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Asymmetric Fluorinated Dimers for Dual Frequency Liquid Crystal Mixtures: Synthesis, Mesomorphism & Electro-optic Properties

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by

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Summary

Dual frequency liquid crystal mixtures are a technology used to achieve faster response times in electro-optical devices. At low driving frequencies the material acts as a positive dielectric, while at high frequencies the materials switches to a negative dielectric due to dielectric relaxation. This allows for voltage driven reorientation of the liquid crystal in two directions, thereby increasing the device switching speed.

This project aimed to synthesise and investigate the mesomorphic properties of a series of asymmetric liquid crystal dimers targeting dual frequency mixtures. The targeted structures feature two mesogenic arms linked by a flexible methylene spacer. One section of the dimeric mesogen has lateral fluorine substituents and the other section has terminal fluorination, to generate dipoles both perpendicular and parallel to the liquid crystal director. The aim is to synthesise materials with one section of the mesogen contributing positive dielectric anisotropy at low driving frequency and the other section contributing negative dielectric anisotropy at high frequencies.

The synthesis of twelve systems is presented in this thesis, these dimers vary in core length, terminal chain and parity of the spacer. The even lengthed spacers give linear shaped dimers, while the odd lengthed spacers give bent shaped materials. Synthesis proceeded through a number of conventional synthetic procedures including low temperature lithiations and Suzuki cross-couplings. Structure and purity was confirmed using NMR, MS, EA and HPLC, with the targeted materials being of high purity. The mesomorphic behaviour was investigated through a combination of optical polarising microscopy, differential scanning colorimetry and x-ray diffraction techniques. The materials exhibit nematic, smectic A, smectic C and in one case a more highly ordered nematic phase (N_x) . Two of the targeted systems, one linear shaped and the other bent shaped both with asymmetric core lengths were further investigated as mixtures with each other and the stability of the N_x phase in mixtures is discussed. For the same two dimers electro-optic measurements were conducted to measure birefringence and to investigate the voltage and frequency response of the materials and it was found that the linear dimer has relatively low crossover frequency making it viable for dual frequency liquid crystal mixtures.

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List of Abbreviations & Symbols

Abbrevi	ations	ITO	indium tin oxide
5CB	4-cyano-4'-pentylbiphenyl	LC_x	unidentified liquid crystal phase
<i>n</i> -BuLi	<i>n</i> -butyllithium	LCD	liquid crystal display
BCO	bicyclooctane	MTC5	2',3'-difluoro-4,4"-dipentyl-
CDCl_3	deuterated chloroform		1,1,4,1 -terpnenyi
CB7CB	4',4'''-(heptane-1,7-diyl)bis([1,1'- biphenyl]-4-carbonitrile)	N N*	nematic phase chiral nematic phase
СН	trans-cyclohexane	N_{cd}	chiral domain nematic phase
Cr	crystal phase	N_{TB}	twist-bend nematic phase
CRT	cathode ray tube	N_u	uniaxial nematic phase
DCM	dichloromethane	N_x	low temperature nematic phase
DF	dual frequency	$\rm Na_2\rm CO_3$	sodium carbonate
DFLC	dual frequency liquid crystal	OLED	organic light emitting diode
DMSO	dimethyl sulphoxide	OPM	optical polarising microscopy
DSC	differential scanning calorimetry	Ph	phenyl
ECB	electrically controlled birefringence	PVA	polyvinyl alcohol
EtOAc	ethyl acetate	Sm	smectic phase
EtOH	ethanol	Sm_{d}	interdigitated smectic phase
FLC	ferroelectric liquid crystal	SmA	smectic A phase
HCl	hydrochloric acid	$\rm SmA_{c}$	intercalated smectic A phase
IPS	in-plane switching	SmC	smectic C phase
Iso	isotropic phase	SmC^*	chiral smectic C phase

${\rm SmC}_{\rm ca}$	smectic C intercalated anticlinic	ε_0	permittivity of free space
$\mathrm{SmC}_{\mathrm{c}}$	intercalated smectic C phase	$arepsilon_{\perp}$	permittivity perpendicular to n
STN	super-twisted nematic	$arepsilon_{\parallel}$	permittivity parallel to n
TFT	thin film transistor	f_c	crossover frequency
THF	tetrahydrofuran	f_H	high frequency
TLC	thin layer chromatography	f_L	low frequency
TMS	tetramethylsilane	f_r	relaxation frequency
TN	twisted nematic	γ_1	rotational viscosity
VA	vertically aligned	J	coupling constants
VHR	voltage holding ratio	K_{11}	splay elastic constant
XRD	x-ray diffraction	K_{22}	twist elastic constant
Symbols		K_{33}	bend elastic constant
A	area of electrode surface	K_{ii}	elastic constants
χ	electronegativity	λ	wavelength
C_o	capacitance (empty cell)	λ_v	wavelength of light in a vacuum
$C_{\mathbb{I},\perp}$	capacitance (paralell/perpendicular)	η_1	viscosity coefficient (η : \parallel to v, \perp to ∇v)
δ	chemical shifts	η_2	viscosity coefficient (η : \perp to v , \parallel to
δ	optical retardance	,-	∇v)
$\Delta \varepsilon$	dielectric anisotropy	η_3	viscosity coefficient (η : \perp to v & ∇w)
ΔH_{N-I}	N-I transition enthalpy	n	v v v
Δn	birefringence	n_e	
d	LC film thickness / cell gap	n_o	orumary refractive index
d	inter-planar distance	ω_1	rotation around the short molecu- lar axis

ω_2	precessional motion about the di- rector
ω_3	rotation about the long molecular axis
ϕ	azimuthal angle
S	order paramater
$ au_o$	relaxation time
θ	scattering angle
$t_{\rm off}$	response time (turn-off process)
$t_{\rm on}$	response time (turn-on process)
T_{N-I}	nematic-isotropic transition
T_c	clearing point
T_m	melting point
∇v	velocity gradient
v	flow velocity
V_H	voltage at high frequency
V_L	voltage at low frequency
V_{th}	threshold voltage

1 Introduction

1.1 The Liquid Crystal Mesophase

Most materials exhibit only the solid, liquid and gas phases. In crystalline solids the molecules are constrained within a lattice and so have both positional and orientational order in three dimensions throughout. Isotropic liquids are completely disordered systems, where the molecules are mobile and can diffuse throughout the bulk with the molecular axis pointing randomly in many possible directions. Liquid crystals are an additional class of materials which have one or more intermediate phases, known as mesophases, between the conventional crystal and isotropic phases (Figure 1.1).¹

In the liquid crystal mesophase the molecules are mobile, much like an isotropic liquid, but also have significant orientational order and in some cases positional order. Unlike isotropic liquids, liquid crystals are anisotropic materials and have a structure such that one molecular axis is significantly different from the other.¹

Below the melting point, (T_m) of a liquid crystal the material is in the crystalline state. Above the T_m the material undergoes a phase transition to one or more, liquid crystal mesophases. At a higher temperature, known as the clearing point, (T_c) there is another transition to the isotropic liquid phase.^{2,3} A phase is enantiotropic when it is exhibited at temperatures above the melting point where as, when it is only displayed below the melting point it is known as a monotropic phase. There are many possible mesophases with varying degrees of positional and orientational order, these are determined by the structure of the liquid crystal material.⁴



Figure 1.1. States of Matter.

¹M. Hird and P. J. Collings. Introduction to Liquid Crystals. Taylor & Francis, London, 1997.

²S. M. Kelly and M. O'Neill. "Liquid Crystals for Electro-Optic Applications". In: Handbook of Advanced Electronic and Photonic Materials and Devices. Academic Press Japan, 2000.

³L. Pohl and U. Finkenzeller. *Physical Properties of Liquid Crystals*. Vol. 1. World Scientific, Singapore, 1990.

⁴J. W. Goodby. "Materials and Phase Structures of Calamitic and Discotic Liquid Crystals". In: *Handbook of Visual Display Technology*. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1243–1287.

1.1.1 Liquid Crystal Classes



Figure 1.2. Liquid crystal classes.

There are two main classes of liquid crystals, thermotropic and lyotropic as shown in Figure 1.2. Transitions between mesophases in thermotropics are dependent upon temperature. In lyotropics both temperature and concentration (within a solvent) determine mesophase transitions. Thermotropic liquid crystals are usually rod shaped (calamitics), disk shaped (discotic) or planar (sanidic) in structure.^{1,5} These are illustrated in Figure 1.3. Some materials such as **108** can be both lyotropic and thermotropic and these are known as amphitropic liquid crystals. The most common type of molecule that forms liquid crystal phases is the calamitic liquid crystal.



Figure 1.3. Structures of a typical calamitic 1, discotic 2 and lyotropic 3 liquid crystal.¹

⁵K. Tarumi, U. Finkenzeller, and B. Schuler. Jpn. J. Appl. Phys. 1992, **31**, 2829–2836.

1.2 History of Liquid Crystal Research

Research into thermotropic liquid crystals first began in 1888 with Austrian, Friedrich Reinitzer. Reinitzer noticed a derivative of cholesterol (Figure 1.4) seemingly had two melting points, one at 146 °C where the solid melted to a cloudy liquid and another at 179 °C forming a clear liquid.⁶ Later in collaboration with Reinitzer, German physicist Otto Lehman was able to observe these transitions through a polarizing microscope he built? It was Lehman who first coined the term "Flüssige Kristalle" (liquid crystals). In 1922 Georges Friedel created the classification of phases we use today — nematic, smectic and cholesteric.⁸



Figure 1.4. Cholesteryl benzoate, the compound Reinitzer dicovered had a liquid crystalline phase.

After a decline during and after the war years research picked up prior to 1960 on both sides of the Iron Curtain. In the Soviet Union I. G. Chystyakov established a group in Moscow. In the United States Glenn Brown wrote a review on liquid crystals and founded the Liquid Crystal Institute at Kent State University.¹ In the UK, George Gray at the University of Hull published a book on liquid crystals titled "Molecular Structure and Properties of Liquid Crystals".⁹ It was George Gray & coworkers that first synthesised the compound shown in Figure 1.5, 4-cyano-4'-pentylbiphenyl **5** or 5CB as it is commonly known.¹⁰ 5CB was the first material with a stable room temperature nematic phase (Cr 24.0 N 35.0 Iso¹ (°C)) and found use in early optical display systems based on the twisted nematic design. Liquid crystal displays began in watches and calculators with just a few pixels, today there are >50 inch television displays with millions of pixels.



Figure 1.5. 4-cyano-4'-pentylbiphenyl — 5CB.

⁶F. Reinitzer. Monatsh Chem, 1888, 9, 421–441.

⁷O. Lehmann. Z. Phys. Chem. 1889, 462–472.

⁸G. Friedel. Ann. Phys. 1922, **18**, 273–474.

⁹G. W. Gray. Molecular Structure and the Properties of Liquid Crystals. Academic Press Inc, 1962.

¹⁰G. W. Gray, K. J. Harrison, and J. A. Nash. *Electron. Lett.* 1973, **9**, 130.

1.3 Physical Properties

Liquid crystals are anisotropic materials, meaning they have different properties in different directions. In the simplest liquid crystal phase, the uniaxial nematic phase (N), locally one molecular axis is orientated in a preferred direction. This preferred direction is known as the director (n), where n = -n. For calamitic materials, the director is parallel to the long molecular axis and equal to the optic axis. This is shown in Figure 1.6² where the director is in the z axis. Conversely, for discotics the director is parallel to the short molecular axis. The orientation of the director changes throughout the bulk material and can be described by continuum theory.



