (IP) remained above 5 eV, the optical band gap was dramatically increased and so altering the electron affinity (EA), 3.61 and 1.80 eV respectively. This interesting result has the effect of changing an electron-accepting material into an electron-donating material with the simple addition of a urazole moiety, when compared to compound **2**.

A number of attributes are required for a compound to be a suitable hole-transporting material. Hole-transport materials should have a low barrier for hole-injection from the anode, shown by the relatively low ionisation potential, 5.31 eV of compound **3**. They should have high optical transparency, that allows the passage of light emitted from the

device, to ensure a high light collecting efficiency. ^[3] These requirements will be helped by the high band-gap (Eg) of 3.61 eV of compound **3**. The material however must also have good film forming properties and unless compound **3** can be deposited under vacuum to form an amorphous material the compound is not easily processable as it cannot be solution processed due to the absence of a mesophase or an amorphous glassy phase. One possibility that has not been researched is the prospect that compound **6** may form microcrystalline domains, depending on processing conditions, that may prove useful for charge-transport properties. ^[4]



Table 4.02 Molecular structure and melting point of compound 3.

The oxidation potentials corresponding to the HOMO levels of compounds **2**, **3** and **6** were measured by cyclic voltammetry as a DCM solution, shown in table 4.03.

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Compound	IP (eV)	E _g (eV)	EA (eV)	
2	5.80	2.28	3.52	
3	5.31	3.61	1.80	
6	5.83	2.29	3.54	

 Table 4.03 Cyclic voltammetry results of compounds 2, 3 and 6.

It is not surprising to see very similar ionisation potentials, optical band-gaps and electron-affinities of compounds 2 and 6, table 4.03, as the perylene chromophore in each compound is identical. This similarity in behaviour is confirmed by comparison of the UV-vis absorption spectra of the two compounds, figure 4.04. There is no noticeable difference apart from their intensities, which have been offset for clarity. The marginal differences in the cyclic voltammetry results may be explained by experimental error or the slight difference in van der Waals forces of attraction between the perylene cores, because of the branched 3,7-dimethyl octyl chains in compound 6.



The UV-vis spectrum confirms an almost identical absorption onset, which would be expected as both materials have similar band-gaps, figure 4.04.

4.2 Scheme 3 and 3a.

A key requirement of OLEDs is the need for electron-transporting materials. There is a lack of suitable materials due to the inherent hole-transporting properties of organic materials. Fluorine substituents have previously been incorporated in lateral positions of aromatic cores in order to have the effect of lowering nematic melting and clearing points, although this gives mixed results.^[5] However little work has been conducted into the effect fluorine substituents have on the electron mobility of 2,7-disubstituted-9,9dialkylfluorene compounds, which led us to synthesise the 2,7,-disubstituted-9,9*di*(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)fluorene class of compounds. The two alkyl chains are orthogonal to the fluorene unit and so act as large lateral substituents, ^[6] which are known to lead to low liquid crystalline temperatures and to the suppression of smectic phases due to steric effects.^[7] Therefore, compound **14** was synthesised to study these effects on the liquid crystalline properties and on the charge-carrier properties compared to those of the corresponding compound MPA043 with alkyl chains in place of the partially perfluorinated chains in compound 14. The greater van der Waals forces of attraction between the fluorine atoms of the perfluorinated chains in compound 14 leads to a higher melting point of 145 °C compared to a melting point of 105 °C for MPA043. This increase may be enough to prevent the direct observation of the expected nematic phase. There is also an absence of a glass transition for compound 14, seen for MPA043 at -10 °C, meaning compound 14 has no self-assembling properties required for good charge mobility. Unfortunately the absence of liquid crystalline phases and a glass transition temperature probably render compound 14 unsuitable for use as an electrontransport material.



Table 4.04 Melting points and transition temperatures of compounds 14 and MPA043.

A further problem is caused by the lack of a significant difference between the electrontransporting properties of compound **14** and those of compound **MPA043**, table 4.05, shown by cyclic voltammetry. This is surprising as the electron affinities of **MPA043** and **14** are 2.49 eV and 2.52 eV respectively. These results show that the perfluorinated chains have no appreciable effect. This is possibly due to the conjugated aromatic chromophore being the dominant force in determining the electron and hole-transporting properties of a material, meaning the alkyl substituents have little effect. This also seems to be confirmed when mainchain fluorinated PPV polymers are considered. ^[8] It was found that although the energy levels are altered by molecular substitution, it has little effect on the charge carrier mobilities or optical properties of related polymers, similar to the behaviour seen for compound **14**.

R	Compound	IP (eV)	E _g (eV)	EA (eV)	
(CH) ₂ (CF ₂) ₅ CF ₃	14	5.70	3.18	2.52	
(CH ₂) ₇ CH ₃	MPA043	5.60	3.11	2.49	

 Table 4.05 Cyclic Voltammetry results for compounds 14 and MPA043.

Comparison of the UV-vis spectra of compound **14** and **MPA043**, figure 4.05, shows no significant difference in the absorption wavelength due to the presence of the perfluorinated chains. This is expected as both compounds have very similar optical band-gaps and so the absorption spectra should be very similar. The only significant difference is the absorption intensity of each compound. Compound **MPA043** has a stronger absorption maximum compared to that of compound **14**. This is probably caused by more efficient inter-molecular packing of **MPA043** causing greater absorption, due to greater aggregation between neighbouring molecules. ^[9]



(approx. 0.0125% wt/wt, DCM).

In an attempt to prepare a similar compound with the same aromatic core, but with a liquid crystal phase, or an amorphous glassy state, compound **14** was converted into compound **18** by removal of the octyloxy chains to form a bis-phenol, which was alkylated in a Williamson-ether synthesis to yield compound **18** with a non-conjugated diene at the ends of the terminal chains. The corresponding non-conjugated diene, compound **18**, has a lower melting point than compound **14**, table 4.06. This was expected due to the longer aliphatic chain and steric hindrance attributable the diene-ester group. This combination of effects results in a greater inter-molecular distance between

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neighbouring chromophores and more non-linear chain conformations, which in turn leads to a lower degree of anisotropy of molecular shape and molecular polarisability.^[10] The branched structure of the photopolymerisable diene end group is also expected to make a significant contribution to lowering the melting and clearing point, due to steric effects. ^[10] Although the melting point of compound **18** is lower than that of **MPA043** there is still no observable liquid crystalline phase or glass transition. This is not surprising when the model structure of the dialkyl-substituted fluorene of compound 18 is viewed, figure 4.07. The alkyl chains at the 9 position on the fluorene are orthogonal to the aromatic chromophore.^[6] This is the case for both compounds **18** and **MPA045**. figure 4.07 and 4.08. However, compound **18** has two perfluorinated chains which seems to make the chains sit further out of plane of the aromatic fluorene, figure 4.07. Although the atomic radius of fluorine is only 12% larger than hydrogen this causes enough intermolecular spacing and disorder to prevent the positional order required for the formation of a liquid crystal phase. In compound **MPA045** this is not the case, the alkyl chains sit closer to the central plane of the chromophore and are straighter, figure 4.08. As discussed earlier the higher van der Waal attractive forces attributable to the fluorine atoms cause a higher melting point for compound 18 compared to that of MPA045. The melting point of compound 18 is actually higher than the clearing point of MPA045. This is possibly high enough to prevent the direct observation of a mesophase. The increased conformational rigidity of perfluorinated chains compared to alkyl chains possibly also has a significant contribution.



Table 4.06 Melting points and transition temperatures of compounds 18 and MPA045.

The DSC thermogram, figure 4.06, confirms the melting point of compound **18**. The base-line of the spectra is relatively flat and a sharp transition peak is observed with no appreciable thermal degradation. The large enthalpy value is characteristic of a melting point. However, no smaller first order transition peak indicative of a liquid crystal to isotropic liquid phase change is seen and there is no second order shift in the base-line indicating a glass transition. The lack of any mesophase was confirmed by optical-polarising microscopy on heating and cooling cycles. All that was seen is a typical crystalline texture on both heating and cooling.



Figure 4.06 DSC thermogram as a function of temperature for compound 18 (scan rate 10° C).



Figure 4.07 MM2 geometry optimised structure of the difluoroalkyl-substitued fluorene of compound 18.



Figure 4.08 MM2 geometry optimised structure of the dialkyl-substitued fluorene of compound **MPA045**.

4.3 Scheme 4 and 4a.

In order to make use of colour rendering and colour tunability over the whole visible spectrum in an OLED, materials that emit other than in the red-green-blue primary regions of the spectrum are also required. ^[11] Therefore, the synthesis of a compound that emits in the yellow region of the electromagnetic spectrum was carried out. In order to achieve this the degree of conjugation or planarity of the molecular core has to be larger than that typically seen for compounds **14** and **18** in order to red-shift the absorption and emission spectra. Therefore, compound **30** incorporating a 4,7-disubstituted benzothiadiazole moiety was synthesised. This molecular modification should have the desired effect of extending the degree of aromatic conjugation to provide yellow emission.

Benzothiadiazole **30** has no observable liquid crystal mesophase, but it is still suitable for device fabrication. This is because it not only forms an amorphous glass at room temperature it is also stable enough to allow polymerisation to be carried out to form an insoluble amorphous polymer network.