Figure 1.6. The molecular structure (5CB) a nematic liquid crystal with a large length-to-breadth ratio. The director, n is in the z axis.²

1.3.1 Order Paramater

In the netmatic phase the average orientation of the molecules relative to the director is the know as the nematic order parameter, S defined as:

$$S = \left(\frac{1}{2}(3\cos^2\theta - 1)\right)$$
(1.1)

where θ is the angle between the director of the liquid crystal and the long molecular axis of an individual molecule. In an ideal, perfectly ordered nematic liquid crystal S = 1, whereas in a isotropic liquid S = 0. For a typical nematic material $0.5 \leq S \leq 0.7$. Like many liquid crystal properties the order parameter is temperature dependent and falls as the temperature approaches the clearing point.^{1,11,12}

¹¹G. H. Brown and P. P. Crooker. Chem. Eng. News, 1983,

¹²C. V. Brown. "Physical Properties of Nematic Liquid Crystals". In: *Handbook of Visual Display Technology*. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1343–1361.



Figure 1.7. Order parameter, S in (a) an ideal nematic, (b) typical nematic, and (c) isotropic liquid¹²

1.3.2 Optical Anisotropy

As previously discussed, for uniaxial calamitic liquid crystals the unique axis is often referred to as the optic axis and coincides with the direction of n. Light behaves differently when propagating parallel or perpendicular to the optic axis and this is the basis of birefringence. Upon entering a birefringent medium, plane polarised light splits into two orthogonal component rays, ordinary and extraordinary each with differing velocities. The electric field vector of the ordinary ray is perpendicular to the optic axis and the refractive index (n_o) is constant, independent of the propagation direction. Conversely, the electric field of the extraordinary ray lies in parallel in plane with the optic axis, thus it's refractive index (n_e) varies with the ray propagation angle, θ . Birefringence (Δn) is the difference between these two refractive indicies:

$$\Delta n = n_e - n_o \tag{1.2}$$

you could mention somewhere that optical anisotropy means that aligned lcs are able to control the polarisation of light. I say aligned so that maybe you can justify mentioning the cell gap where you define optical retardance

Max Δn occurs when $\theta = 90^{\circ}$, where the field of the extraordinary ray is parallel to the optic axis. Most calamitic liquid crystals have a positive Δn resulting in a delayed extraordinary ray versus the ordinary ray as it travels through the liquid crystal medium. Birefringence means that aligned liquid crystals are able to control the polarisation of light and so are responsible for the transmission of light in optical devices and the interference colours seen under optical polarising microscopy (OPM). Interference between the two rays results in the varied coloured appearance of the liquid crystal texture under OPM. The relative phase difference between these rays is known as the optical retardance, δ and can be described by the following:

$$\delta = \frac{2\pi\Delta nd}{\lambda_v} \tag{1.3}$$

where d is the liquid crystal film thickness (or cell gap) and λ_v is the wavelength of light in a vacuum.

Figure 1.8 shows that the refractive indices are temperature dependent. Upon exceeding the T_c the material becomes isotropic, thus birefringence no longer occurs. When light enters parallel to the director it only traverses one axis so the difference in velocities of the refractive indices will be zero, thus there is no change in polarisation and birefringence will not occur.^{1,2,13,14}



Figure 1.8. Schematic of optical anisotropy versus temperature.

Figure 1.9. Schematic of dielectric anisotropy versus temperature.

1.3.3 Dielectric Anisotropy

The interaction between a liquid crystal and an electric field is dependent upon the dielectric anisotropy ($\Delta \varepsilon$) of the material. Dielectric anisotropy is defined as:

$$\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \tag{1.4}$$

where ε_{\parallel} and ε_{\perp} are the dielectric permittivities parallel and perpendicular to the director (n) of the liquid crystal. The permittivities are a result of the polarisability of the material, which has two components. Firstly, on application of an electric field there is the creation of an induced dipole within the material. Secondly, the electric field can orient the permanent dipole moments. The dielectric anisotropy can be positive or negative, and this is determined by the relative magnitudes of the dielectric constants, parallel and perpendicular to the liquid crystal director. The sign and magnitude of $\Delta \varepsilon$ required for a device depends on the specific device type. Dielectrics and birefringence are linked through the relationship, $n_o = n_{\perp} = \sqrt{\varepsilon_{\perp}}$ and $n_e = n_{\parallel} = \sqrt{\varepsilon_{\parallel}}$. Where the two indices of refraction equal the square root of the corresponding dielectric constants.

¹³D. Demus et al. Handbook of Liquid Crystals. Wiley-VCH, 1998.

¹⁴P. W. Benzie and S. J. Elston. "Optics of Liquid Crystals and Liquid Crystal Displays". In: *Handbook of Visual Display Technology*. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1365–1385.

Figure 1.9 shows how $\Delta \varepsilon$ is dependent on temperature, above the T_c the material is isotropic and the dielectric anisotropy is destroyed. The sign and magnitude of $\Delta \varepsilon$ is determined by multiple factors, but most importantly the anisotropy of permanent dipoles within the liquid crystal structure.^{2,15}

In addition to the temperature dependence, dielectric permittivities are frequency dependent^{1,2} A given liquid crystal has one or more relaxation frequencies where there is a dispersion of the dielectric.¹⁶ This property can be used in dual frequency liquid crystals, and will be described in greater detail in Section 1.8.1.

1.3.4 Elastic Constants

An electric field or a solid surface can impose a distorting force upon a liquid crystal phase. This distortion or elastic behaviours is determined by three elastic constants, K_{11} , K_{22} and K_{33} each representing resistance of the material to the splay, twist and bend deformations respectively.^{1,2,17} It is often the ratios between these constants which are important.¹ For example, a low value of the K_{33}/K_{11} ratio can be an effective method to reduce the required transmission voltage in an optical display.¹⁸



Figure 1.10. Idealised schematic showing the elastic distortions in the nematic phase, (a) the undistorted nematic and the (b) splay K_{11} , (c) twist K_{22} , (d) bend K_{33} distortions.

¹⁵D. Pauluth and K. Tarumi. J. Mater. Chem. 2004, **14**, 1219–1227.

¹⁶I. C. Khoo and S. T. Wu. *Optics and nonlinear optics of liquid crystals*. World Scientific. 1993.

¹⁷G. Vertogen and W. H. de Jeu. *The Physics of Liquid Crystals Fundamentals*. Springer, Berlin, 1988.

¹⁸C. L. Kuo et al. Appl. Phys. Lett. 1996, **68**, 1461–1463.

1.3.5 Viscosity

Viscosity can be described as the internal friction of a fluid and governs the rate of flow of the fluid. Viscosity in liquid crystal materials is another anisotropic property and is dependent upon the direction of flow within the bulk fluid with respect to the director of the material. There are three parameters, known as shear viscosity coefficients (also Miesowicz coefficients), used to describe the viscosity of a nematic phase — η_1 , η_2 and η_3 . The first, η_1 has the director perpendicular to the flow velocity (v), but parallel to the velocity gradient (∇v) . Whereas, for η_2 , the director is parallel to v, but perpendicular ∇v . Finally for η_3 , the director is perpendicular to the both v and ∇v . These geometries are illustrated in Figure 1.11.^{12,19-22}



Figure 1.11. Geometries for the three viscosity coefficients (a) η_1 , (b) η_2 and (c) η_3 ¹²

The bulk viscosity of an unaligned nematic phase is an average of these three parameters. When the material is within a cell for optical displays, the constrained environment of the cell walls limits bulk fluid flow and so means there is an alternative rotational viscosity (γ_1) which for a nematic phase is associated with the rotational motion of the director (rotation perpendicular n). Typical values of γ_1 for commercial liquid crystal mixtures are $\gamma_1 = 0.05 - -0.45$ Pas.^{2,12}

¹⁹T. E. Faber. *Fluid Dynamics for Physicists*. Cambridge University Press, Cambridge, 1995.

²⁰D. A. Dunmur, A. Fukuda, and G. R. Luckhurst. *Physical Properties of Liquid Crystals: Nematics*. Ed. by D. A. Dunmur, A. Fukuda, and G. R. Luckhurst. INSPEC, 2001.

²¹J. W. Goodby et al. "Low Molecular Weight Liquid Crystals I". in: Handbook of Liquid Crystals. Ed. by D. Demus et al. Wiley-VCH, 1998. 1–525.

²²S. V. Pasechnik, V. G. Chigrinov, and D. V. Shmeliova. Liquid Crystals: Viscous and Elastic Properties. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Oct. 2009.

1.4 Calamitic Materials

As previously stated, calamitic liquid crystals are composed of rod-shaped molecules. The word calamitic is derived from the Ancient Greek word " $\kappa\alpha\lambda\alpha\mu\sigma\varsigma$ " (kalamos) meaning reed or pen. As the name suggests these materials have a molecular length that is significantly larger than the breadth, thus have a length-breadth ratio much greater than one.

1.4.1 Calamitic Mesophases

1.4.1.1 Nematic Phase

The nematic phase, N shown in Figure 1.12 (a) is the least ordered of the liquid crystal mesophases, it only has long range orientational order and no positional order. The molecules are arranged parallel to each other so that the long axis are all in the same average direction. This is the unit vector known as the director (n). The rod like molecules are able to freely rotate about their long molecular axis and to some degree their short axis. The rotation about the short axis is much slower (10^5 Hz) than that about the long axis $(10^{11} \text{ Hz})^{13}$ In the bulk of the nematic phase there are equal amounts of molecules pointing in one direction to the other, +n and -n are equivalent. The nematic phase appears at temperatures above the other phases and is less viscous than those below it. Nematic liquid crystals can undergo a reorientation on the application of a electric field, known as electro-optical switching, which will be discussed further in Section 1.7 (page 42).⁴



Figure 1.12. (a) nematic, (b) smectic A and (c) smectic C mesophases.

1.4.1.2 Smectic Phase

Smectic phases (Sm) have both orientational and positional ordering, depicted in Figure 1.12 (b & c). The molecules are arranged into layers, where for the Smectic A phase the long axis is approximately perpendicular to the layer plane. There is no translational periodicity in the planes of, or between the layers, so there is only very short range positional order over ~ 1.5-2.5 nm.²¹ However, the interlayer forces are relatively weak, and thus are able to move past one another, making the layers themselves very diffuse. A result of the layering present in smectic liquid crystals is that they generally have

higher viscosity and appear at lower temperature ranges than nematic liquid crystals. There are many types of smectic phases, different types are characterised by their varying packing formations and tilt angles. For example, in SmA liquid crystals the director is perpendicular to the layers however, in SmC liquid crystals the molecules have a tilt angle associated with them, the director is not 90° to the layer plane^{4,23}

1.4.1.3 Chiral Phases

Related to the nematic phase is the chiral nematic phase (N^*) , which displays a helical structure (Figure 1.13). Chiral molecules within the liquid crystal cause the director to become twisted as it progresses through the liquid crystal medium. It is the rotation of the local director along a single axis (helix axis) that creates the helical structure. Like the nematic phase there is no positional order, only a localised orientational order. The distance needed for the director to rotate by an angle of 360° through the bulk is known as the pitch. At higher temperatures the helix tightens reducing the pitch, at low temperatures the helix unwinds giving a longer pitch. A small concentration of chiral nematic liquid crystal molecules can be added as a dopant to nematic liquid crystal to bestow chiral properties to the nematic phase. Increased concentrations lead to higher twisting power.