When compared to **PV080**, see table 4.07, benzothiadiazole **30** has a lower melting point, possibly due to greater inter-annular twisting between the thiadiazole core and neighbouring fluorenes. This is confirmed when the modelled structures of both compounds are compared, figure 4.09 and 4.10, as the structures show there is much greater inter-annular twisting between the thiadiazole and fluorenes of benzothiadiazole **30** than the biphenyl and fluorenes of **PV080**. This is likely to be caused by steric hinderance attributable to the bulky thiadiazole moiety compared to that of the smaller biphenyl group. The modelled structures are viewed as if above the molecule with the plane of the molecule running perpendicular to the page. The dihedral angle between fluorenes and benzothiadiazole is found to be 44 degrees for benzothiadiazole **30** and 15 degrees for **PV080**. It is this lower dihedral angle present in **PV080** that allows the formation of a nematic phase. The greater length of the biphenyl moiety present in **PV080** leads to a higher aspect ratio, (length-to-breadth ratio), for **PV080** than that of

benzothiadiazole **30**. The large aspect ratio is likely to result in the presence of the monotropic nematic phase seen on cooling at 55 $^{\circ}$ C.

	~~~o-/	C ₃ H ₇	A C ₃ H ₇	C ₃ H ₇	C ₃ H ₇ C			= //
Chromophore A	Compound	Tg		Cr		N		Ι
N ^S N	30	•	25	•	77		-	•
	PV080		-	•	147	(•	55)	•

Table 4.07 Melting points and transition temperatures of compounds 30 and PV080.



Figure 4.09 MM2 optimised geometry structure of compound 30.



Figure 4.10 MM2 optimised geometry of structure of compound PV080.
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Plate 4.04 shows the room temperature amorphous glass, when viewed between cross polarisers. The glass is seen as a dark orange region. Once crystallised the same region shows a typical crystal texture, plate 4.05, with a degree of paramorphism.



Plate 4.04 Room temperature amorphous glassy phase of compound 30.



Plate 4.05 Crystallised glassy phase of compound 30 after seven days at RT.

N ^S N 30 :	5.51	2.45	3.06

 Table 4.08 Cyclic voltammetry results for compound 30.
 Compound 30.
 Cyclic voltammetry results for compound 30.
 Cyclic voltammetry results for

The cyclic voltammagram of benzothiadiazole **30**, figure 4.11, shows the process is reversible with a ionisation-potential of 5.51 eV and electron-affinity of 3.06 eV.



Figure 4.11 Cyclic voltammagram of compound 30.

The compound is an orange solid with bright yellow photoluminescence. The optical band-gap, table 4.08, shows that absorption should begin around 510 nm. This is confirmed by the UV-vis spectra, figure 4.12.



It is clear from the UV-vis absorption spectra that there are two main peaks of absorption with maximums of 432 and 322. The first at 432 is due to the presence of the benzothiadiazole moiety and the second at 322 is due to the  $\pi$ - $\pi$ ^{*} transition of the fluorene moiety. This region of absorption is typical of many materials synthesised during this thesis as many contain the fluorene chromophore.

## 4.4 Scheme 5a.

A high electron-affinity value is required for materials that are to be used as electron transport materials. The benzothiadiazole moiety is often used to induce a high electron-affinity in electron-transport materials designed for use in OLEDs. With this is mind the benzothiadiazole chromophore of compound **PV013** was replaced by a benzoxadiazole core to produce compound **42**. This modification would facilitate the study of the effect of changing the electron-rich sulphur of benzothiadiazole **PV013** for an electron-deficient oxygen on the mesomorphic behaviour and the other physical properties of benzoxadiazole **42**. The electron deficient oxygen atom in benzoxadiazole **42** would be expected to increase the electron affinity. This would hopefully render benzoxadiazole **42** suitable as an electron transport material, whilst maintaining the desired self-assembling properties of **PV013**. The use of the benzoxadiazole moiety in electron-transport materials for OLEDs has not been extensively studied. In contrast there is an increased understanding of benzothiadiazole derivatives used for this purpose. ^[12]



Table 4.09 Transition temperatures of compounds 42 and PV013.

The benzoxadiazole **42** exhibits a higher clearing point and a lower melting point than those of the corresponding benzothiadiazole, table 4.09. Therefore the temperature range of the smectic A phase is much broader. Smectic phases are generally observed for apolar

liquid crystals with two or more aromatic rings connected by a C-C single bond. ^[5] This increase in mesomorphic range is more than likely due to the lower dihedral angle, 39 °, of the benzoxadiazole than that of the corresponding benzothiadiazole, 42 °. This means the phenyl rings of the benzoxadiazole lie more in the plane of the molecule with less inter-annular twisting, figure 4.15 and 4.15 respectively. The lower dihedral angle is probably due to the smaller atomic radius of the oxygen atom compared to that of the sulphur atom. This should cause less steric interaction. The electron-deficient oxygen atom may result in a greater electrostatic attraction between neighbouring hydrogen atoms. This may induce the phenyl rings to lie more in the central plane. These effects may allow a greater degree of order within the smectic A phase for the benzoxadiazole **42**.

The DSC thermogram of benzoxadiazole **42** shows typical first order transition peaks for the melting point of 60  $^{\circ}$ C and 98  $^{\circ}$ C for the clearing point, figure 4.13.



Plate 4.06 shows the typical focal-conic texture and dark homeotropic regions of a smectic A phase of benzoxadiazole **42**, which formed from batonnets on cooling from the isotropic liquid.



Plate 4.06 Typical focal-conic texture of smectic A phase of compound 42 at 87 °C.

The ionisation potential and electron affinity of the benzothiadiazole **PV013** are lower, 5.64 and 2.98 eV, than those of the benzoxadiazole, 5.72 and 3.17 eV, table 4.10. This is a reflection of the presence of the electron-deficient oxygen atom in place of the electron-rich sulphur atom in the aromatic core of **PV013**. This results in a difference in the optical band-gap and therefore the PL spectrum so that the benzothiadiazole **PV013** exhibits green light in the PL spectrum. However, the benzoxadiazole **42** with an oxygen atom in place of the sulphur atom, emits orange light,  $\lambda_{max} \approx 540$  nm, i.e. the emission is red-shifted, 40 nm, compared with that of the corresponding benzothiadiazole,  $\lambda_{max} \approx 500$  nm, **PV013**. This can be attributed to the narrowing of the HOMO-LUMO band gap of the benzoxadiazole, which is shown by the optical band-gap, Eg, values of the benzoxadiazole, 2.55 eV, and benzothiadiazole, 2.66 eV, due to the electron-deficient oxygen atom. This is confirmed when the modelled structures are compared as the lower dihedral angle of benzoxadiazole **42** means the planarity increases creating extended conjugation and so lowering the band-gap. This has been confirmed experimentally to be a difference of 0.11 eV.

The results discussed above show that the aims of increasing the EA and so making a material more suitable as an electron transport material in an OLED have been achieved.

Ring A	Compound	IP (eV)	E _g (eV)	EA (eV)	
	42	5.72	2.55	3.17	
N N	PV013	5.64	2.66	2.98	

However, the EA is still slightly too low for practical applications and the ionisation potential slightly too high.





Figure 4.14 MM2 optimised geometry of benzothiadiazole PV013.



Figure 4.15 MM2 optimised geometry of benzoxadiazole 42.

## 4.5 Scheme 6 and 7.

Many materials based on phenyl-pyridines, phenyl-pyrimidines and phenyl-tetrazines are known to exhibit liquid crystalline behaviour, often with smectic phases. ^[12, 13] The presence of electronegative nitrogen atoms in these derivatives may lead to a high electron affinity and hence a high mobility of electrons. ^[14] These properties render nitrogen heterocycles with liquid crystalline behaviour as interesting potential candidates for use as electron transport materials in OLEDs. The tetrazines are interesting as potential red-emitting materials.



Table 4.11 Melting points and transition temperatures of compounds 37, PV071 and 46.



Figure 4.16 DSC thermogram of compound 37.

As the transition temperatures show, table 4.11, the 2,5-disubstituted pyridine **37** and pyrimidine **PV071** exhibit a smectic C mesophase. Surprisingly the tetrazine **46**, shows no mesophase just a high melting point. The high melting point may be expected as the molecule is anticipated to be more planar in nature, figure 4.21, compared to the pyridine **37** and pyrimidine **PV071**, figures 4.19 and 4.20. This means there is more inter-annular twisting between the phenyl rings and the pyridine or pyrimidine rings compared to the tetrazine ring and phenyl rings. This increase in melting point is possibly the reason for the lack of an observable mesophase.

During initial investigations of tetrazine **46** using DSC, figure 4.17, it was believed that a mesophase was present due to what was thought to be a melting peak at 54  $^{\circ}$ C and a clearing peak at 109  $^{\circ}$ C. However, on closer inspection using optical microscopy and with the aid of the second heating cycle of the DSC it became clear that what was occurring was a change in the crystal structure of the compound. With each additional cycle the peak at 54  $^{\circ}$ C became smaller, leaving on the third cycle just the melting peak at 109  $^{\circ}$ C. This is also confirmed by the shift in the super-cooled crystallisation peak from a value of 102  $^{\circ}$ C to 93  $^{\circ}$ C from first to second cooling cycle.



Figure 4.18 shows a further DSC thermograph of tetrazine **46**. It is immediately noticeable that above 140 °C a dramatic change occurs, followed on cooling by the loss of the crystallisation peak and on heating the melting peak, seen in figure 4.17. This is caused by polymerisation of the compound whilst in the liquid state, thus creating an intractable insoluble polymer network. This spontaneous polymerisation may be inhibited by the addition of a small quantity of sublimed sulphur to the material. This inhibition technique was used for the less-stable methacrylate polymerisable groups utilised later in this thesis.



Figure 4.18 DSC thermograph of compound 46.

Molecular modelling using MM2 geometry optimisation of compounds **37**, **PV071** and **46** shows that when each molecule is viewed from above, down the molecular axis with the molecule perpendicular to the page subtle differences in structure can be seen, figures 4.19, 4.20 and 4.21. As the number of nitrogens is increased the molecule becomes more planar due to intra-molecular interactions between the nitrogen atoms and the neighbouring hydrogen on the adjacent phenyl ring. Whilst this may enhance the electron transport due to greater intermolecular  $\pi$ - $\pi$  overlap, it may result in high values for the melting and clearing points as the number of nitrogen atoms in the nitrogen heterocycle increases for the same reasons. Unfortunately, it also has the effect of increasing aggregation between neighbouring chromophores, which results in a high degree of quenching of the excited state. Thus, the photoluminescence and electroluminescence efficiency is often low for liquid crystalline nitrogen heterocycles with more than one nitrogen atom in any given aromatic ring of the molecular core.^[15]



Figure 4.19 MM2 optimised geometry of pyridine 37.



Figure 4.20 MM2 optimised geometry of pyrimidine PV071.



Figure 4.21 MM2 optimised geometry of tetrazine 46.

As expected increasing the number of nitrogen atoms within the compound increases the EA of the material, table 4.12. It can be seen that while the pyridine **37** has an EA of 2.37 eV and the pyrimidine **PV071** a value of 2.40 eV, the EA of the tetrazine **46**, with four