Figure 1.13. Chiral nematic phase, N^{*}.

Figure 1.14. Chiral smectic C phase, SmC^* .

Pitch, P

Chiral smectic liquid crystals exist, such as the SmC^{*}. Chiral smectics have similar properties to the chiral nematic phase; the SmC^{*} phase has a director that rotates as it progresses through the liquid crystal medium (Figure 1.14).²³ However, the smectic nature means that there is also a tilt angle present. It is the precession of the tilt angle that results in the helical structure seen in chiral smectics. SmC^{*} liquid crystals can display ferroelectric properties, when the helical structure is unwound.

²³P. J. Collings. Liquid Crystals: Nature's Delicate Phase of Matter. Princeton University Press, 2002.

1.4.2 Calamitic Structure & Properties

The rod shaped molecules comprising calamitic liquid crystals can typically have a number of different structural features, as shown in Figure 1.15. Core units (A & B) — often aromatics, terminal groups (R & R'), linking groups (X, Y & Z) and lateral substituents (M & N). A liquid crystal may contain all or just a few of these features. Different groups and their locations can have a massive affect on the physical properties of the liquid crystal.



Figure 1.15. Structure of a typical calamitic liquid crystal. Core units A & B, terminal groups R & R' and linking groups X, Y & Z.

1.4.2.1 Core Units

The core unit of a calamitic liquid crystal is in general defined as the linear rigid backbone of the material. The cores of most liquid crystal mesogens are based on aromatic ring structures such as 1,4-phenyl, 2,5-pyrimidinyl, and 2,6-naphthyl, (Figure 1.16) however alicyclic cores are also common.¹³



Figure 1.16. Typical aromatic core units, (a) 1,4-phenyl, (b) 2,5-pyrimidinyl, and (c) 2,6-naphthyl¹

The length and type of the core plays a large role in the mesophase properties of a liquid crystal material. Figure 1.17 shows the effect of the different aromatic core structures mentioned above on transition temperatures. Using 5CB, **5** as the standard we can see that in the terphenyl analogue, **6** the addition of another aryl group has greatly increased the melting point. The added length has substantially increased the length to breadth ratio, this results in a particularly high T_{N-I} giving a material with a wide nematic phase range. The pyrimidine core unit on compound **7** has a higher T_{N-I} than 5CB as there is less steric hinderance between the rings and it can adopt a planar conformer enhancing longitudinal polarisability. However the polarity of the N atoms leads to a higher melting point, resulting in a monotropic nematic. Finally, the naphthyl derivative, **8** extends both the length and breadth of the material. While not as long as the terphenyl system the added length still results in a material with a higher T_{N-I} though it is reduced because of the added breadth.¹



Figure 1.17. Effect of the aromatic core on mesophase temperatures.¹

As mentioned above, in addition to aromatic cores alicyclic cores are common in many liquid crystal materials. Two examples of these are *trans*-cyclohexane (CH) and bicyclooctane (BCO). Again, 5CB **5** will be used to compare the effect of these cores on the transition temperatures (Figure 1.18). By replacing the aromatic phenyl (next to the pentyl chain) with a cyclohexane ring (**9**) both the melting point and the T_{N-I} have increased, using a bicyclooctane (**10**) the effect is greater still. The increased T_{N-I} is a result of the alicyclic structures anti-parallel pair having reduced overlap and therefore a larger length to breadth ratio. The bicyclooctane system also benifits form this effect, but adittionally has reduced flexiblity - further increasing the transition temperatures. This gives a general trend for the formation nematic phases Ph < CH < BCO. An interesting comparison is **9** with **11** where the cyclohexane is next to the terminal cyano, this shows a very low T_{N-I} value, the alternating polarisability of the material does not support the liquid crystal phase.¹



Figure 1.18. Effect of alicyclic core on mesophase temperatures.¹

1.4.2.2 Terminal Substituents

The properties of a liquid crystal material are highly dependent on the terminal substituents. The variety of terminal groups in liquid crystals is vast, but the most common are straight hydrocarbon chains or small polar groups.¹ Polar groups result in substantial intermolecular attraction which stabilises the molecular orientation of the liquid crystal. There is a general order for the relative efficiency of a terminal group to form nematic phases, Ph > NHCOCH₃ > CN > OCH₃ > NO₂ > Cl > Br > N(CH₃)₂ > CH₃ > F > H.¹ Both the cyano group, fluorine and alkyl/alkoxy units as substituents will be discussed in more detail below.

The cyano group is particularly useful as it is highly polar, so generates a positive dielectric anisotropy $(\Delta \varepsilon)$. It also extends the conjugation of the molecule resulting in a higher birefringence (Δn) . Another particularly useful effect of the terminal cyano group is that it allows for anti-parallel correlation between two alkylcyanobiphenyl molecules, this interaction effectively extends the molecular length and polarisability of the paired mesogens promoting the liquid crystal phases.²⁴

Fluorine, and the carbon-fluorine bond have some unique properties that make it an attractive substituent for use in liquid crystal materials. Fluorine is the most electronegative element in the periodic table, having a value of $\chi = 3.97$ on the Pauling scale.²⁵ Once bound to carbon the resulting C-F bond is one of the strongest in organic chemistry, having a dissociation energy of 441.3 kJ mol⁻¹.²⁶ The high electronegativity of fluorine causes (a) the C-F bond to be greatly polarized, giving rise to a large dipole and (b) the bond to be very un-polarizeable. Compared to the cyano unit, the terminal fluorine substituent is much less favourable to liquid crystalline phase stability — it does not enhance the length to breadth ratio and is not very polarisable. Fluorine will be discussed more thoroughly later, as a lateral substituent in Section 1.4.2.4.

1.4.2.3 Terminal Alkyl & Alkoxy

Like polar groups, hydrocarbon chains in the terminal position confer a large effect on the liquid crystal properties. Unlike the polar groups already discussed non-polar moeties have little effect on $\Delta \varepsilon$ and Δn but they do have significant power to alter transition temperatures and elastic constant ratios (K_{33}/K_{11}) . Straight chain alkyl or alkoxy groups are the most widespread and these will be discussed in detail. Table 1.1 lists the homologous series of alkylcyanobiphenyls and the transition temperatures for the liquid crystal phases. A number of trends can be seen.

Firstly, longer chains add greater flexibility to the mesogen which reduces melting points (12–16. With very short chains (compounds 12–15) the melting points are very high masking liquid crystal phases and so only virtual or monotropic nematic phases are seen. With very long chains melting points increase due to substantial van der Waals intermolecular forces of attraction. The longer chains promote microphase separation (segragation) - where the aromatic cores and aliphatic chains tend to separate, placing the molecules into a layered arrangement that leads to smectic behaviour. At extreme lengths this effect can completely remove any nematic phase behaviour as seen in $C_{10}H_{21}$ chain (20).

In terms of liquid crystal phase stability, the longer alkyl chains extend the molecular length and are able to interact with each other, this stabilises the nematic phase. In opposition to this however, is the disruption to molecular packing due to the greater flexibility of the chain, this reduces the liquid crystal phase stability and in the case of 20 has entirely removed the nematic character. Compounds

²⁴G. W. Gray and S. M. Kelly. J. Mater. Chem. 1999, 9, 2037–2050.

²⁵A. L. Allred. J. Inorg. Nucl. Chem. 1961, **17**, 215–221.

²⁶D. O'Hagan. Chem. Soc. Rev. 2008, **37**, 308–319.

Compound	R	Transition Temperatures $^{\circ}\mathrm{C}$	
12	CH_3	Cr 109 [N 45] Iso	
13	$\mathrm{C_2H_5}$	Cr 75 [N 22] Iso	
14	$\mathrm{C_3H_7}$	${\rm Cr}$ 66 (N 26) Iso	
15	$\mathrm{C}_{4}\mathrm{H}_{9}$	${\rm Cr}$ 48 (N 17) Iso	
5	$\mathrm{C}_{5}\mathrm{H}_{11}$	Cr 24 N 35 Iso	
16	$\mathrm{C_6H_{13}}$	${\rm Cr}$ 15 N 29 Iso	
17	$\rm C_7H_{15}$	${\rm Cr}$ 30 N 43 Iso	
18	$\mathrm{C_8H_{17}}$	Cr 22 SmA 34 N 41 Iso	
19	$\mathrm{C}_{9}\mathrm{H}_{19}$	Cr 42 SmA 48 N 50 Iso	
20	$C_{10}H_{21}$	Cr 44 SmA 55 Iso	

Table 1.1. Effect of terminal chain length on transition temperatures.¹

18, 19 and 20 show smectic A phases, this is because the particularly long chains enhance microphase segragation, enabling the lamellar packing required for the layered smectic phases.

Looking at the transition temperatures of the series an odd-even effect is seen, the even chained materials have a lower T_{N-I} and melting point. This is because the addition of the even methylene deviates from the linear structure of the mesogen (in addition to the greater flexibility). The odd-even effect is illustrated when looking at compounds 5 and 16.



Figure 1.19. Comparison of alkyl and alkoxy terminal chains on transition temperatures.

If an alkyl terminal group is replaced by an alkoxy there is a substantial rise in the mesophase transition temperatures. This is illustrated in Figure 1.19. In the alkyl system (16) the Ph–CH₂–alkyl bond angle is 117.1°, in the alkoxy analogue (21) the Ph–O–alkyl bond angle is 119.0°. This larger bond angle means that the alkoxy systems are more linear in shape and are able to pack better, raising both the melting point and the nematic phase stability. Additionally, the lone electron pair on the oxygen atom of the alkoxy systems is able to partake in the mesomeric effect, which strengthens the anti-parallel accosiation, again raising the transition temperatures.

1.4.2.4 Lateral Substituents

A lateral substituent is one that comes off the side of the long molecular axis. A huge array of lateral substituents have previously been incorporated for liquid crystal materials including, F, CN, NO₂ and CF₃ but by far the most commonly targeted is fluorine.^{27,28} As previously mentioned, fluorine is very electronegative, thus when attached laterally is very useful for generating negative dielectric anisotropy, $\Delta \varepsilon$. The particular location of a lateral fluorine on a material has a large influence on the mesophase behaviour. These effects will be detailed in the following sections.²⁹



Figure 1.20. Effect of lateral fluorination and the resulting broadening of the material on liquid crystal phase transitions and dielectric anisotropy.

Figure 1.20 illustrates how broadening a material by the addition of lateral fluorines effects the transition temperatures and dielectric properties. Compound 22 has both a high melting point & T_{N-I} value and a moderate value of $\Delta \varepsilon$, the single fluorine in the terminal position does not broaden the material. The addition of a second fluorine atom in compound 23 has broadened the molecule and as a result there has been a large fall in both the melting point and the T_{N-I} value. The second fluorine has produced only a small increase in $\Delta \varepsilon$ as it contributes equally to ε_{\perp} and ε_{\parallel} . The third fluorine on 24 has further broadened the molecular shape and as expected has lowered the phase transitions to a greater extent. The $\Delta \varepsilon$ of this last material is much higher than the first two. This is due to the fact that the third fluorine dipole is opposite the second and it's contribution to ε_{\perp} cancels out the one opposite, both lateral fluorines now only contribute to ε_{\parallel} resulting in the much higher $\Delta \varepsilon$.

²⁷M. Hird, G. W. Gray, and K. J. Toyne. *Mol. Cryst. Liq. Cryst.* 1991, **206**, 187–204.