nitrogen atoms present in the heterocyclic ring is high, 3.88 eV. The increased planarity of the tetrazine **46** due to the lower dihedral angle, as previously discussed, increases the degree of conjugation and in effect lowers the band gap. High electron affinity renders the tetrazine **46** a potential electron-transport material, although the lack of a mesophase or glass transition suggests that this might not be the case in practice due to the defects at crystal grain boundaries in the solid state.

Ring A	Compound	IP (eV)	Eg (eV)	EA (eV)	
N	37	5.70	3.33	2.37	
$-\langle N \\ N $	PV071	5.87	3.47	2.40	
N=N N=N	46	6.07	2.09	3.88	

Table 4.12 Cyclic Voltammetry results for compounds 37, PV071 and 46.

The electrooxidation and electroreduction processes of the tetrazine **46** are reversible, figure 4.22. This behaviour shows that the tetrazine **46** exhibits a high degree of electrochemical stability.



Figure 4.22 Cyclic voltammagram of compound 46.

The tetrazine **47** was synthesised to study the effect of chain length on the mesomorphic behaviour of this class of tetrazines and hopefully induce liquid crystalline behaviour. Tetrazine **48** had been previously synthesised was used in the synthesis of compound **49**, scheme 7a. Table 4.13 shows that unlike tetrazine **46**, both the tetrazines **47** and **48** possess a smectic C mesophase and tetrazine **48** also exhibits a nematic phase.

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 Table 4.13 Melting points and transition temperatures for compounds 46, 47 and 48.

Tetrazine **47** exhibits a crystal to smectic C first order transition at 74 °C, plate 4.07, and a smectic C to isotropic liquid transition at 132 °C. On cooling the isotropic liquid a smectic phase was observed at 123 °C and the smectic to crystal transition was observed at 64 °C, i.e., recrystallisation. There appears to be no amorphous glassy phase, but on heating three small peaks are seen, which are believed to be crystal-crystal transitions. Tetrazine **47** with the same molecular core as tetrazine **46** exhibits an observable smectic C phase due to the longer alkoxy spacer chain and significant steric effects attributable to the bulky non-conjugated diene moiety at the end of the chains, which leads to a low melting point.



Plate 4.07 shows the typical texture of the smectic C phase present for tetrazine **47** between 74 and 132 °C. The Schlieren texture is clear and on cooling from an isotropic liquid, no droplets consistent with the formation of a nematic phase are observed.



Plate 4.07 Schlieren texture of Smetic C phase of compound 47 at 125 °C.

Tetrazine **48** exhibits both a smectic C and a nematic mesophase as confirmed by DSC, figure 4.24, and optical-polarising microscopy, plate 4.08. Two crystal first order transitions are present at 82 °C and 96 °C respectively, as confirmed by optical-polarising

microscopy. A smectic C mesophase is observed above 132 °C followed by a smectic C to nematic transition at 188 °C on heating. The material becomes an isotropic liquid at 196 °C. On cooling all the transitions exhibit a degree of hysteresis. However, no amorphous glassy phase is formed. Thus, the material is probably unsuitable for device applications. At room temperature the material forms a disordered crystal phase. As it is not a reactive mesogen, it cannot be polymerised in either the smectic or the nematic mesophase.





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As confirmation that tetrazine **48** does indeed possess a nematic phase droplets were observed on cooling from an isotropic liquid, as shown in plate 4.08. The droplets coalesced to form a Schlieren texture with four and two-point disclinations.



Plate 4.08 Nematic droplets of compound 48 at 188 °C.

It can be concluded that tetrazines have been shown to form smectic and nematic mesophases with high a electron-affinity and relatively low melting and clearing points.

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## 4.6 Scheme 6a and 7.

The absence of efficient liquid crystalline electron-transport materials led to the synthesis of compounds **49** and **53** as potential electron-transport materials. The 3,6-disubstitued pyridazine moiety was chosen as aromatic nitrogen heterocycles often have good electron-transport properties. ^[16] Furthermore the predicted V-shaped nature of the materials was believed to have a good chance of producing an amorphous glassy phase, because of steric-effects and potentially a very high viscosity. Molecular modelling using MM2 geometry optimisation showed the structure was a V-shape. This molecular shape could be expected to induce a high value of the viscosity required for formation of an amorphous glassy phase. The induction of a glass transition above room temperature is important as neither material would be expected to possess a mesophase due to their low aspect (length-to-breadth) ratio. Compound **53** also contains four pyridine rings in place of the four phenyl rings in compound **49**. The presence of more electron-deficient nitrogen atoms could lead to a greater value of the electron affinity.



 Table 4.14 Melting points and transition temperatures of compounds 49 and 53.

The DSC thermograph, figure 4.25, of compound **49** shows two transition peaks on each heating cycle and two peaks on each cooling cycle. The entropy values of each peak are high suggesting that the first transition on heating, 64 °C, is a crystal-to-crystal transition and the second the melting point. It is only during optical-polarising microscopy on cooling that a more ordered focal-conic fan-like structure is seen, plate 4.09. When this plate is mechanically sheared a granulated Schlieren-like texture is seen, plate 4.10 and when the material is heated again to an isotropic liquid and quenched rapidly at 50 °C per minute, a third texture is seen, which is also Schlieren-like but with some focal-conic areas, plate 4.11. The fact that the material can be sheared once this focal-conic-like structure is present is further indication of the presence of an ordered smectic phase, rather than of crystalline behaviour. Compound **49** has what has been termed a siamese twin structure. ^[17, 18] Therefore, a mesophase is perhaps possible if the structure formed is the most extended conformation. ^[19] However, siamese compounds reported previously are nematic, not smectic materials. This maybe due to the lower aspect ratio of **49** compared to previously reported materials.





Plate 4.09 Focal-conic fan structure of a smectic x phase of compound 49.



Plate 4.10 Schlieren texture of the ordered smectic phase of compound 49.



Plate 4.11 Schlieren type texture of the ordered smectic of compound 49.

X-ray Diffraction would need to be carried out to confirm whether the compound had the long range order expected of a highly ordered smectic phase.

Compound **53** has a very high melting point, 289 °C, and a supercooled recrystallisation temperature of 209 °C, shown by figure 4.26. Although under rapid quenching an amorphous glass is formed with a glass transition temperature at 154 °C. This compares



favourably with the high glass transitions seen for many electron-transport^[16] and hole-transport materials.^[20]

Figure 4.26 DSC thermograph of compound 53.

The CV data, figure 4.27, for compound **53** suggests, somewhat surprisingly, that rather than being an electron-transport material, due to the low ionisation potential and the large band-gap, material **53** may be more suitable as a hole-transport material. Unfortunately, the significant change in the oxidation process from cycle one to cycle two shows that the oxidation is irreversible, possibly suggesting that the material is electrochemically unstable. This irreversible behaviour is also seen for compound **49** leading to the conclusion that the central pyridazine moiety is unstable under these conditions.



Figure 4.27 Cyclic voltammagram of compound 53.

Comparison of the UV-vis absorption spectra of compounds **48** and **49** show the differences between the absorption spectra of the tetrazine of compound **48** and the pyridazine compound **49**. The first noticeable difference is the loss of a weak absorption at 550 nm, due to the loss of the  $\pi$ - $\pi^*$  transition of the tetrazine ring. The second noticeable difference is the blue-shift in the absorption of the peak at 301 nm of compound **49**. This is probably due to the loss of planarity between the central pyridazine ring and neighbouring phenyl ring, figure 4.30, With greater inter-annular twisting, as shown by molecular modelling using MM2 geometry optimisation. A higher degree of inter-annular twisting results in less  $\pi$ - $\pi$  overlap of the aromatic cores of adjacent aromatic rings.



Molecular modelling using MM2 geometry optimisation suggests that the most stable conformations of compounds **49** and **53** may be a V type structure, figure 4.29 and 4.30. This is caused by inter-annular twisting between one of the phenyl or pyridine rings and pyridazine ring and a planar configuration between the other phenyl or pyridine ring and the pyridazine ring, figure 4.30. This inter-annular twisting of one ring and not the other is difficult to explain. However, if the optimised geometries for both **49** and **53** are studied, it is clear that inter-molecular electrostatic repulsion between the hydrogen in the 2-position of the pyridazine and the hydrogen in the 2-position of the pyridazine and the hydrogen in the 2-position of the central benzene rings may cause a V-shaped outward splay of one side of the molecule. This then brings the opposite sides of the molecule closer together therefore forcing the twist in the rings at that side in order to reduce electrostatic interactions with the central benzene ring.

This predicted conformation allows a prediction of molecular stacking to be made, figure 4.31, for compound **49**. If this type of packing were indeed to take place it would explain the formation of ordered smectic phase seen during optical-polarising microscopy and DSC. Confirmation of this ordered packing could be obtained by X-ray diffraction, as the layer spacing could be calculated. These studies are ongoing.



Figure 4.29 MM2 optimised geometry of compound 53



Figure 4.30 MM2 optimised geometry of compound 49.



Figure 4.31 Proposed packing configuration of compound 49.

# 4.7 Scheme 9, 10 and 11.

The tetrazine compounds **60**, **61** and **64** were synthesised using similar techniques as seen in schemes 6, 7 and 8. These materials were also synthesised as potential electrontransport materials and red-emitting materials with the expectation of forming smectic or nematic mesophases.

Compound **61** exhibits a nematic phase, table 4.15. Compound **60** possesses a, second order, amorphous glass transition at 20 °C. No mesophase or amorphous glassy phase is observed for compound **64**. This behaviour may be partially explained by the fact that the phenyl ring gives a lower aspect ratio inhibiting the formation of the nematic phase or smectic phases. In contrast the biphenyl group present in compound **61** increases the aspect ratio, which increases the chance of formation of liquid crystalline phases.

C ₈	H ₁₇ O A	C ₆ H ₁₃	N C ₆ H ₁₃	C ₆ H.	13 C ₆ H ₁₃	A	_OC ₈ H ₁₇	
Ring A	Compound	Tg		Cr		Ν		Ι
C ₈ H ₁₇ O-	60	•	20	•	97	(•	-25)	•
	61		-	•	208	•	235	•
	64		-	•	136		-	•

 Table 4.15 Transition temperatures and melting points of compounds 60, 61 and 64.