²⁸M. Hird and K. J. Toyne. Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A, 1998, **323**, 1–67.

²⁹M. Hird. Chem. Soc. Rev. 2007, **36**, 2070–2095.



Figure 1.21. Effect of lateral substituent position on mesophase behaviour, inner core versus outer edge.

Whether a lateral substituent is in an inner core or outer edge position has a substantial effect liquid crystal phase behaviour, Figure 1.21. The non-fluorinated terphenyl, 25 has a very high clearing point but only shows a narrow smectic phase range due to the equally high melting point. The addition of a fluorine into an outer edge position as on compound 26 widens the SmA phase, this is mostly a result of the outer edge fluorine filling a void next to the alkyl chain offsetting the molecular broadening, and so enhancing intermolecular attractions and lamellar packing ability. The fluorine in 27 on the other hand is in a inner core location. In this position the full force of the molecular broadening is felt and the material accordingly has a substantially lower melting point and T_{N-I} . Another consequence of the inner core position is that it introduces interannular twisting, disrupting the polarisability of the core. Subsequent lowering of the liquid crystal phase stability, reveals the N phase. In compound 28 the inner core positioned chlorine atom due to it's much larger size has further broadened the molecule, greatly reducing the mesophase stability, this material is only nematic, over a short range.



Figure 1.22. Ortho-difluoro positioning and the effect on mesophase behaviour.

The ortho-diffuoroterphenyls have recieved much research attention as negative dielectric materials.

The location with the two fluorines or the to one another means that their longitudinal dipoles cancel, thus they don't contribute to ε_{\parallel} and as a result have a negative $\Delta \varepsilon$ (for compound **30** $\Delta \varepsilon = -0.7$ at 114°). Similar effects are seen with the diffuoroterphenyl systems shown in Figure 1.22. In **29** both the fluorines are on an outer ring or the to one another. The outer edge fluorine fills a vacant space and so smectic phases are generated. The inner core fluorine enables the full effect of the molecular broadening to be felt and also introduces interannular twisting. Both of these result in lower melting and T_{N-I} values. In addition poorer lamellar packing depresses the smectic phase and thus the exhibition of a nematic phase is seen. When both of the fluorines are located in inner core positions on the centre ring as in **30** there is a reduction in the melting point and the phase stability of the smectic phases, so much so that this material only displays a nematic phase.³⁰ This is due to excess interannular twisting causing a reduction in polarisability of the molecule. However, if the alkyl chains are sufficiently long then the interaction between them leads enhanced microphase segragation and the reappearance of the smectic phases, this is shown by **31**.

1.5 Dimeric Materials

Liquid crystal dimers are materials that consist of two mesogenic units separated by a flexible spacer. The first liquid crystal dimers were synthesised by Völander in 1927,³¹ these were the α,ω -bis(4-alkoxyphenyl-4'-azophenyl)alkanedioates shown in Figure 1.23. At the time their importance was not realised, it wasn't until the 1980s that they became the focus of research activity again with the work of Griffin and Britt³² who first discovered the transitional effects of the spacer length and parity.



Figure 1.23. Vörlander's dimer, the first reported liquid crystal dimer material.

Initially dimers were used as model compounds for the important main chain liquid crystal polymers which showed unusual liquid crystal mesophase behaviour. It was thought that dimers could act as an intermediate between polymers and monomers. However, liquid crystal dimers show interesting properties on their own, often showing new phases or subphases of common phases when compared to conventional calamitic materials.

³⁰G. W. Gray et al. J. Chem. Soc., Perkin Trans. 2, 1989, 2041–2053.

³¹D. Vörlander. Z. Phys. Chem. 1927, **126**, 449.

³²A. C. Griffin and T. R. Britt. J. Am. Chem. Soc. 1981, **103**, 4957–4959.

1.5.1 Dimer Mesophases

1.5.1.1 Dimer Nematic Phases

The standard nematic phase exhibited by liquid crystal dimers is analogous to that seen in conventional calamitics. The molecules have no positional order but are orientated with their long molecular axis in one direction. In some cases, the bent dimers with odd spacer chain lengths can show an additional nematic-type phase (N_x) seen below uniaxial nematic (N_u) one. This phase has additional order, and was first thought to be a type of smectic phase due to it's optical texture.³³ However, later studies confirmed this as a nematic phase.³⁴ The exact structure of the N_x phase is still under substantial debate and multiple models have been proposed including, twist-bend $(N_{TB})^{35-37}$ and chiral domains (N_{cd}) .³⁸ Figure 1.24 (b) shows a model of the proposed N_{TB} phase, where "the director follows an oblique helicoid, maintaining a constant oblique angle with the helix axis and experiencing twist and bend".³⁷



Figure 1.24. (a) nematic phase structure of a symmetrical liquid crystal dimer, (b) N_{TB} phase model.³⁹

1.5.1.2 Dimer Smectic Phases

Like conventional calamitic materials, liquid crystal dimers exhibit smectic phases. Figure 1.25 shows some of the possible SmA packing arrangements seen for symmetric and asymmetric dimers. For symmetrical systems the most simple arrangement is the monolayer (a), where the terminal chains and flexible spacers phase separate so that the mesogenic units are 'attached' to mesogens in the same layer. The second organisation (b) is where the spacer and terminal chains are intermixed

 $^{^{33}{\}rm P.}$ J. Barnes et al. Liq. Cryst. 1993, ${\bf 13},\,603{-}613.$

³⁴V. P. Panov et al. *Phys. Rev. Lett.* 2010, **105**, 167801.

³⁵M. Cestari et al. Phys. Rev. E, 2011, 84, 031704–20.

³⁶R. J. Mandle et al. J. Mater. Chem. C, 2014, 2, 556.

 $^{^{37}\}mathrm{V.}$ Borshch et al. Nat. Commun. 2013, 4, 1–8.

³⁸A. Hoffmann et al. Soft Matter, 2015, **11**, 850–855.



randomly so that different parts of the molecule overlap, this is called an intercalated smectic A phase. Another possible form is the horseshoe-like conformation.⁴⁰

Figure 1.25. SmA structure of liquid crystal dimers (a) symmetrical monolayer, (b) symmetrical intercalated, (c) asymmetric intercalated (d) asymmetric interdigitated.

In asymmetric dimers, where one mesogenic unit differs from the other, the different units are mixed between the smectic layers. In these systems, monolayer, intercalated (c) and horseshoe-like arrangements are possible, like they are for symmetric dimers. In addition a interdigitated system (d) is also possible, where parts of the molecule overlap. Intercalated smectic C phases are also found in liquid crystal dimers. However, these tilted systems have only been observed for asymmetric systems.⁴⁰

1.5.2 Dimer Structure & Properties

This section will discuss the relationships between the molecular structure and the properties of liquid crystal dimers. As described earlier, a liquid crystal dimer is where two mesogenic cores are separated by a flexible spacer. There are three main types of dimer, linear where the two mesogens are linked through terminal positions, H-shaped where there is lateral attachment and T-shaped where one mesogen links terminally and the other laterally. This work focuses on rod-type (calamitic) mesogens with terminal linking, starting with symmetrical dimers.

The length and parity of the spacer in dimeric materials can have dramatic effect on the transitional properties. The α,ω -bis(4-cyanobiphenyl-4'-yloxy)alkanes (BCBOn) series will be used to demonstrate this as it has been the most extensively researched.^{41–43} As shown in Figure 1.26 a dimer adopts either a linear shape (**32**), when the spacer contains an even number of atoms or a bent

⁴⁰C. T. Imrie. "Liquid Crystal Dimers". In: Liquid Crystals II. Springer Berlin Heidelberg, Berlin, Heidelberg, 1999. 149–192.

⁴¹J. W. Emsley et al. Mol. Cryst. Liq. Cryst. 1984, **102**, 223–233.

⁴²G. R. Luckhurst. *Liq. Cryst.* 2005, **32**, 1335–1364.

⁴³C. T. Imrie and P. A. Henderson. Chem. Soc. Rev. 2007, **36**, 2096–2124.

shape (33) when there is an odd number of atoms in the chain. The linear compound (32) has significantly higher transition temperatures than the bent shaped odd dimer (33), Figure 1.27 (a).



Figure 1.26. Comparison of spacer parity with molecular shape.
In general the linear dimers have significantly higher transition temperatures than the equivalent bent shaped dimers Figure 1.27 (a) demonstrates this odd-even effect very well. For T_{N-I} values there is a marked attenuation of this effect and for spacers longer than n = 6 there is no longer any alteration. For melting points there is no apparent attenuation (at least till n = 21). The alteration in melting point has been contributed to the ease the linear dimers to pack in the crystal lattice.⁴² The entropy change for the nematic-isotropic transition ($\Delta S_{NI}/R$) also shows alteration with parity of the spacer, as shown in Figure 1.27 (b). The transitional entropy change can be up to three times larger for the even dimers. Unlike the T_{N-I} values, there is a only small degree of attenuation for entropy.



Figure 1.27. The dependence of (a) the melting (\circ) and, T_{N-I} (\bullet) transition temperatures, (b) entropy (\bullet) change of the N-I transition ($\Delta S_{NI}/R$), on the parity and length of the spacer group.⁴²

In addition to the odd-even effects of the spacer group, dimers exhibit many of the same structureproperty trends as calamitic materials (Section 1.4.2).⁴⁰ An example is illustrated in Figure 1.28. For a dimer with a methylene only spacer (**35**), the transition temperatures are much lower, than the corresponding alkoxy (**34**).⁴⁰ The larger bond angle of the Ph–O–CH₂ bond means that the alkoxy dimer is more linear in shape than the corresponding alkyl spaced dimer and this greater linearity allows for better molecular packing thus raising the transition temperatures. Lateral substituents such as methyl groups or fluorine lower transition temperatures due to broadening the molecular shape. This effect is demonstrated by compounds **36** and **37** in Figure 1.29.^{40,44,45}

 $^{^{44}{\}rm C.}$ T. Imrie. Liq. Cryst. 1989, 6, 391–396.

⁴⁵R. W. Date et al. *Liq. Cryst.* 1992, **12**, 203–238.



Figure 1.28. Effect of changing the linking spacer group on transition temperatures. Bond angles are exaggerated.



Figure 1.29. Effects of broadening a dimer on transition temperatures.

All of the systems discussed so far have been symmetrical dimers, but many asymmetric systems have also been studied previously. By using two different mesogens, the properties of the material can be tailored to a greater extent. Flexible spacer linking groups allows two very different mesogens to be incorporated into the same material. Compounds **38** and **39** were part of a series of materials synthesised by R. J Mandle⁴⁶ in the investigation of the N_x/N_{TB} phase.



Figure 1.30. Dimers reported by R. J Mandle,⁴⁶ featuring lateral and longitudinal dipoles.

 $^{^{46}\}mathrm{R.}$ J. Mandle et al. Liq. Cryst. 2015, 1–9.

Material series, 40 and 41 were synthesised to study the flexoelastic and viscoelastic properties of dimer materials⁴⁷ In combination with work by Ferrarini & Luckhurst⁴⁸ it was found that both odd and even lengthed dimers can adopt a range of conformations including bent and linear, but it is the relative proportions of each conformer that is important. The even dimers are mostly linear in shape and the odd dimers mostly bent.



Figure 1.31. Dimers originally reported by S. Morris, featuring both terminal and lateral fluorination. Transition temperatures for 40 are taken from later work by D. O. Lopez ,⁴⁹ whereas for 41 the transition temperatures listed are on cooling.