Compound 61 has an interesting DSC thermograph, figure 4.32 and 4.33. The first trace shows the material on heating to 250 °C. It is on this heating cycle that the nematic to isotropic phase transition can be seen at 235 °C. Then on cooling a crystallisation peak can be seen at 155 °C, plate 4.14, followed by a crystal phase transition at 90 °C. On the second heating cycle the morphology of the material has clearly changed by being cooled from an isotropic phase. Two crystal transition peaks appear at 104 and 123 °C, that were not present on the first heating cycle. This behaviour is followed by the crystal to nematic transition at 200 °C, which is 8 °C lower than on the first heating cycle. The presence of the nematic phase is confirmed on repeated heating and cooling cycles by opticalpolarising microscopy, plate 4.12. To confirm that the changing DSC thermograph was because of a change in material morphology once cooled from an isotropic melt a second DSC was run with new material, figure 4.33. This time the material was heated to 220 °C, above the crystal to nematic transition but below the nematic to isotropic transition. This prevented a change in morphology occurring, which is seen in the DSC thermograph, figure 4.32. The nematic to crystal transition on both cooling cycles are observed at 176 °C and the crystal to crystal transition at 92 °C appears at the same temperature on both cycles. On heating two crystal to crystal transitions appear that were observed in the first DSC thermograph, figure 4.32, at 141 and 177 °C. However, the main difference with the second trace is the crystal to nematic transition, which occurs at the same temperature, 208 °C, on both cycles. The two heating cycles are not identical unlike the cooling cycles. On the second heating cycle no transitions are seen at 141 and 177 °C, but one is seen at 100 °C. This must be a more kinetically stable crystal phase as it occurs at 104 °C in the first trace and 100 °C in the second, so even though the material has not been cooled from an isotropic liquid it forms this crystal phase, which is seen on both occasions during optical-polarising microscopy. This is not the first material to exhibit this type of behaviour, as it is also seen for compounds 46, 47 and 48, all of which contain the tetrazine chromophore. This molecular reordering within different crystalline phases may be a common property induced by the presence of the planar tetrazine ring.



Polarised optical microscopy provided confirmation that compound **61** does indeed possess a nematic phase. Nematic droplets were observed on cooling from the isotropic liquid to a temperature just below the nematic clearing point, as shown in plate 4.12. The droplets then coalesced after further cooling to form a characteristic Schlieren texture with four and two-point disclinations.



Plate 4.12 Droplets representing the nematic phase of compound 61 formed on cooling from the isotropic liquid.



Plate 4.13 Part-crystallised part-Schlieren texture of the nematic phase of compound 61 at 177  $^{\circ}$  C.



Plate 4.14 Crystal structure of compound 61 at 129 °C formed on cooling from the Schlieren texture of the nematic phase.

Compound **64** does not exhibit an observable liquid crystal mesophase or an amorphous glass, figure 4.34. This is probably because the aspect ratio, is too low to induce mesophase formation. The addition of an extra phenyl ring in compound **61**, successfully induces a nematic mesophase, probably due to a higher aspect ratio, and a high melting point at 208 °C. The van der Waals forces of attraction between the aromatic cores are likely to be significant for compound **64**, which would also account for this increase compared to the melting point of compounds **60** and **64**.



Compound **60** exhibits an amorphous glassy phase, 20 °C, after cooling after the first heating cycle. No melting peak is seen on heating during the second cycle. The material is in a glassy state at room temperature. However, the glass is meta-stable, which is not seen in the DSC thermograph as no exothermic crystallisation peak is present, on heating, but crystallisation does occur gradually over time. Recrystallisation is complete after about seven days. Plate 4.15 shows the slow crystallisation of the amorphous glass. The crystal growth can be seen amongst the dark amorphous glass regions after five days.





Plate 4.15 Part crystal, part amorphous glass of compound 60 at room temperature.

As can be seen from the UV-vis absorption spectra, figure 4.36, there is very little difference in the absorption maxima of compounds **60**, **61** and **64** at 400 nm. This absorption peak is likely to be caused by a  $\pi$ - $\pi^*$  transition of the fluorene part of the aromatic core. Such a peak is observed in other fluorene-containing materials. The very weak absorption at 555 nm is due to the tetrazine part of the chromophore, figure 4.37. The absorption peaks that change with differing structure are the ones present at 296, 281 and 278 nm. This behaviour is attributable to differences in the nature of the aromatic ring in the pyridine, biphenyl and phenyl compounds **60**, **61** and **64**. The peaks are offset for clarity although there is no appreciable difference in the absorption intensity.



Figure 4.36 UV-vis absorption spectrum of compounds 60 (red) and 61 (green), 64 (blue).



**Figure 4.37** Enhanced UV-vis absorption spectrum of the  $\pi$ - $\pi^*$  transition of the tetrazine chromophore.

## 4.8 Schemes 11, 12 and 13.

Compounds **68** to **86** were synthesised in attempts to optimise the values of the physical properties of a well-researched compound **GJR130**, figure 4.38. Small structural variations in molecular structure should enable a study of the effect that these variations have on the physical properties of these materials, especially the quantum efficiency and also mesomorphic behaviour.



Figure 4.38 Chemical structure of reactive mesogen GJR130.

It was expected that altering the number of methyl substituents and changing their position would increase the intermolecular distance and thus reduce the degree of molecular aggregation and thereby lower the amount of quenching of excitons and improve the quantum efficiency of PL and EL, especially within a thin film. If this approach to molecular structural variation proved successful, it could be applied to other potentially useful materials in order to improve their quantum efficiencies. It would also have the effect of lowering the melting and clearing points of reactive mesogens due to steric effects attributable to the presence of the large methyl-groups in lateral positions in the molecular core, ^[21] making them easier to process during device fabrication.



Ring	R	Compound	Tg		Cr		N		Ι
$X = CH_3$ $Y = H$ $Z = H$	CH ₃	68	•	85	•	196	•	220	•
$X = CH_3$ $Y = H$ $Z = H$	C ₈ H ₁₇	72	•	35	•	121	•	137	•
$X = CH_3$ $Y = H$ $Z = H$	-(CH ₂ ) ₅ C-O	70	•	33	•	89		-	•
$X = CH_3$ $Y = H$ $Z = H$	-(CH ₂ ) ₁₀ C-O	71		-	•	105		-	•
$X = H$ $Y = CH_3$ $Z = H$	CH ₃	76		-	•	157	(•	125)	•
$X = H$ $Y = CH_3$ $Z = H$	C ₈ H ₁₇	80	•	17	•	111	(•	80)	•
$X = H$ $Y = CH_3$ $Z = H$	-(CH ₂ ) ₅ C-O	78		-	•	1	•	16	•
$X = H$ $Y = CH_3$ $Z = H$	-(CH ₂ ) ₁₀ C-O	79		-	•	-10	•	9	•
$X = H$ $Y = CH_3$ $Z = CH_3$	CH ₃	84	•	88	•	159	(•	111)	•
$X = H$ $Y = CH_3$ $Z = CH_3$	C ₈ H ₁₇	87	•	26	•	120	(•	95)	•
$X = H$ $Y = CH_3$ $Z = CH_3$	-(CH ₂ ) ₅ Ċ-O	86	•	22	•	<-40	•	30	•

 Table 4.16 Transition temperatures and melting points of compounds 68 to 87.

Compounds **72**, **80** and **87** differ only in the position of the methyl substituent. Compound **72** shows an enantiotropic nematic phase, whereas compounds **80** and **87** only posses a monotropic nematic phase. Compound **72** has the highest melting point, 121 °C, than those of compound **80**, 111 °C and **87**, 120 °C. This is surprising as the position of the methyl group in compound **72** should cause inter-annular twisting between the phenyl ring and thiophene. This twisting should lower the melting point of the compound because of a lower degree of planarity along the aromatic core, which should lead to weaker van der Waals forces of attraction. This behaviour is not observed for this material and others shown in table 4.16.



Figure 4.39 DSC thermograph of compound 80.




Plate 4.16 Nematic droplets exhibited by compound 72.



Plate 4.17 Schlieren texture of nematic phase of compound 80.



Plate 4.18 Room temperature Schlieren texture of a nematic glass of compound 86.

Figure 4.41 shows the glass transitions, melting points and clearing points of the comparable compounds **72**, **80**, **87** and **GJR092**. The first noticeable point is the absence of a glass transition for compound **GJR092** compared to the other materials. This can more than likely be explained by the greater viscosity of the laterally-substituted materials due to the steric effects of the additional methyl groups. The second point is that the materials with methyl substituents exhibit lower melting and clearing points

compared to those of the analogous material **GJR092**. Again this can be explained by steric hindrance resulting in weaker van der Waals interactions between neighbouring molecules. Finally the materials with the methyl substituent located next to the alkoxy position, i.e., compounds **80** and **87**, exhibit monotropic nematic phases, c.f., compound **68**, which possesses an enantiotropic nematic phase as well as a higher melting and clearing point. This is possibly due to a shielding effect by the methyl groups of the oxygen of the alkoxy group preventing it from participating in van der Waals interactions in an efficient way. Interestingly compound **80** with one methyl group. This trend seen in other comparable compounds, table 4.16, may be due to the increased symmetry of compound **87** leading to closer packing.



Figure 4.41 Graph showing the glass transitions, melting points and clearing points of compounds 72, 80 and 87.

The UV-vis absorption spectra, figure 4.46, of compounds **GJR092**, **72**, **80**, and **87** show only a slight variation in the absorption maximum between compound **72** and the compounds **80**, **87** and **GJR092**. This would be expected as the additional methyl groups have very little effect on the conjugation of the aromatic core so the band-gap should be

unaltered. However, the methyl group in compound **72** is positioned next to the thiophene ring. This induces inter-annular twisting, which in turn slightly reduces the degree of aromatic conjugation and so lowers the band-gap. Thus the initial absorption of compound **72** is the lowest of the four compounds. The absorption of compound **87** is the weakest compared to that of the other three materials. This phenomenon could be explained by a degree of steric-hindrance, caused by the additional methyl group, which may prevent aggregation between neighbouring chromophores.



Figure 4.42 UV-vis Absorption Spectrum of compounds GJR092 (blue), 72 (pink), 80 (red), and 87 (green) (approx. 0.0125% wt/wt, DCM).



Figure 4.43 MM2 optimised geometry of compound GJR130.



Figure 4.44 MM2 optimised geometry of compound 87.



Figure 4.45 MM2 optimised geometry of compound 80.



Figure 4.46 MM2 optimised geometry of compound 72.

Table 4.17 show	vs the solution	and thin-film	quantum	efficiencies	of compounds 7	0, 71,
72 and GJR130	).					

Compound	Photoluminescence	Photoluminescence	Photoluminescence	
	Quantum Efficiency	Quantum Efficiency	Quantum Efficiency	
	of Toluene Solution	of Film on Quartz (%)	of Film on Quartz	
	(%)		(after	
			photopolymerisation)	
			(%)	
70	69.3	18.6	16.9	
71	66.7	20.5	16.6	
72	64.3	20.6	-	
GJR130	71.1	22	28	

Table 4.17 Solution and thin-film quantum efficiencies of compounds 70, 71, and 72.

Figure 4.47 shows the differences in the photoluminescence spectrum of **GJR130** and **70** in solution, as thin-films and as a cross-linked thin-film.



Figure 4.47 PL spectrum of compounds 70 and GJR 130 in solution, thin-film and cross-linked thin-film.

The PL quantum efficiencies of compounds 70 and 71 are slightly higher than that of compound 72. This is probably due to the presence of the sterically bulky diene alkoxy chains creating space between neighbouring aromatic chromophores, thus producing less aggregation and so lowering the degree of internal quenching and improving the quantum efficiency. The quantum efficiency of the materials as thin-films is much lower than that of the same compounds in solution. This is because of the greater degree of aggregation between neighbouring chromophores in a solid film compared to in a solution. Compounds 70 and 71 are UV polymerisable so the quantum efficiency was also measured after an insoluble polymer network was created by photopolymerisation. In this case the efficiency of the polymer networks is lower than that of the unpolymerised thinfilms. This behaviour is inconsistent with previously reported results where an increase in efficiency after the photochemical crosslinking process has been explained by a possible reduction of the exciton diffusion coefficient or a reduction in the density of traps.^[22] This reduction in efficiency on crosslinking compounds 70 and 71 may be attributable to the fact that both compounds do not possess a mesophase, so polymerisation may have formed a highly aggregated polymer network increasing the amount of internal quenching of the photoluminescence present. It may also be due to a small amount of photochemical degradation as a result of intense UV laser absorption.

## 4.9 Scheme 14

A further aim of this research was to produce materials capable of emitting circularly polarised light from either a chiral nematic or a chiral smectic mesophase. Non-polymerisable chiral nematic compounds in the glassy state are required for organic lasers ^[23, 24] and for circularly polarised photoluminescence and electroluminescence ^[25] for applications in optical information displays.

Compound **77**, which is not mesomorphic, was used in the synthesis of compound **90** to try and realise a chiral nematic mesophase as a means of generating plane polarised light. One possible way to achieve this is to introduce a chiral centre in the long alkyl spacers of the aliphatic chains at each end of the chromophore. This can be achieved incorporating 3 $\beta$ -cholestanol attached to an alkyl spacer group in a similar base-esterification reaction used for the synthesis of compound **29**. The presence of two cholesteryl groups in trimers incorporating a non-mesomorphic core in the centre of the molecular structure has been used previously to induce smectic mesophases. ^[26]

Compound **90** is termed a trimeric thermotropic liquid crystal as the molecular structure consists of three mesogenic cores. Trimeric liquid crystals incorporating cholesterol have demonstrated interesting liquid crystal properties with high glass transition temperatures.^[26]



Table 4.18 Transition temperatures of compound 90.

Table 4.18 shows that the trimeric liquid crystal **90** exhibits a chiral nematic phase and a glass transition at significantly higher temperatures than those at which the chiral nematic glass, originally used to demonstrate highly-efficient emission of circularly polarised light, was observed. ^[25] The presence of the two optically-active cholestanyl groups should suppress any tendency of compound **90** to crystallise due to a combination of steric intermolecular interactions and a high degree asymmetry as well as inducing a very high viscosity essential for glass formation.



Figure 4.48 Chemical structure of compound MPAC3.

A similar material, **MPAC3**, synthesised in previous work by Aldred ^[7] exhibits a chiral smectic C phase as well as a chiral nematic phase. This is unusual for compounds containing fluorene moieties with two alkyl chains at the 9-position. The lack of a smectic C mesophase in compound **90** could be due to the methyl group present at the three position of the phenyl ring or the fact that the alkyl spacer of compound **90** is shorter. The effect of the methyl group, although not insignificant, is unlikely to have much effect on mesophase formation compared to the large bulky dihydrocholesteryl groups. However, this difference in mesomorphic behaviour may be explained when the alkyl spacer length connecting the three mesogenic units is compared between the two compounds. The compound shown in figure 4.48 has an even-even configuration, which

means the molecular structure results in a parallel orientation of the long molecular axis of the three mesogenic units. This is likely to promote the ordered stacking of the terminal aliphatic cores resulting in some form of well-ordered microphase separation. Compound **90** has an odd-odd configuration, figure 4.49. This may prevent the formation of well-ordered structure and prevent the formation of a smectic phase. This difference in conformations has previously been shown to effect the ordering of liquid crystal phases.^[27]



Figure 4.49 Schematic representation of even-even, odd-odd and even-odd conformation. [27]

Plate 4.19 shows the droplets formed on cooling compound **90** from the isotropic liquid phase to the chiral nematic phase. Dark isotropic regions between the droplets are visible and the droplets have characteristic curved surfaces showing that the phase is fluid and liquid-like. Brownian motion was also apparent on mechanical shearing.

Plate 4.20 shows a pseudo focal-conic fan texture, which is similar to that observed for the smectic A phase. Other areas of the sample showed a typical fingerprint texture, plate 4.21. The focal-conic fan structure shows the typical dark cross of the ellipse and hyperbola, when viewed through cross-polarisers.



Plate 4.19 Droplets of a chiral nematic phase of compound 90.



Plate 4.20 Pseudo focal-conic fan texture of chiral nematic phase of compound 90.



Plate 4.21 Finger-print texture of chiral nematic phase of compound 90.

Upon shearing of the glass cover slip whilst the pseudo focal-conic fan texture was present, plate 4.20, a Grandjean texture appeared, plate 4.22. This is typical of a chiral nematic phase that forms a pseudo focal-conic fan texture.



Plate 4.22 Pseudo focal-conic fan and Grandjean texture of a chiral nematic phase of compound 90.

As a new approach to OLEDs a device was fabricated using compound 90 as the emissive layer. The EL spectrum of the OLED device of compound 90 is shown in figure 4.50, which shows blue EL. The OLED was fabricated on a glass substrate, 25 mm x 45 mm x 1 mm, covered with an ITO transparent anode and a poly(3,4ethylenedioxythiophene) poly(styrenesulfonate) EL grade layer, 45 nm thickness. A thinfilm of compound 90 was spin-coated onto the PSS/PEDOT layer from toluene solution then baked at a temperature close to the clearing point. A hole-blocking layer of TPBi, 13 nm was deposited on top of compound 90, followed by the deposition of lithium fluoride, 0.6 nm then aluminium, 83 nm as a combined cathode. The OLED EL was measured after five minutes of electrode deposition. This is thought to be the first OLED fabricated using a trimeric liquid crystal. Although the efficiency and brightness of this particular OLED are poor, 0.01 CdA⁻¹ and 10 Cd/m⁻² respectively, the use of a trimeric liquid crystal incorporating three conjugated chromophores would substantially improve the device efficiency and brightness. A further development could be to combine three different chromophores to colour tune the EL output. The advantage of three separate chromophores is the possibility of inducing very high glass transition temperatures, which could conceivably lead to better device stability.



Figure 4.50 EL spectrum of an OLED using compound 90 as the emissive layer.

Molecular modelling using the MM2 geometry optimisation, figure 4.51, shows how the presence of the bulky dihydrocholesteryl groups help induce a high glass transition compared to similar materials, table 4.16. They act as large substituents that prevent close packing and allow the material viscosity to overcome the force of crystalliation.



Figure 4.51 MM2 optimised geometry of compound 90.

## 4.10 Scheme 15

Reactive mesogens with methacrylate groups at the end of the terminal alkoxy groups polymerise much more quickly than the corresponding materials with non-conjugated dienes as the polymerisable group at the end of the chains. Although methacrylate reactive mesogens have been synthesised previously none of these materials have been incorporated into a polymerised OLED by our research group so far. This led us to synthesise a methacrylate reactive mesogen compound **100**, table 4.19, to be incorporated into an OLED. The use of reactive mesogens with methacrylate moieties as the polymerisable group should lead to much shorter processing times for the fabrication of OLEDs containing such materials. This may in turn lead to less photochemical damage and to much longer device lifetimes.



Table 4.19 Transition temperatures of compounds GJR090, GJR092, GJR130, MPA134 and 100.

The DSC thermograph of compound **100**, figure 4.52, shows broad transition peaks and an unstable baseline, which seems to be due to the presence of a small quantity of sublimed sulphur in the aluminium pan. The traces of sulphur are present to allow multiple heating and cooling cycles to be carried out without polymerisation of the methacrylate groups. Optical microscopy without sulphur reveals that the phase transitions occur very quickly, with the formation of the nematic phase from nematic droplets at 90 °C occurring within 0.1 °C. This is a good indication that the material has a high purity and shows that the DSC transition values correlate very well with those seen using optical-polarising microscopy. The DSC thermograph clearly shows a second order

glass transition at 6  $^{\circ}$ C. However the glass is meta-stable as on heating the glass crystallises, shown by the large exothermic peak at 50  $^{\circ}$ C.



The Schlieren texture present, plate 4.23, on cooling of compound **100** formed from droplets during the transition from liquid to nematic phase.



Plate 4.23 Schlieren texture of the nematic phase of compound 100.



Figure 4.53 Graph showing transition temperatures of compounds GJR090, GJR092, MPA134 and 100.

Molecular modelling using MM2 geometry optimisation shows why compound 100 forms a nematic liquid crystal phase. The molecular core is completely planar, with a large aspect ratio, partly because of the long alkyl spacer connecting the methacrylate moiety to the conjugated aromatic core, figure 4.54.



Figure 4.54 MM2 optimised geometry of compound 100.

The OLED using compound **100** showed blue electroluminescence, figure 4.56, although brightness and efficiency were found to be poor, 300 cdm² and 0.2 cdA⁻¹ respectively, figure 4.55. The OLED was fabricated on a glass substrate, 25 mm x 45 mm x 1 mm, covered with an ITO transparent anode and a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) EL grade layer, 45 nm thickness. A thin-film of compound 100 was spin-coated onto the PSS/PEDOT layer from toluene solution then baked at a temperature close to the clearing point. A hole-blocking layer of TPBi, 12 nm, was deposited on top of compound 100, followed by the deposition of lithium fluoride, 0.6

nm, then aluminium, 57 nm, as a combined cathode. The OLED EL was measured after five minutes of electrode deposition. The poor data achieved from the OLED of compound **100** is mainly attributable to the de-wetting of the material when it was deposited by spin-coating on the device substrate. The de-wetting of the material prevented the polymerisation of compound **100** to form an insoluble polymer network during device fabrication. This inability to form a uniform thin layer made a significant contribution to the poor performance of the OLED containing the reactive mesogen **100** as the emissive layer.



Figure 4.55 The luminance-voltage plot and the current density-voltage of an OLED incorporating compound 100 as the emissive layer.



Figure 4.56 EL spectrum of an OLED using compound 100 as the emissive layer.

**Results and Discussion** 

## 4.11 Scheme 16, 17, 17a, and 17b.

The compounds **111**, **108** and **105** incorporating 1,4-disubstituted phenyl rings, 2,5disubstituted thiophene rings and 2,7-disubstituted-9,9-dialkyl fluorenes in the aromatic core. They differ only in the nature of central ring A, see table 4.20. They serve to demonstrate the control over the electroluminescent properties of liquid crystals by molecular design and synthesis. Compounds **111**, **108** and **105** were synthesised to provide red, green and blue emitting materials respectively, in order to realise a full colour RGB OLED. It was anticipated that the presence of an *E*-2,3-*bis*(4-thiophen-2-ylphenyl)but-2-enedinitrile chromophore, figure 4.57, in the centre of the molecule, ring A, see table 4.20, would produce a red emitting material. The thiophene moiety was included in the chromophore to induce planarity and lead to a significant red shift and to prevent the material exhibiting red/orange, rather than red emission.



Figure 4.57 Structure of E-2,3-bis(4-Thiophen-2-yl-phenyl)but-2-enedinitrile chromophore.