Figure 1.32. Dimers reported by Z. Ahmed in the investigation of the N_{x} phase.

Compounds 42 and 43 were designed and synthesised to investigate the structural features required to promote the formation of the N_x phase.⁵⁰ Currently, only bent shaped dimers with odd spacer lengths have been found to exhibit the N_x phase. Lateral fluorine substitution on the mesogenic core and terminal polar groups were found to stabilize the phase. Some materials show additional highly ordered liquid crystal phases below the N_x . This work included the synthesis of double bend materials such as 43 which feature one bent mesogen in addition to the spacer group.

⁴⁷S. Morris et al. *Phys. Rev. E*, 2007, **75**, 041701.

⁴⁸A. Ferrarini et al. Chem. Phys. Lett. 1993, **214**, 409–417.

⁵⁰Z. Ahmed, C. Welch, and G. H. Mehl. *RSC Adv.* 2015, **5**, 93513–93521.



Figure 1.33. Chiral dimer reported by E. Gorecka.

Work by E. Gorecka investigated a chiral dimer system, 44 linking a chiral mesogen via spacer to a non-chiral mesogen. The higher temperature phases are chiral nematic on heating, while blue phases on cooling. At lower temperatures, this material exhibits a N*-N_x phase transition,⁵¹ where the N_x phase disrupts the chiral twist giving a system with splay-bend modulation.



Figure 1.34. Dimer reported by G. Tamba, linking conventional calamitic to bent core mesogen.

Additional double-bend dimer materials include the banana-calamitic dimers, such as 45, investigated by G. Tamba. These systems link a conventional calamitic mesogen with a bent core group and can exhibit an N_x phase.⁵²

⁵¹A. Zep et al. J. Mater. Chem. C, 2013, 1, 46–49.

⁵²M. G. Tamba et al. *Ferroelectrics*, 2014, **468**, 52–76.

1.6 Dimers as Dopants for Liquid Crystal Display Mixtures

K. Araya studied a series of symmetrical fluorinated dimers as dopant materials for liquid crystal display mixtures in order to target faster relaxation times.⁵³ Figure 1.35 shows some of the materials investigated, these included different length and parity spacers, and changing the location and amount of fluorine substitution. The dimers were doped into a nematic host (ZLI-4792), and their influence on relaxation time was explored. In general the dimers reduced the relaxation time of the mixture. The reason for this is that the flexibility of the dimer reduces the order parameter, thus influencing the rotational viscosity and the field induced relaxation time. It was found that the shorter, odd lengthed spacers resulted in faster relaxation times than the even and longer dimers.



Figure 1.35. A series of fluorinated ether linked dimers reported by K. Araya.

⁵³K. Araya et al. J. Mater. Chem. 2006, **16**, 4675.

1.7 Electro-Optic Devices

Liquid crystals are have found use in a wide variety of products, including liquid crystal displays (LCD), filters, lasers and shutters. These devices rely on the electro-optical effects that liquid crystals possess, including field-induced director-axis reorientation, dynamic scattering and the guest-host effect. Of theses field-induced directer-axis reorientation is probably the most common and shall be further discussed.

1.7.1 Liquid Crystals in Magnetic & Electric Fields — Fréedericksz Transition

For electro-optic devices the most important property of liquid crystals is the ability of the director to be re-orientated by an external electric or magnetic field. This effect can be described by the Féedericksz transition. The Fréedericksz⁵⁴ transition is the field induced reorientation of the director field and can be described for the three geometries shown in Figure 1.36. These are the distortions representing splay (a), bend (b) and twist (c). Here, the nematic liquid crystal (with positive $\Delta \varepsilon$) is confined in a cell, where the surfaces impose a boundary condition that orients the bulk so that there is a uniform director field. Upon application of a field (magnetic or electric) above a certain field strength the nematic is distorted.⁵⁵ For an electric field this distortion happens at the threshold voltage (V_{th}).⁵⁶



Figure 1.36. (Top) Initial surface alignment, director oriented by the surface, (bottom) Fréedericksz transitions for (a) splay, (b) bend, (c) twist distortions under the influence of an electric field, B above the V_{th} .

⁵⁴V. Fréedericksz and V. Zolina. Trans. Faraday Soc. 1933, **29**, 919–16.

⁵⁵W. Helfrich. Mol. Cryst. Liq. Cryst. 1973, **21**, 187–209.

⁵⁶D. Demus et al. "Fundamentals". In: *Handbook of Liquid Crystals*. Ed. by G. W. Gray et al. Wiley-VCH, 1998. 1–943.

1.7.2 Display Devices

Liquid crystals are the dominant display technology in use today, liquid crystal devices replaced the old CRT displays, and compete with plasma and OLED displays. A basic LCD device, consists of a liquid crystal mixture sandwiched between glass substrates, with polarisers, transparent electrodes and alignment layers. More advanced displays include additional components such as colour filters, backlights and TFT circuits. The polariser setup is used to stop light transmitting through the device in the dark state. When the polarisers are set up orthogonal to one another the plane polarised light produced by by the first is then blocked by the second. The electrodes are usually made of indium tin oxide (ITO) which is deposited as a thin film by vapour deposition. The alignment layer is used to orient the liquid crystal material into a homeotropic (normal to the substrate surface) or homogeneous (planar to the surface) configuration. Homeotropic alignment is usually achieved by using a surfactant, such as lecithin whose tail groups align normal to the cell surface. The liquid crystal molecules then align between the tail groups. An alternative method uses a hydrophobic polymer layer which promotes homeotropic alignment (often used for VA mode). Homogeneous planar alignment most often uses a polymer such as polyvinyl alcohol (PVA), which orients the liquid crystal planar to the surface. A rubbing technique is then used to set a uniform azimuthal direction.

All liquid crystal display devices operate on the basis of voltage driven reorientation of the liquid crystal material. There are a wide number of competing LCD technologies, such as twisted nematic (TN), vertically aligned (VA), in-plane switching (IPS), super-twisted nematic (STN) and ferroelectric liquid crystal (FLC). Each alignment type has it's own benefits & drawbacks, some of which will be discussed in the following sections.

1.7.2.1 LCD Material Requirements

Liquid crystals must have certain properties, depending on the type of display technology to be used in LCDs. However, all types must have the same set of basic properties. A broad nematic phase range so that the liquid crystal can still function within the operating temperature of the device, typically -40–100 °C. The clearing point of the liquid crystal should be at a least 10 °C higher than the maximum operating temperature of the device.^{15,57} The liquid crystal should display a dielectric anisotropy, $\Delta \varepsilon$ in order for the liquid crystal to respond to an applied switching voltage. This can be positive or negative depending on the type of display mode. For the desired electro-optical effect the liquid crystals must display birefringence, Δn . Upon switching the orientation of the liquid crystals, there is a change in the optical path which is defined as $d\Delta n$ (where d = cell gap). This leads to changes in the transmission of the display between 5 % and 95 % (devices are rarely perfect so 0-100 % is not currently achieveable). Higher Δn allows for a smaler cell gap, reducing switching times.

⁵⁷M. Klasen-Memmer and H. Hirschmann. "Liquid Crystal Materials for Devices". In: *Handbook of Visual Display Technology*. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1315–1342.

The operating voltage is proportional to the square root of the ratio between elastic constants (K_{ii}) and dielectric anisotropy. For liquid crystals to be used in high speed displays such as TVs, they must have a suitably fast switching time. The switching time of a liquid crystal is proportional to the molecules rotational viscosity (γ_1) and the cell gap, d. Therefore the liquid crystal must have low γ_1 . In an active-matrix LCD each pixel is driven by a thin film transistor (TFT) which charges the pixels via signal pulses. The applied voltage must be sustained till the next pulse(one frame time). The voltage drop during a single frame is characterised by a voltage holding ratio (VHR) which is the ratio of voltages at the beginning and end of a frame time. High VHR are needed for flicker free images.

There are some mutually exclusive requirements associated with liquid crystals for displays. The requirement for high clearing points and nematic phase ranges are often at odds with the low rotational viscosity, thus it can be problematic to design a material that has both suitable operating range and fast switching speeds. Another problem is in combining low birefringence with high dielectric anisotropy and low viscosity. As a result of these contradictions a single liquid crystal cannot meet all the requirements for LCD use. Mixtures of 10–20 or more different liquid crystals are typical. Current research leans towards reducing the rotational viscosity while still maintaining or improving upon the other properties ($\Delta \varepsilon$, Δn , VHR).^{15,57}

1.7.2.2 Electrically Controlled Birefringence & Vertically Aligned Mode

Electrically controlled birefringence (ECB) devices were first developed in the 1970's.⁵⁸ As the name suggests ECB devices use an electric field to reorientate the liquid crystal, thus changing the effective birefringence. This works on the basis of the Fréederickzs transition described earlier. (Section 1.7.1). ECB devices can have a number of different forms depending on the initial alignment of the liquid crystal.⁵⁹ The most important and widely used of these is the vertically aligned (VA) cell. First described in 1972 by Soref,⁶⁰ this device uses a negative dielectric anisotropy nematic liquid crystal aligned homeotropically in a cell between crossed polarisers as shown in Figure 1.37(a). This cell design is normally dark, the plane polarised light propagates parallel to the optic axis (director) so there is no optical retardation. On application of an electric field between the surfaces above the V_{th} the liquid crystal reorients towards the homogeneous / planar alignment with increasing field strength (Figure 1.37b). With the optic axis now not parallel to the incident light, the effective birefringence changes and optical retardation occurs thus transmitting light through the second polariser^{2,15,59,61}

⁵⁸M. F. Schiekel and K. Fahrenschon. Appl. Phys. Lett. 1971, **19**, 391.

 ⁵⁹H. Yoshida. "Vertically Aligned Nematic (VAN) LCD Technology". In: Handbook of Visual Display Technology. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1485–1505.
 ⁶⁰R. A. Soref and M. J. Rafuse. J. Appl. Phys. 1972, 43, 2029.

⁶¹I. C. Khoo and S.-T. Wu. "Electro-Optical Properties of Liquid Crystals". In: Optics and Nonlinear Optics of Liquid Crystals. WORLD SCIENTIFIC, 1993. 100–268.



Figure 1.37. Schematic of a vertically aligned display device in the off/dark state (a) and the on/light state(b). Where E is the electric field, P the polariser direction and A is the alignment direction.²

Initially VA devices were less common due to a lack of suitable negative dielectric materials (low viscosity, etc). Later however, they saw a resurgence once more suitable materials were developed and the advantages of the VA device could be realised. Compared to other technologies such as twisted nematic displays, VA devices have improved contrast ratios, excellent brightness, wider viewing angles (with surface modification)⁶² and good performance-cost ratio.¹⁵ Additionally vertically aligned systems can be used simultaneously in reflective and transmissive modes in transflective devices.⁵⁹ One drawback to some VA devices is that the field induced planar alignment is random, leading to disinclination lines and defects (William's Domains) reducing the optical performance, however this can be reduced by modifications to the alignment surface. Additionally dynamic scattering in certain materials can lead to a non-uniform alignment.⁵⁹

1.7.2.3 Twisted Nematic (TN)

The twisted nematic electro-optic effect was first reported by Schadt in 1971.⁶³. Initially twisted nematics were only used in low density displays, due to the inability of multiplexing. However, during the 80s the advent of TFTs and STNs allowed high density displays to be realised, after which TN devices became the dominant display technology.