Compound **111** shows very weak photoluminescence in solution, figure 4.58. This was not unexpected as it has been reported elsewhere that the *E*-2,3-diphenyl-but-2-enedinitrile chromophore has a greater photoluminescence intensity in the solid state than in solution. ^[28] However, a thin-film of compound **111** also exhibits very poor PL characteristics, unlike the green and blue films, figure 4.59.

It has been previously reported that compounds incorporating bithiophene moieties next to a fluorene moieties may exhibit green luminescence. ^[10] Therefore compound **108** was designed as a green-emitter using an intermediate required for the synthesis of compound **111**.



Figure 4.58 Photograph of solutions of compounds 111 (red), 108 (green) and 105 (blue) under long-wave UV light (1% wt/wt in DCM).



Figure 4.59 Photograph of compounds111 (red), 108 (green) and 105 (blue) under long-wave UV light in thin-films.

Compounds **111**, **108** and **105** exhibit a nematic mesophase above a glass transition. The liquid crystalline transition temperatures of the compounds **111**, **108** and **105** depend on the nature of the chromophore A, see table 4.20. The clearing point decreases from compound **111** to **108** to **105**, as does the glass transition temperature, table 4.20.



Table 4.20 Transition temperatures of compounds 105, 108 and 111.



Figure 4.60 Graph showing the glass transition, melting point and clearing points of compounds 105, 108 and 111.

Figure 4.61 shows the DSC thermogram of compound **105**. The first heating cycle shows a large melting peak for the crystal to nematic phase transition at 131 °C. The material

clears to form an isotropic liquid at 166 °C. On the second heating cycle the second order transition of the glass transition can be seen at 41°C. However, unlike compound **111**, the glass state is meta-stable as crystallisation occurs on heating to 77 °C, as evidenced by a large exothermic peak. This is confirmed by the presence of a second melting peak of the crystal to nematic transition, which shows the material has crystallized to form a solid. On cooling the nematic phase appears at 163 °C, but no crystal phase appears on cooling as the nematic mesophase forms a glassy phase instead of recrystallising.







Plate 4.24 Nematic droplets of compound 105.



Plate 4.25 Schlieren texture of a nematic phase of compound 105.

Figure 4.62 shows the DSC thermograph of compound **108**. The first heating cycle shows a large melting peak for the crystal to nematic phase change at 206 °C. The material clears to form an isotropic liquid at 214 °C. On cooling the nematic phase appears at 210 °C, but no crystal phase appears on cooling as the nematic mesophase forms a glass. On the second heating cycle the second order transition of the glass transition can be seen at 54 °C. However, unlike compound **111**, the glass state is meta-stable as crystallisation occurs on heating, 120 °C, seen by a large exothermic peak. This is confirmed by the presence of a second melting peak of the crystal to nematic transition, which shows the material has crystallised to form a crystalline solid.



Figure 4.62 DSC thermograph of compound 108.



Plate 4.26 Room temperature Schlieren texture of a nematic glass of compound 108.

Figure 4.63 shows the DSC thermograph of compound **111**. The first heating cycle shows two crystal to nematic peaks. The second peak is much larger than the first peak. The smaller peak is probably due to the presence of a small quantity of the *cis* compound. This is expected as it has been previously reported that the central fumaronitrile moiety can from the less stable *cis*-configuration during the purification procedure on contact with silica gel. ^[28] Once this product has melted it is likely that it forms the more thermodynamically favorable *trans* compound, whilst in the fluid nematic phase. This

behaviour is confirmed by observing at the clearing point. Only one peak is evident and the smaller melting peak is not observed on the second heating cycle. On cooling a supercooled nematic phase appears at 238 °C, but no crystal phase appears on cooling and the nematic phase forms a glass directly. The second heating cycle shows a clear second order transition in the form of a glass transition at 74 °C. This appears to be a stable glassy phase as no crystallisation peak is observed above this peak and no melting peak is observed. However, the nematic to isotropic peak is seen as expected as the glass clears to form an isotropic liquid. The amorphous state present is not typical of redemitting fluorophores as they are prone to aggregation due to either attractive dipoledipole interactions or effective intermolecular  $\pi$  stacking. ^[29] Thus this material possesses favourable processing properties, even if the transition temperatures are high. This morphological behaviour is particularly favourable for device processing in that the amorphous glass formed is a nematic glass, shown by plate 4.28.





Plate 4.27 Nematic droplets of compound 111 at 239 °C.



Plate 4.28 Room temperature Schlieren texture of a nematic glass of compound 111.

So far only the ionisation potential of compound **111** has been measured by cyclic voltammetry. As compounds **108** and **105** are very similar to previously recorded materials, measuring the optical band gap using the optical absorption spectrum allowed the electron affinity to be calculated, table 4.21. The narrow band-gap, 2.05 eV, is typical of a red-emitting material. This low value also makes compound **111** suitable as a

material for organic photovoltaics. Very few organic materials have a band-gap lower than 2 eV meaning that only around 30% of solar radiation is absorbed. However, **111** has one of the lowest band-gaps of the materials synthesised during this thesis. At an initial absorption of 600 nm a material should have a band-gap of 2 eV. This is confirmed when the UV-vis absorption of compound **111** is studied. The broad absorption peak begins at 590 nm, meaning a band-gap of 2.05 eV would be expected.

Compound **111** is electrochemically stable according to the cyclic voltammogram, which shows that the electroreduction and electrooxidation processess are reversible. The electron-accepting nature of the cyano groups helps to raise the EA of compound **111**, which gives it a relatively small band-gap compared to other materials synthesised in this thesis.

Chromophore A	Compound	IP (eV)	E _g (eV)	EA (eV)
S NC	111	5.36	2.05	3.31

 Table 4.21 Energy levels of compound 111.

The UV-vis absorption spectra of compounds **105**, **108** and **111** show a distinct variation in the absorption spectra of each compound. This is expected as the central chromophore has been altered to produce materials for a RGB OLED. Compound **111** has a very wide absorption spectrum, which covers the whole of the visible region from 600 to 300 nm. The initial absorption spectrum of compound **108** begins at 470 nm. This means it will have an approximate band-gap of 2.6 eV, which is typical of a green-emitting material. The initial absorption spectrum of compound **105** begins at 425 nm meaning it will have an approximate band-gap of 2.9 eV. This is a small value for a blue-emitting material, when compared with other blue-emitters, such as compound **14**, which has a band-gap of 3.18 eV. This behaviour is explained when the photoluminescence spectrum is studied. A second green shoulder appears, so compound **105** is not actually a true blue-emitter, although it appears so to the human eye, figure 4.62.



Figure 4.64 UV-vis absorption spectrum of compound 111 (blue) 108 (red) and 105 (green).

Molecular modelling using MM2 geometry optimisation, figure 4.65, 4.66 and 4.67, clearly shows why each compound exhibits a nematic mesophase. The side-on-view of each molecule shows extended planarity along the aromatic core. This large aspect ratio leads to the formation of a nematic mesophase. However, the presence of the orthogonal alkyl chains at the 9-position of the fluorene core prevents the formation of any more ordered mesophases, such as a smectic phase, being present. It is not surprising that compound **111** is the only one of all three compounds that exhibits a stable amorphous glassy phase. The difference between compound **111** and **108** and **105** is the pronounced bend in the aromatic core of the molecule, when viewed after MM2 geometry optimisation. This probably has the effects of increasing the viscosity due to steric-effects the inhibition of intermolecular  $\pi$ - $\pi$  stacking and the prevention of crystallisation on heating. ^[29]



Figure 4.65 MM2 optimised geometry of compound 105.





Figure 4.66 MM2 optimised geometry of compound 108.



Figure 4.67 MM2 optimised geometry of compound 111.

The device characteristics of three separate OLEDs fabricated incorporating either compound **105**, **108** or **111** are shown in figures 4.68 to 4.72.

The OLED for compound **105** was fabricated on a glass substrate, 25 mm x 45 mm x 1 mm, covered with an ITO transparent anode and a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) EL grade layer, 45 nm thickness. A thin-film of compound **105** was spin-coated onto the PSS/PEDOT layer from toluene solution then baked at a temperature close to the clearing point. A hole-blocking layer of TPBi, 15 nm, was deposited on top of compound **105**, followed by the deposition of lithium fluoride, 0.6 nm, then aluminium, 80 nm, as a combined cathode. The OLED EL was measured after five minutes of electrode deposition.



Figure 4.68 EL spectrum of an OLED using compound 105 as the emissive layer.



Figure 4.69 The luminance-voltage plot and the current density-voltage of an OLED incorporating compound 105 as the emissive layer.

Compound **105** shows blue EL, figure 4.68, although a large green-shifted shoulder gives rise to blue-green EL emission. This may be due to the increased planarity of this aromatic core compared to that of regular polyfluorene due to the presence of the thiophene moiety. The brightness of emission of 30 cd m⁻² is poor, 4.69 This may be due

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to poor device fabrication or crystallisation of the mesophase, while under working conditions due to the low glass transition of 41  $^{\circ}$ C.

The OLED using compound **108** was fabricated on a glass substrate, 25 mm x 45 mm x 1 mm, covered with an ITO transparent anode and a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) EL grade layer, 45 nm thickness. A thin-film of compound **108** was spin-coated onto the PSS/PEDOT layer from toluene solution then baked at a temperature close to the clearing point. A hole-blocking layer of TPBi, 15 nm, was deposited on top of compound **108**, followed by the deposition of lithium fluoride, 0.6 nm, then aluminium, 80 nm, as a combined cathode. The OLED EL was measured after five minutes of electrode deposition.



Figure 4.70 EL spectrum of an OLED using compound 108 as the emissive layer.



Figure 4.71 The luminance-voltage plot and the current density-voltage of an OLED incorporating compound 108 as the emissive layer.

Figure 4.71 shows that the OLED incorporating compound **108** has a much higher, 600 cd m⁻², brightness compared to that of the OLED incorporating compound **105**. The higher brightness could be attributable to a higher glass transition temperature of 54 °C preventing crystallisation during device operation. The EL spectrum shows broad green emission similar to that seen from OLEDs using analogous materials as the emissive layer, figure 4.70. ^[10]

It has been reported previously that the fumaronitrile moiety shows very poor EL, although this does have advantages in allowing compound **111** to be incorporated into a White-Light Organic Light-Emitting Diode, see later. However, this means no recordable EL is seen so the EL spectrum is not shown for compound **111**.

Figure 4.72 shows the typical OLED configuration used for compounds **105**, **108** and **111**.



Figure 4.72 Device structure for OLED using either compounds 105, 108 or 111, as emissive layer.