A twisted nematic device uses a positive dielectric anisotropy nematic liquid crystal placed between crossed polarisers. The liquid crystal is aligned homogeneously, planar to the electrode surfaces. However, unlike previous designs in a TN device the liquid crystal is aligned so that the director on one surface is orthogonal to the other surface. This alignment regime results in the liquid crystal director gradually twisting by 90° as it moves through the bulk (Figure 1.38a). In the field off state the TN cell is normally transmissive, the twisted nematic liquid crystal acts as a waveguide and rotates the plane of polarised light by 90° enabling passage through the second polariser. Application of an electric field above the V_{th} results in a deformation of the liquid crystal director as it reorientates to align with the field (Figure 1.38b). Polarised light is not rotated by the distorted twist and so is

⁶²A. Takeda et al. SID Int. Symp. Dig. Tech. Pap. 1998, **29**, 1077–1080.

⁶³M. Schadt. Appl. Phys. Lett. 1971, 18, 127.

extinguished by the second polariser, giving the dark mode of the device. The TN device as described is normally transmissive, however if parallel polarisers are used instead, the device can be used in the normally dark mode, this set-up is used for reflective devices.



Figure 1.38. Schematic of a twisted-nematic display device in the off/light state (a) and the on/dark state (b). Where E is the electric field, P the polariser direction and A is the alignment direction.

TN-LCD combined efficient multiplexing, long life and low cost and became the dominant liquid crystal display technology. However, there are a number of drawbacks associated with TN devices. The twisted alignment regime is compatible both right-handed and left-handed twist arrangements, that give domains that persist into the on-state where they are highly visible. This was solved in later devices, with modification of the surface alignment with pre-tilt (~1°) and addition of long pitch N* dopants. Large operating voltages are needed to completely orient the liquid crystal homeotropically and the molecules at the alignment layers are still orientated homogeneously even at high voltages, meaning that the perfect black state cannot be achieved, resulting in reduced contrast ratios. In addition, TN devices have poorer viewing angles when compared to other technologies.^{2,64}

1.7.2.4 In-Plane Switching (IPS)

In both display technologies discussed so far, the electrodes have been on opposite surfaces of the cell. An in-plane switching (IPS) device uses an alternative arrangement first reported by Soref in 1974.⁶⁵. In this device both electrodes are on the same surface and run parallel to each other in lines. In this case the electric field is applied parallel with the surfaces. In the off-state a positive dielectric liquid crystal is aligned homogeneously to the surface and parallel to the electrodes as shown in Figure 1.39a. In this state, between crossed polarisers the display is dark as the liquid crystal is orientated so that the optic axis is parallel to one of the polarisers.

⁶⁴P. Raynes. "Twisted Nematic and Supertwisted Nematic LCDs". In: *Handbook of Visual Display Technology*. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1433–1444.

⁶⁵R. A. Soref. J. Appl. Phys. 1974, **45**, 5466.



Figure 1.39. Schematic of an in-plane switching display device in the off/dark state (a) and the on/light state(b). Where E is the electric field, P the polariser direction and A is the alignment direction.²

When a voltage above the V_{th} is applied the liquid crystal rotate in plane with the surface to align with the field. This moves the optic axis away from the direction of the polariser by an angle ϕ (Figure 1.40) TN and VA devices control transmission by changing the effective birefringence, whereas in IPS it is a change in azimuthal angle, ϕ . And it is the "*electric field not the voltage* that drives the liquid crystals in IPS mode".⁶⁶ As the liquid crystals are reorientated in plane the most important elastic constant is twist, K_{22} . The strong surface alignment effects mean that the molecules close to the surfaces are not reorientated.^{65–67} IPS displays have the intrinsic advantage of good viewing angles, due to the homogeneous dependency of $d\Delta n$. Drawbacks of IPS devices include lower brightness and poorer contrast ratio.^{2,15}



Figure 1.40. IPS, from above, showing angle ϕ .

⁶⁶M. Oh-e and K. Kondo. Appl. Phys. Lett. 1995, **67**, 3895–4.

 ⁶⁷H. Hong. "In-Plane Switching (IPS) Technology". In: *Handbook of Visual Display Technology*. Ed. by J. Chen,
 W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1469–1483.

1.8 Dual Frequency Liquid Crystals

There is an increasing demand for faster response times in liquid crystal electro-optic devices.^{68–70} Various approaches to reduce the response time have been used, including high field strength, thin cells, π -cells and overdrive/undershoot voltage driving regimes. All accelerate the turn on process. However, none are able to accelerate the relaxation process, which is governed by the restoration of elastic force.⁶⁹ Once route to achieve acceleration of both the turn on and off processes, is found in dual frequency liquid crystal (DFLC) mixtures. DFLC mixtures allow the voltage drive of both the turn-on and the turn-off switching, which increases the effective response times of devices.⁷⁰ A dual frequency liquid crystal is a material that possesses different dielectric response at different frequencies. Typically the material is switched into one orientation at a low frequency (f_L) , then the other at a higher frequency (f_H) .⁷⁰

1.8.1 Dielectric Relaxation

DFLC devices take advantage of relaxation processes in the dielectric permittivities of the materials. Dielectric relaxation is the response of a dielectric medium to an external oscillating electric field, where delay of the medium to respond to the field is known as dielectric relaxation. The dielectric constants parallel (ε_{\parallel}) and perpendicular (ε_{\perp}) experience a fall in magnitude as frequency of an applied voltage is increased. The frequency at which the permittivity falls is known as the relaxation frequency, f_r .



Figure 1.41. Schematic plot of ε_{\parallel} and ε_{\perp} against frequency showing the rotational modes ω_1, ω_2 and ω_3 .⁵⁶

Figure 1.41⁵⁶ shows the different modes responsible for dielectric relaxation. ω_1 is rotation of the long molecular axis around the short axis and leads to a fall in ε_{\parallel} . This happens at a much lower frequency than the other modes since this rotational mode is strongly hindered at higher frequencies. ω_2 is the precessional motion about the director and effects both ε_{\parallel} and ε_{\perp} . ω_3 is rotation around the long molecular axis this effects only the ε_{\perp} .^{13,71} The permittivity perpendicular to the director

⁶⁸H. Xianyu et al. *Liq. Cryst.* 2007, **34**, 1473–1478.

⁶⁹H. Xianyu, S. Gauza, and S.-T. Wu. *Liq. Cryst.* 2008, **35**, 1409–1413.

⁷⁰H. Xianyu, S.-T. Wu, and C.-L. Lin. *Liq. Cryst.* 2009, **36**, 717–726.

⁷¹S. V. Shiyanovskii and O. D. Lavrentovich. Liq. Cryst. 2010, **37**, 737–745.

is almost constant up to the MHz region. On the other hand permittivity parallel, ε_{\parallel} falls at lower frequencies. The consequence of this means that it is only the positive dielectric materials that change $\Delta \varepsilon$ with frequency (below MHz region) and so it is positive dielectric materials that are responsible for the frequency dependent switching in DFLC mixtures.^{70,72–74}

1.8.2 Crossover Frequency



Figure 1.42. Temperature and frequency dependence on ε_{\parallel} and ε_{\parallel} showing the crossover frequency, f_c where $\Delta \varepsilon$ changes sign.⁷⁴

In a DFLC material there is a frequency at which the $\Delta \varepsilon$ changes sign, this is known as the crossover frequency (f_c). This frequency depends on a number of factors, including the relaxation frequencies of the individual mixture components. Additionally, while higher temperatures will result in lower viscosity (faster responce times) they greatly increase the f_c of a material. This is illustrated in Figure 1.42.⁷⁴ This means the f_H will have to be set higher, which can lead to increased dielectric heating of the material, further increasing the f_c .

⁷²M. Schadt. Mol. Cryst. Liq. Cryst. 1981, 66, 319–336.

⁷³M. Schadt. J. Chem. Phys. 1972, **56**, 1494–5.

⁷⁴M. Schadt. Mol. Cryst. Liq. Cryst. 1982, **89**, 77–92.

1.8.3 DFLC Switching Times

The key reason a DFLC device is able to achieve fast response times is because of the relatively high voltages used. DFLC materials are generally more viscous than a typical nematic mixture for other devices, so require higher operating voltages to compensate ($V \gg V_{th}$). Additionally threshold voltage is related to the $\Delta \varepsilon$ so it also changes with frequency.

For a homogeneous (planar aligned) cell the switching time can be described by:

$$\tau_{\rm on} \sim \frac{\tau_o}{\left(V_L/V_{th,L}\right)^2 - 1} \tag{1.5}$$

and

$$\tau_{\rm off} \sim \frac{\tau_o}{\left(V_H/V_{th,H}\right)^2 - 1} \tag{1.6}$$

where

$$\tau_o = \gamma_1 d^2 / K_{33} \pi^2 \tag{1.7}$$

where V_H and V_L are the driving voltages at high and low frequency, $V_{th,H}$ and $V_{th,L}$ are the corresponding threshold voltages, γ_1 is rotational viscosity, d is the cell gap and K_{33} is the bend elastic constant^{70,75}

As an example, if a mixtures $\tau_o = 196$ ms, in order to reduce the switching time to 0.5 ms, a voltage switching ratio of $V/V_{th} = 14$ is needed. Therefore, if the $V_{th} = 3.5$ V_{RMS} a driving voltage of V = 49 V_{RMS} is required to achieve the desired switching time. If material with lower threshold is used, $V_{th} = 3$ V_{RMS} the driving voltage required is lower, at V = 42 V_{RMS}. Thus materials with lower V_{th} are preferred in order to keep power requirements low $(P = (1/2)fCV^2)$.

 $^{^{75}{\}rm H.}$ Xianyu et al. Liq. Cryst. 2008, ${\bf 35},$ 1129–1135.

1.8.4 DFLC Materials

In 1974 Bücher reported the first mixture where the director could be reorientated parallel or perpendicular to to the electrode surfaces by changing the frequency of the applied voltage.⁷⁶ The mixture was comprised of a 1:1 ratio of the phenyl benzoyloxybenzoate derivatives shown in Figure 1.43 (50 and 51 were previously investigated by Van Meter⁷⁷). These ester linked mesogens, both featured a laterally substituted chlorine and only differ in the length of the terminal alkyl chains.



Figure 1.43. Bücher DFLC mixture, 1:1 ratio of of the above materials.

The liquid crystal mixture was placed into a cell with crossed polarisers and aligned homogeneously to the surfaces, in the normally transmissive state. Upon application of a 50 Hz field the $\varepsilon_{\perp} = 5.9$ and $\varepsilon_{\parallel} = 12.0$ giving a positive dielectric material ($\Delta \varepsilon = 5.1$). In this state the liquid crystal orientates homeotropically so that optic axis lies parallel with the field producing the dark state. At a higher frequency of 100 kHz the ε_{\perp} remains the same but ε_{\parallel} falls to $\varepsilon_{\parallel} = 3.7$ giving $\Delta \varepsilon = -2.2$. Now a negative dielectric, the material reorientates with the director normal to the field returning to the transmissive state. In addition to the homogeneous cell setup described DFLCs can be used in homeotropic cells also. In this case a high frequency voltage initially reorientates from homeotropic to homogeneous, then a low frequency can be use to return to the homeotropic orientation.

The majority of DFLC mixtures use a combination of two classes of materials, positive compounds and negative compounds. Negative compounds have a lateral dipole and a negative $\Delta \varepsilon$ that remains mostly constant with driving frequency, these are responsible for the large negative $\Delta \varepsilon$ at high frequencies. Positive compounds have a longitudinal dipole and positive $\Delta \varepsilon$ that falls with increased driving frequency. The positive compounds are responsible for the frequency dependence of the mixture. The following sections will discuss some of the previously reported DFLC materials.

⁷⁶H. K. Bücher, R. T. Klingbiel, and J. P. Van Meter. *Appl. Phys. Lett.* 1974, **25**, 186.

⁷⁷J. P. Van Meter and B. H. Klanderman. Mol. Cryst. Liq. Cryst. 1973, 22, 285–299.

1.8.4.1 Positive Compounds



Figure 1.44. Previously investigated positive compounds, showing the effect of terminal groups and core structure on electro-optic properties.

As previously mentioned positive compounds need to have a large positive dielectric anisotropy therefore they often feature polar groups in the terminal position. Figure 1.44 shows a number of materials previously reported by Xianyu.^{70,78} These all have the same basic core structure comprised of an aromatic core, ester linking groups, lateral fluorine substitution and polar terminal groups.

Comparing compounds 52 and 53 with 54 and 55 it can be seen that replacing the cyclohexane ring with an aromatic increases birefringence and $\Delta \varepsilon$, due to the greater degree of π -conjugation in the aromatics. The terminal cyano and isothiocyanate contribute to Δn with the NCS groups having the larger effect. The CN group gives a larger $\Delta \varepsilon$ due to it's stronger dipole moment. Additionally the CN materials have much lower relaxation frequency (f_r) than the NCS materials. The inclusion of the ester linking group contributes to the ε_{\parallel} but increases viscosity. Lateral fluorine substitution is commonly used to lower melting points and if correctly placed can contribute to ε_{\parallel} . The CN materials are suitable for DFLC mixtures where large Δn and high $\Delta \varepsilon$ are required. Alternatively the lower relaxation frequency of the NCS groups allows the material to be used at elevated temperatures.



Figure 1.45. Positive compounds for DFLC, showing the effect of core length on the electo-optic properties.

⁷⁸H. Xianyu et al. *Liq. Cryst.* 2009, **36**, 1401–1408.

Compound 56 in Figure 1.45 illustrates the effect of an additional the aromatic core. The longer material has a much higher T_{N-I} and the extended π -conjugation results in higher birefringence. The additional length of the core further hinders rotation about the short axis therefore four ring system generates a extremely low f_r , making it ideal for use in higher temperature devices where it can benefit from a greatly reduced visco-elastic constant. The double ester materials such as 57 benefit from low f_r and high $\Delta \varepsilon$. Though low birefringence and a relatively high visco-elastic coefficient (due to the double ester and fluorines) mean materials of this type are less useful. However, the very high $\Delta \varepsilon$ can be useful for mixture formulations.^{70,78}

1.8.4.2 Negative Compounds

In order for a DFLC mixture to switch signs of $\Delta \varepsilon$ at high frequency a moderate negative $\Delta \varepsilon$ is required (though this also depends upon the $\Delta \varepsilon$ of the positive compound). This can be more difficult to achieve as in general negative compounds have a much smaller magnitude of $\Delta \varepsilon$. Therefore, in most DFLC mixtures the negative compounds form the majority (70 %) component of the mixture. A common method for generating a negative $\Delta \varepsilon$ is via lateral substitution with of the aromatic cores with fluorines. When both fluorines are placed next to each other, as in Figure 1.46 & Figure 1.47 the individual contributions to ε_{\parallel} cancel out and only the ε_{\perp} is expressed. Additionally as mentioned in previously, lateral fluorines lower the melting point of the liquid crystal and due to their polarity, increase viscosity.



Figure 1.46. Negative DFLC compounds, with lateral fluorination to give negative $\Delta \varepsilon$

The terphenyl materials shown in Figure 1.46 both have moderate birefringence. The two fluorines on **58** give a relatively small negative $\Delta \varepsilon$. The additional fluorines on **59** have given a higher $\Delta \varepsilon$ but have undesirably, drastically increased the rotational viscosity of the material and reduced the nematic to a monotropic phase.



Figure 1.47. Negative DFLC compounds, with lateral fluorination and tolane structure.

If higher birefringence is required, tolane based materials are an alternative, such as those shown in Figure 1.47 investigated by Xianyu et al^{15,70,79} The tolane moiety extends the length of the delocalised π -system, which grants higher Δn with **61** having the greatest Δn due to the additional phenyl ring. Comparing the tolanes (**60** & **61**) to the terphenyls (**58** & **59**) with the same number of lateral fluorines show that the tolane mesogens have significantly higher $\Delta \varepsilon$ than the terphenyls.

1.8.5 DFLC Applications

Dual frequency liquid crystal materials can be found in number of different electro-optic technologies a few of which will be outlined below.

1.8.5.1 Cholesteric Liquid Crystal Displays

In 1999, M. Xu and D. Yang reported the development of a bistable reflective display using a DF cholesteric material. The two, zero-field stable states are (1) Bragg reflecting planar texture and (2) a non-reflecting focal conic texture. Application of a low frequency voltage switches from the planar to the focal conic texture, while a high frequency field returns the material to the planar arrangement.⁸⁰ Further work by F. Lin and W. Lee reported a colour-reflective system where a complete RGB pixel was realised. This system utilised three distinctive cholesteric pitches so that the Bragg reflections occurred at the correct wavelengths to give red, green and blue colours, see Figure 1.48.⁸¹



Figure 1.48. Reflectance of the RGB cells in a cholesteric reflective device when varying frequency of the applied field.⁸¹

⁷⁹S. Gauza et al. *Liq. Cryst.* 2008, **35**, 1401–1408.

⁸⁰M. Xu and D.-K. Yang. Jpn. J. Appl. Phys. 1999, **38**, 6827.

⁸¹F.-C. Lin and W. Lee. Appl. Phys. Express, 2011, 4, 112201.

1.8.5.2 Guest-Host Liquid Crystal Displays

Guest-Host displays employ liquid crystals and dichroic dyes contained within a polymer network, absence of polarisers results in a display with high brightness and wide viewing angles. Y. H. Lin demonstrated a DFLC guest-host system where the addition of a DFLC material enables faster response times. Figure 1.49 shows a schematic of the device in three states. At V=0 the liquid crystal and dye are orientated homeotropically, normal to the surfaces. In this configuration the cell does not scatter light and is in the normally white state (a). At a voltage above the threshold with a low frequency the molecules tilt slightly away from the field, reflectance is slightly reduced due to light scattering. At $f > f_c$ and $V > V_{th}$ (c) the liquid crystal is a negative dielectric and reorients with the field into the planar position, orientating the dye with it. In this orientation the dye is absorbing and gives the black state. Low frequency fields orient the liquid crystal and dye back to the homeotropic position, returning the cell to the white state.⁸²



Figure 1.49. Schematic of a dual frequency guest-host device. (a) no applied field — white state (b) applied field at $f < f_c$ — reduced reflectance (c) applied field at $f > f_c$ — black state.⁸²

1.8.5.3 Optical Retarders

A. B. Golovin, S. V. Shiyanovskii, and O. D. Lavrentovich developed a fast switching dualfrequency liquid crystal optical retarder, driven by an amplitude and frequency modulated voltage. This device employed a dual frequency nematic material combined with special boundary conditions and driving scheme to achieve particularly fast switching. The addressing scheme can be used in retarders, spatial light modulators, polarization rotators, beam deflectors and displays.⁸³

1.8.5.4 HAN Devices

In 2004, Y. Q. Lu investigated a dual frequency HAN cell for photonic applications, particularly targeting a variable optical attenuator. Compared to conventional HAN devices this achieved much faster response times and lower operating voltages, while doubling the maximum phase modulation. The cell also show three stable states so are potentially suitable for ternary photonic devices.⁸⁴

⁸²Y. H. Lin et al. J. Display Technol. 2005, 1, 230–233.

⁸³A. B. Golovin, S. V. Shiyanovskii, and O. D. Lavrentovich. Appl. Phys. Lett. 2003, 83, 3864-4.

 $^{^{84}{\}rm Y.-Q.}$ Lu et al. Appl. Phys. Lett. 2004, ${\bf 85},\,3354\text{--}4.$

1.9 Characterisation of Liquid Crystals

A variety of techniques are used to identify and characterise the mesophase behaviour liquid crystalline materials, including polarising microscopy, differential scanning calorimetry, and X-ray diffraction. It is often only a combination of these techniques that a liquid crystal phase can be correctly identified.

1.9.1 Polarized Optical Microscopy

Optical Polarising Microscopy (OPM) is a method used to observe the characteristic textures displayed by liquid crystal materials. OPM is the oldest and most widely used technique and is the first method used to identify liquid crystals.

A basic polarising microscope system is shown in Figure 1.50 it comprises: an eyepiece, polariser(analyser), objective lens, sample, polariser and light source.



Figure 1.50. Basic components of a polarising microscope.

The basic technique involves placing a sample onto a glass slide where it is illuminated and viewed between crossed polarisers. When no material or a non-birefringent material is present the light is not affected and is extinguished by the 2^{nd} polariser. When light passes through a birefringent sample such as a liquid crystal, it is affected by multiple factors, the sample thickness, material birefringence, phase modulation, the director orientation and any defects.

The different liquid crystal phases display one or more characteristic optical textures that can be used, in conjunction with other techniques to accurately identify the mesophase type. Nematic liquid crystals can be seen under optical polarizing microscopy and can show a number of characteristic defect textures, Schlieren, threaded or marbled, these are illustrated in Figure 1.51.⁸⁵

 $^{^{85}}$ I. Dierking. Textures of Liquid Crystals. Wiley-VCH Verlag GmbH, Mar. 2004.



Figure 1.51. Textures of the nematic phase (N), (a) Schlieren, (b) thread, (c) $marble^{85}$

The Schlieren texture is characterised by brush like bands emanating from point or line singularities. Where the brushes appear black the liquid crystal is orientated parallel to one polariser or another. There are different types of point singularities, depending on the number of brushes and the sign of the rotation (+ rotate with the polariser, – against). The defects are assigned an s value, which is equal to the number of brushes divided by four. Therefore a 4-brush singularity has $s = \pm 1$ whereas a 2-brush defect has $s = \pm 1/2$, these are shown in Figure 1.52. For nematics the Schlieren defects texture contains a mixture of both $s = \pm 1$ and $s = \pm 1/2$ singularities.⁸⁶



Figure 1.52. Defect singularities in the nematic phase.⁸⁶

Like the nematics, smectic phases have some characteristic textures as shown in Figure 1.53⁸⁵. SmA phase often displays a fan (a) or focal conic texture (b). SmC can show a broken fan texture (c). The tilted smectic C phase can additionally show a Schlieren defect texture, though this only contains $s = \pm 1$ type singularities.⁸⁶

⁸⁶J. W. Goodby. "Introduction to Defect Textures in Liquid Crystals". In: Handbook of Visual Display Technology. Ed. by J. Chen, W. Cranton, and M. Fihn. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012. 1–23.



Figure 1.53. Textures of smectic phases (a) fan texture of SmA (b) focal conics of SmA, (c) broken fan texture of the tilted SmC.