### 4.12 White-Light Organic Light-Emitting Diodes

Signifcant research effort has focused on the development of White-light Organic Light-Emitting Diodes (WOLEDs) over the past decade.^[30] They are seen as an important application for display technologies and offer potential applications as novel lighting sources that are less expensive and more efficient than conventional incandescent and fluorescent illumination sources. ^[31-34] Several routes have been utilised to produce an emission spectrum that covers most of the visible spectrum, necessary to achieve whitelight. They include stacked ^[33] or multilayer ^[35] OLED structures with separated molecular emitters. This has been improved recently to incorporate three different emitters mixed together in one emissive layer to obtain stable colour balance at a high external EL and OE.^[36] However, this method requires careful adjustment of concentrations because of energy transfer from the higher-energy blue emitter to the lower-energy green emitter as well as green to red. WOLEDs have also been developed using many kinds of polymer-based materials such as polyaniline, ^[37] polymer blends, ^[38] doped polymers, ^[39] co-polymers ^[40] and side-chain polymers. ^[41] White light emission has been generated by eximer/exiplex emission from small molecules ^[42] and polymers. ^[43] Hybrid inorganic/organic WOLEDs ^[44] and white-light emission for assemblies of iridium and europium complexes have also been reported. ^[45] Mixtures of liquid crystalline oligomers in the glassy state have been used to generate white-light and polarized white-light by Förster energy transfer in LC-WOLEDs. ^[46]

A WOLED was fabricated using binary mixtures of electroluminescent (blue and red) liquid crystals synthesised during this thesis and other analogous materials. This new approach to WOLEDs uses insoluble electroluminescent liquid crystalline polymer networks. ^[47] The materials used were compounds **86**, figure 4.77 and **111**, figure 4.78. Compound **86** is a reactive mesogen, which when polymerised forms a highly cross-linked electroluminescent network. Compound **111**, is a nematic liquid crystal that forms a stable nematic glass at room temperature. Compound **111** incorporates a central fumaronitrile moiety, which has shown to be a very efficient chromophore for red-emitting materials. ^[28] The blue and red electroluminescent materials were originally

combined in the hope of achieving red electroluminescence from compound **111** doped in **86** by Förster energy transfer.





Figure 4.74 Chemical structure of compound 111.

The binary nematic mixture formed a glassy nematic phase at room temperature on cooling from the fluid nematic phase, which spontaneously orients on suitable alignment surfaces. Complete miscibility of the mixture components is shown in figure 4.75, which shows a good correlation between the experimental values and the best fit. The mixtures also show a typical Schlieren texture characteristic of a nematic phase when viewed between crossed polarisers, plate 4.29. The mixtures are homogeneous and exhibit no phase separation across the mixture phase diagram.



Figure 4.75 Miscibility diagram of binary mixtures of compound 86 and 111.



Plate 4.29 Typical Schlieren texture of a 7:1 binary mixture of compounds 86 and 111.

The electroluminescence spectrum of the glassy mixture of compound **111** (12%) and **86** (88%) for different values of applied voltage is shown in figure 4.76. The OLED was fabricated on a glass substrate, 25 mm x 45 mm x 1 mm, covered with an ITO transparent anode and a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) EL grade layer, 45 nm thickness. A thin-film of the mixture was spin-coated onto the PSS/PEDOT layer from toluene solution then baked at a temperature close to the clearing point. A hole-blocking layer of TPBi, 15 nm, was deposited on top of the mixture,

followed by the deposition of lithium fluoride, 0.6 nm, then aluminium, 80 nm, as a combined cathode. The OLED EL was measured after fifteen minutes of electrode deposition The emission covers most of the visible spectrum and is white, broad and does not vary with applied voltage as often occurs for mixtures of small molecules and polymers. The peak EL intensity corresponds to yellow light ( $\lambda_{max} = 575$  nm) with maximum sensitivity to the human eye. The CIE coordinates (0.362, 0.358) of this mixture are shown in figure 4.77 as D1. The reference white point corresponds to perfect white light and the hollow square represents emission from a white, fluorescent light from a lamp. The purity of the white light emission from the 1:7 mixture is superior to that of the fluorescent light reference.



Figure 4.76 EL spectrum of binary mixture of compound 86 and 111.



Figure 4.77 CIE coordinates of binary mixtures D1, D2, D3, White-light and Fluorescent light.

Figure 4.78 shows the device characteristics of the white single-pixel LC-WOLED fabricated by spin-casting and photolithography of the binary mixture of **111** and **AW001**. The LC-WOLED has a turn-on voltage of 4.0 V and a linear response with increasing voltage. The luminance is 190 cd m⁻² at 8 V and 850 cd m⁻² at 14 V. The inset shows the maximum device efficiency is 0.4 cd A⁻¹. This level of efficiency is too low for practical applications. However, it does establish proof of principle for a new approach to white electroluminescence based on liquid crystalline polymer networks. Significant improvements in performance can be realistically expected by better matching of the energy levels of device-components, more efficient blue-emitting RMs, a better electron-injecting layer and superior device fabrication procedures. ^[48]



Figure 4.78 The luminance-voltage plot and the current density-voltage for the cross-linked nematic polymer network formed by photochemically polymerising the compounds 111 (12%) and AW001.

Figure 4.79 shows that the EL spectrum from the non-polymerised nematic mixture of **111** and **AW001** is not a linear combination of the EL spectra from the individual components. Although the EL spectrum is white, the PL spectrum from the mixture is red because of Förster energy transfer from **AW001** to **111**. The intermediate EL spectrum may indicate carrier-induced excimer/exciplex formation. This interesting phenomenon is under further investigation.



Figure 4.79 The electroluminescence emission of (a) the blue-emitting compound AW001
(b) the red-emitting component 111 and (c) the non-polymerised nematic mixture 111 (12%) and AW001 (88%).

Figure 4.80 shows the polarised EL spectrum of the cross-linked nematic polymer network formed by photochemically polymerising the nematic mixture of compounds **111** and **AW001**. Alignment is achieved by mechanically rubbing the underlying PEDOT layer. A maximum polarisation ratio  $EL_{\parallel}/EL_{\perp}$  of 9:1 at 600 nm is observed where  $EL_{\parallel}$  and  $EL_{\perp}$  refer to the analyser aligned parallel and perpendicular to the rubbing direction of the alignment layer. The  $EL_{\parallel}/EL_{\perp}$  ratio integrated over the whole spectrum is 8:1. Although these values are not very high in absolute terms they are sufficiently large to allow polarised emission with a very high polarisation ratio, 100:1, to be fabricated using an additional clean up polariser. These are much cheaper than conventional polarisers and offer a cost-effective approach to WOLEDs with polarised emission. Analogous materials have demonstrated a polarisation ratio of 30:1 using green light-emitting liquid crystals orientated on rubbed PEDOT ^[49] and so significant improvements can be expected.



Figure 4.80 Polarised EL from the cross-linked nematic polymer network formed by photochemically polymerising the nematic mixture of 111 (12%) and AW001. a) and b) show EL∥ and EL⊥respectively.

The actual device configuration is shown in figure 4.81.



Figure 4.81 Device structure for WOLED using a binary mixture of compounds 86 and 111, as emissive layer.

# **Organic Photovoltaics**

## 4.13 Scheme 18.

Perylene bis-imides were initially used as red vat dyes and then as pigments. This is due to their migrational stability, thermal stability and chemical inertness. ^[50] More recently perylene bis-imides have been found to be some of the best *n*-type semiconductors, which is related to the high electron affinity of the perylene moiety. ^[51, 52] The characteristic properties of perylene bis-imides has also led to investigation of perylene as suitable materials for photovoltaics. ^[53]

Perylenes are suitable candidates for use as *n*-type liquid crystalline semiconductors in photovoltaic devices. The perylene moiety could also be incorporated into a reactive mesogen so that a polymer network could be formed giving all the advantages already discussed.

Charge separation is achieved in solar cells by ionisation of the photogenerated exciton at a heterointerface between electron-donating material with a low ionisation-potential and electron-accepting species with a high electron-affinity. This lead to the synthesis of compound **117**, which is a liquid crystalline perylene bis-imide. It exhibits an enantiotropic nematic phase, table 4.22, and a glassy nematic phase when quenched.



**Table 4.22** Transition temperatures of compound 117.

Optical-polarising microscopy shows the presence of nematic droplets on cooling from the isotropic liquid to the nematic phase, which coalesce to form a Schlieren texture, plate 4.31, with two and four point brush disclinations. It can be seen that the droplets are circular and fluid, which is typical of a nematic mesophase as it forms from an isotropic liquid, plate 4.30.



Plate 4.30 Droplets of a nematic phase on cooling from an isotropic liquid of compound 117.



Plate 4.31 Schlieren texture of a nematic phase of compound 117 at 200 °C.

Molecular modelling using MM2 geometry optimisation shows compound **117** has a *trans*-configuration in relation to the perylene moiety, figure 4.82. This bend in the molecule and the sterically-hindered alkyl chains at the 9-position of the fluorene is likely to be sufficient enough to disrupt efficient  $\pi$ - $\pi$  stacking of the perylene moiety which has the effect of lowering the melting point and allowing the formation of a nematic phase due to the aspect ratio, of the molecule. This is significantly larger compared to that of the perylene bis-imide synthesised in scheme 20, compound **127**.



Figure 4.82 MM2 optimised geometry of compound 117.

Figure 4.83 shows the UV-vis absorption spectrum of compound **117**. The spectrum shows absorption across most of the visible spectrum, 300 - 550 nm. The three absorption peaks seen at 527, 491 and 455 nm are typical of the  $\pi$ - $\pi$ ^{*} absorption bands of

the perylene bis-imide core. ^[54] The absorption maximum at 527 nm with a stronglypronounced vibronic fine structure is observed, which belongs to the  $S_0$ - $S_1$  transition, with a transition dipole moment along the long molecular axis. This agreement with previously reported peak positions with other substituents on the imide nitrogen is explained by the presence of nodes in the HOMO and LUMO at this position. ^[55]

Compound **117** shows no fluorescence, which has also been seen previously in perylene bis-imides and is an indication of the intense aggregation present between the perylene chromophores. ^[54]



Figure 4.83 UV-vis absorption spectrum of compound 117.

### 4.14 Scheme 19.

Compound **124** was synthesised as an alternative photovoltaic material. It was expected a liquid crystal phase or glass transition would be formed.



 Table 4.23 Melting point and glass transition of compound 124.

The DSC thermograph of compound **124**, figure 4.84, shows a crystal to isotropic transition, 244 °C, which is confirmed by optical-polarising microscopy. On cooling no crystallisation peak is observed and an amorphous glass is formed from the isotropic liquid. This is seen on the second heating cycle by a small shift in the baseline, 130 °C. No melting peak is seen at 244 °C on the second heating cycle. This shows that the glassy state is stable to heating and no exothermic crystallisation peak is observed. Although the melting point is high compound **124** still forms a stable amorphous glass when spin cast in thin-films, which allows device fabrication to be carried out at room temperature when compound **124** is spin cast from a suitable solvent such as toluene.



Cyclic voltammetry was used to measure the ionisation potential of compound **124**.

Measuring the optical absorption spectrum, then allows the electron-affinity to be calculated, table 4.24. The CV data shows the high electron-affinity and low band-gap make compound **124** a suitable material for use in a photovoltaic device.

Compound	IP (eV)	E _g (eV)	EA (eV)	
124	5.38	2.12	3.26	

 Table 4.24 Cyclic voltammetry results for compound 124.

Molecular modelling using MM2 geometry optimisation, figure 4.85, of compound **124** shows again that the compound forms a *trans*-like configuration. As expected the alkyl chains at the 9-position of the fluorene core lie orthogonal to the core, which increases the inter-molecular spacing. No mesophase could be determined for compound **124**. This behaviour is due to the lower aspect ratio compared to compound **117**. If the methoxy group was replaced with a longer alkyl chain or alkyl spaced polymerisable group this would increase the aspect ratio and possibly induce a mesophase. Work is ongoing to test this hypothesis.



Figure 4.85 MM2 optimised geometry of compound 124.

The UV-vis absorption spectrum of compound **124**, figure 4.86, shows a broad absorption over most of the visible region, 250 - 560 nm, which makes these perylene materials potentially suitable compounds for use in organic photovoltaics.



Figure 4.87 shows the UV-vis absorption spectra of compounds **117** and **124**. The two materials have almost identical spectra between 450 and 550 nm. This is due to the absorption of the perylene core, which is present in both compounds, hence giving a very similar absorption pattern. The difference between the spectra of the two compounds

appears below 450 nm. This difference is caused by the variations in the chromophore attached to the perylene. As MM2 geometry optimisation shows, there is more interannular twisting between the perylene core, phenyl ring and fluorene in compound **117**, than that between the perylene core and the thiophene and fluorine moieties in compound **124**. This additional twisting slightly lowers the degree of conjugation along the backbone of the molecule and results in a blue shift of the maximum absorption peak to 369 nm from 379 nm observed for compound **117**.



Figure 4.87 UV-vis absorption spectrum of compounds 117 and 124.

**Results and Discussion** 

#### 4.15 Scheme 20.

Compound **127** was synthesised as an alternative to compound **MPA340**, table 4.25, as the melting point of compound **MPA340** is high, which makes device processing difficult. Longer dodecyl alkyl chains were attached to the 9-position of the fluorene fragment in compound **127.** This was designed to lower the melting point to make device processing easier and to induce an amorphous glassy state and to alter the charge separation properties by altering the diffusion length as an electron-accepting species. The melting point should be lowered as the greater alkyl chain length will reduce the van der Waals forces of attraction between the molecular cores. The charge-carrier diffusion path-length will also be altered as the alkyl chains lie orthogonal to the planar fluorene core, figure 4.89. This increases the intermolecular spacing between the fluoreneperylene core, which adopts a slight *trans*-configuration, which disfavours close-packing, for compound 127 compared to MPA340. This interpretation is confirmed when the optical behaviour of thin-films of each compound are compared. MPA340 is maroon in colour, whereas compound 127 is red. This behaviour suggests a greater degree of  $\pi$ - $\pi$ stacking within the material for compound **MPA340**, which leads to a greater degree of internal quenching. Thus MPA340 appears darker in colour than compound 127.



Table 4.25 Melting points of compounds 127 and MPA340.

The DSC thermograph of compound **127** shows a first-order transition at 201 °C. This is a melting peak and no mesophase is observed, on cooling. The recrystallisation peak appears at 169 °C. The material has no amorphous glassy phase, so is unsuitable for device fabrication. However, it has been found that compound **MPA340** forms an amorphous glass, when quenched from an isotropic liquid in thin films, which also seems to be the case for compound **127**.







Figure 4.89 MM2 optimised geometry of compound 127.



Figure 4.90 MM2 optimised geometry of compound MPA340.

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## **5.** Conclusions

Novel liquid crystalline materials, including reactive mesogens to be used as lightemitting, charge-transporting or charge-accepting materials for use in OLEDs and or photovoltaic devices have been synthesised. Such compounds with photopolymerisable end groups could be cross-linked to form an insoluble polymer network that allows the fabrication of multi-layer OLEDs or phase-separated photovoltaic devices. Some materials synthesised are capable of being aligned in the liquid crystalline state. This has allowed some materials to be aligned to allow the generation of linearly or circularly polarised light.

Perylenes show promising charge-transport properties as well as having the ability to form liquid crystalline phases. Therefore, compound **6** was synthesised incorporating branched alkyl chains in a perylene tetraester material. Compound **6** has a lower melting point than an analogous material and produced a soluble material for deposition by spin-coating. The material also exhibited high electron-transport properties making compound **6** a possible liquid crystalline electron-transport material.

The incorporation of perfluorinated chains in the 9-position of a fluorene moiety led to the synthesis of compound **14**, then subsequently compound **18**. Unfortunately the perfluorinated chains did not have the desired effect of significantly altering the energy levels or charge-mobility of the compound. This was also compounded by the fact that the nematic liquid crystal phase expected was not present. Therefore the self-assembling properties required for good charge mobility are not present. This shows perfluorinated chains are possibly not suitable when incorporated in the 9-position of a fluorene moiety as liquid crystalline electron-transport materials.

The charge-transporting properties of benzothidiazoles are well known. Therefore compound **30** was synthesised. However, the compound did not possess a liquid crystal phase, although a meta-stable glassy phase was present that could be used to form an insoluble amorphous polymer network. The compound was synthesised as a

yellow emissive material in an OLED. The compound does possess yellow PL under a UV lamp, although the actual PL and EL was not measured.

The charge-transporting properties of benzothidiazoles are well known. Therefore this led to the synthesis of an analogous material incorporating the benzoxadiazole moiety with an oxygen atom in place of the sulphur atom in the heterocyclic ring, compound **42**. The material as expected possessed a smectic A liquid crystal phase similar to the analogous benzothiadiazole. The smectic A liquid crystal range was increased when compared to the analogous benzothiadiazole. The PL emission of the benzoxadiazole was red-shifted compared to the benzothiadiazole. A change in the energy levels of the benzoxadiazole was also seen. Therefore compound **42** is seen as a more suitable liquid crystalline electron-transport material than the analogous benzothiadiazole.

Heterocyclic materials containing nitrogen atoms have been shown to exhibit suitable charge-transporting properties. A number of materials were synthesised incorporating nitrogen heterocyclic rings in order to study the effect of the presence of a number of nitrogen atoms on the liquid crystalline properties and the energy levels of the materials produced. As expected an increase in the number of nitrogens in a heterocycle changed the liquid crystal transition temperatures. An increase in the number of nitrogen atoms increased the electron-affinity. This led to the synthesis of a tetrazine, compound **47**, with high electron-affinity and relatively low smectic C liquid crystalline transition temperatures. This material shows very little PL or EL due to the high aggregation of the tetrazine aromatic cores, but the material could be useful as a liquid crystalline electron-transport material.

A Siamese type structure was synthesised in order to explore the liquid crystalline properties of these types of materials and their electron-transporting properties. Compound **49** exhibits an ordered smectic phase and interesting charge-transport properties. The energy levels of the material suggests that the material is actually more suitable as a hole-transport material than the expected electron-transport material.

The effect of incorporating methyl groups into a fluorene-containing molecular core on the liquid crystalline properties of these materials was studied. The intention was

to produce materials with a low degree of aggregation of neighbouring chromophores. This should in turn result in high PL and EL efficiency, although this effect was not seen when the PL quantum efficiency was compared to an analogous material. The effect of varying the position and number of the methyl groups on the liquid crystalline properties was studied. The nature of the alkoxy-chains attached in a terminal position to the aromatic core was varied in order to study its effect on glass formation and the liquid crystalline behaviour of these materials. The liquid crystalline behaviour of the materials synthesised was unexpected as the inter-annular twisting expected in compounds **68**, **70**, **71** and **72** did not lower the melting and clearing points of the nematic phase present compared to analogous materials synthesised. This has been explained by the shielding effect of the methyl groups on the alkoxy-chains preventing the oxygen atom participating in van der Waals interactions. This has shown to be a useful tool for lowering liquid crystal transition temperatures in our materials that possess alkoxy-chains attached in a terminal position.

The first OLED fabricated using a chiral nematic trimeric liquid crystal, compound **90**, was obtained. The OLED proved to have low brightness and efficiency but showed that trimeric LC-OLEDs producing circularly polarised light is possible.

Three liquid crystalline materials were synthesised, which would facilitate the fabrication of a full-colour LC-OLED. Compounds **105**, **108** and **111** vary only in the nature of the central aromatic moiety. This structural change is sufficient to red-shift emission from blue to green to red, shown by the EL from the OLEDs fabricated. These structures exhibited nematic liquid crystal phases and high glass transition temperatures.

The combination of compound **86** and **111** as a binary nematic mixture gives unexpected white-light when incorporated into an OLED as the emissive layer. The nature of the white-light obtained is not voltage dependent and not due to Förster energy transfer. The cross-linked nematic polymer mixture of compound **AW001** and **111** when incorporated into an OLED as the emissive layer on a rubbed PEDOT layer generated polarised white-light emission with a polarisation ratio of 9:1. This

approach to WOLEDs involves deposition from solution and patterning by photolithography and potentially by inkjet printing.

Three perylene *bis*-imides were synthesised as electron-acceptors for use in organic photovoltaics. Perylene *bis*-imides were chosen because of the perylene broad UV-vis absorption spectrum and high-electron affinity. Perylene *bis*-imides could also be used as an electron-transport layer in OLEDs. One of the materials, compound **117**, exhibited a nematic liquid crystal phase. This could improve the charge-mobility properties of the material due to its self-assembling properties, although its liquid crystal transition temperatures are high causing device processing problems. The high transition temperatures are particularly relevant as the material is not a reactive mesogen.

## Appendix A

#### **Publications**

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