1.9.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) a sensitive and powerful technique for studying liquid crystals. It can provide a wide range of thermodynamic data including phase transition temperatures, enthalpy, heat capacity, specific heat and latent heat.⁸⁷ This makes it an ideal method for discovering new phase transitions and finding the enthalpies of those transitions. However, DSC is not usually used for the identifying the type of liquid crystal mesophase as microscopy and x-ray diffraction are more powerful.⁵⁶

DSC works by applying a constant heating (or cooling) rate to a reference sample. A servo system forces the test sample temperature to match that of the reference sample by varying the applied input power to the test sample. At a endothermic transition more power has to be applied to the test sample to maintain the heating rate. This power differential is converted into the enthalpy change associated with a corresponding transition.^{88,89}

⁸⁷G. A. Bonvallet. Differential Scanning Calorimetric Study of the Nematic Liquid Crystal 5CB. PhD thesis. The College of Wooster, June 1999.

⁸⁸D. A. Skoog, F. J. Holler, and S. R. Crouch. *Principles of Instrumental Analysis*. Brooks/Cole Publishing Company, 2007.

⁸⁹W. Steinmann et al. "Thermal Analysis of Phase Transitions and Crystallization in Polymeric Fibers". In: Applications of Calorimetry in a Wide Context - Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry. Ed. by A. A. Elkordy. InTech, Jan. 2013. 1–30.



Figure 1.54. Schematic of a DSC instrument.⁸⁹

1.9.3 X-ray Diffraction

X-ray diffraction (XRD) is a useful technique in liquid crystal research and aids in identification of phases. A wide range of structural information can be gained including, molecular length, layer spacing in smectic materials and tilt angle in the tilted phases.⁵⁶ XRD is based on the principle of Bragg's Law. When x-rays interact with atoms arranged in planes there can be both constructive and destructive interference. Constructive interference happens when the interplanar distance is an integer of the wavelength. This is represented by the Bragg equation below:

$$n\lambda = 2d\sin\theta \tag{1.8}$$

where n is a positive integer, λ the wavelength of the incident beam, d the interplanar distance and θ the scattering angle.



Figure 1.55. Bragg diffraction of x-ray beams.

The illustrations in Figure 1.56 show the characteristic diffraction patterns, under aligned conditions for different mesophase types. In the isotropic phase the fluidity and lack of orientational or positional order results in an extremely diffuse diffraction pattern. The nematic phase (a) shows two diffuse peaks, one in the small angle and a more intense wide angle. These are equivalent to molecular

width and length respectively.⁵⁶ The peaks are very diffuse as the positional order only extends over a distance of a few molecules. In the case of the SmA phase (b), the wide angle is less diffuse due to the increase in order, additionally the small angle is now much more intense due to the layered structure of the phase. This has a periodicity that is slightly less than the molecular length. Usually only the first one or two Bragg peaks are visible, due to weak layering tendency. For an unaligned SmC phase, the diffraction pattern is very similar to the SmA, except that there is a contraction of the layer spacing due to the tilted nature of the phase. Using an aligned sample however, enables the direct conformation and measurement of the tilt angle (θ) as shown in (c).



Figure 1.56. Schematic showing possible XRD scattering patterns for nematic (a), smectic A (b) and smectic C (c) phases.

1.9.4 Electo-optic Characterisation

In addition to the thermal transitional properties of liquid crystals there are a many electro-optic properties that can be investigated. Some of these include, birefringence, dielectric anisotropy and viscosity. Characterisation methods for these will be described in brief in the following sections.

1.9.4.1 Optical Anisotropy / Birefringence

There are a number of different methods available to find the birefringence, δn of a liquid crystal material. Two of these are described below, the first uses an Abbe Refractometer, whereas the second a Berek compensator.

Abbe Refractometer The Abbe Refractometer is a optical device used for the measurement of refractive indices based on the critical-angle effect. A thin film of liquid crystal material is placed between two prisms in a homeotropic alignment. One prism is for illumination the other for measuring the critical angle. The sample is illuminated by monochromatic light and viewed through an eyepiece where an achromatic boundary is centred and readings taken. The refractive indices ordinary and extraordinary are measured individually, and Δn can be determined by: $\Delta n = n_e - n_o^{.90}$

Berek Compensator Method This method involves the direct measurement of the optical retardance of the material on a microscope using a Berek Compensator. The compensator uses a plate of uniaxial crystalline material, usually calcite or magnesium fluoride whose optic axis is perpendicular plate surface. The plate can be tilted to a precise angle via a scaled dial. Tilting of the plate affords the introduction of a phase difference between the ordinary and extraordinary rays, allowing one to offset (compensate) for the optical retardance of a birefringent sample, in this case a liquid crystal. This results in a minimisation of transmitted intensity, which is seen as a dark band or fringe in the sample. With the fringe centred in the field of view an angle reading is taken. This procedure is repeated in the opposite direction yielding two angles, θ_1 and θ_2 . Using the two tilt angles the mean tilt angle, θ can be found:

$$\theta = \frac{|\theta_1 - \theta_2|}{2} \tag{1.9}$$

Calibration tables supplied with the compensator list retardance, δ from a given value of θ . With cell thickness, d and retardation, δ known, the birefringence can be calculated;

$$\Delta n = \delta/d \tag{1.10}$$

⁹⁰G. J. Cross. The Synthesis and Evaluation of Highly Polarisable Organic Materials for Third-Order Nonlinear Optical Applications. PhD thesis. Hull, 1997.

1.9.4.2 Dielectric Anisotropy

The dielectric anisotropy ($\Delta \varepsilon$) of a material can me found through a number of methods including automated testing systems such as those manufactured by Instec Inc, by dielectric spectroscopy or via the capacitance method.

The capacitance method relies on the fact that a electro-optic cell filled with a dielectric material such as a liquid crystal acts as a parallel plate capacitor. A Bridge circuit device is used to measure resistance/capacitance. The initial step required measuring the capacitance of two empty electrode coated cells (C_o) , followed by filling of the cells with the liquid crystal to be tested. One with planar surface alignment (ε_{\perp}) the other with homeotropic alignment $(\varepsilon_{\parallel})$. The capacitance of the two filled cells $(C_{\parallel,\perp})$ is then measured and the dielectric constants are calculated through the following equations:

$$C_o = \varepsilon_0 A/d \tag{1.11}$$

$$C_{\parallel,\perp} = \varepsilon_{\parallel,\perp} A/d \tag{1.12}$$

which can be rearanged to:

$$\varepsilon_{\parallel,\perp} = \frac{C_{\parallel,\perp}}{C_0} \tag{1.13}$$

where ε_0 is the permittivity of free space, A is the area of the electrode surface and d is the thickness of the liquid crystal material. This method relies on excellent alignment of the liquid crystal to achieve reliable results. This can be improved by using magnetic fields.^{61,73}

1.9.4.3 Viscosity

The individual shear viscosity coefficients, n_1 , n_2 & n_3 and also rotational viscosity, γ_1 can be measured through a number of methods. These include mechanical methods such as capillary flow and moving plate, in addition to non-mechanical methods based on light scattering, the Fréedericksz effect and ultrasounds.^{12,19–22} Viscosity measurments were not undertaken in this work and therefore individual methods will not be discussed further.

2 Aims

2.1 Asymmetric Dimers for DFLC Mixtures

Existing DFLC materials are multi-component systems featuring both positive and negative compounds. Instead of having a binary mixture the aim was to create a single material with features of both types of compound. Dimers present the opportunity to have a material with different structureal units in a single component, where one section acts as the positive compound and the other as the negative (Figure 2.1). Dimer materials also exhibit some unique properties as detailed in the preceding chapter.



Figure 2.1. Basic structure of target materials, with one section acting as a positive compound and the other a negative

The primary aim of this project is to synthesise and investigate the mesomorphic properties for the series of fluorinated asymmetric dimers listed in Table 2.1.

$F \longrightarrow (CH_2)_n \longrightarrow (CH_2)_n \to R$			
Compound	n	R	Shape
90	8	$\mathrm{C}_{5}\mathrm{H}_{11}$	linear
91	8	$\rm C_7H_{15}$	linear
92	8	$\mathrm{OC}_4\mathrm{H}_9$	linear
93	9	$\mathrm{C}_{5}\mathrm{H}_{11}$	bent
94	9	$\mathrm{C_7H_{15}}$	bent
95	9	OC_4H_9	bent

 Table 2.1. Primary target asymmetric dimer materials.

Targeting materials with differing parity spacer groups generates two different systems. Based on the distribution of preferred conformations the even lengthed spacer gives linear shaped dimer, whereas the odd spacer forms a bent material. These were selected as the shape of the material has a substantial effect on the properties. The spacer group is an alkane chain of either eight or nine methylene groups. Spacer lengths too short would give materials with higher melting points and reduced liquid

crystalline behaviour, whereas significantly long chains cause the differences in properties between the spacer parity to be reduced.

A terphenyl core structure was selected for both mesogenic arms, this gives the material a large length to breadth ratio and thus should give substantial liquid crystalline behaviour, additionally the cores are sufficiently long to give a large Δn . The negative mesogenic arm incorporates lateral fluorine substituents on the central aromatic ring for generating a lateral dipole, contributing to the (ε_{\perp}) of the system. Additionally in the terminal position an alkyl or alkoxy chain is selected, relatively short chains are selected to limit promotion of smectic behaviour while keeping melting points low. The positive arm used terminal and lateral-terminal fluorines to give the longitudinal dipole. The key feature of this moiety is the 1-bromo-2,3-difluorobenzene unit. Fluorines in this position impart a longitudinal dipole and thus contribute to the parallel dielectric constant (ε_{\parallel}) of the material.

Following synthesis and characterisation of the mesomorphic behaviour, the secondary aim of the project was to investigate some electro-optic properties and determine viability as DFLC materials.

3 Synthetic Discussion

3.1 Synthetic Routes & Schemes

The synthetic route to the target materials converged from three starting points — the methylene spacer group, the positive arm and the negative arm before the being coupled together in consecutive Suzuki cross-coupling reactions.

3.1.1 Synthesis of the Methylene Spacer Group



b = DEG, (i) hydrazine monohydrate (ii) KOH (iii) HCl 36 %

Scheme 3.1. Synthesis of spacer groups 67 and 68 starting with a Friedel Crafts acylation of bromobenzene with diacyl chlorides, followed by reduction of the diketones via Wolff Kishner procedure.

Synthesis began by targeting the central spacer groups 67 and 68, using modified procedures form the work of Jaunin⁹¹ and Kantor.⁹² The first step was a Friedel Crafts acylation⁹³ of bromobenzene, 62 with suberoyl chloride, 63 or azelaoyl chloride, 64 to create the diketones, 65 and 66. Bromobenzene was used both in excess and as a solvent to ensure that it was added to both sides of the diacylchloride, the excess was easily removed later under vacuum and recrystallisation. An appreciable amount of dibromobenzene was isolated, this was found to be a mixture of two isomers.

⁹¹R. Jaunin and T. Baer. Helv. Chim. Acta, 1957, **40**, 2245–2248.

⁹²S. W. Kantor, T. C. Sung, and E. D. T. Atkins. *Macromolecules*, 1992, 25, 2789–2795.

⁹³C. Friedel and J. M. Crafts. C. R. Hebd. Seances Acad. Sci. 1877, 1392–1395.

The dibromobenzene side product from a Friedel Crafts of bromobenzene is well known.⁹² Initial preparations used column chromatography to purify the material, however in subsequent repeats recrystallisation proved equally effective and any remaining impurities were removed following the reduction step.



Figure 3.1. Friedel Crafts acylation mechanism, proceeding via intermediate acylium ion.

The mechanism for the Friedel Crafts acylation is shown in Figure 3.1. The reaction proceeds through a acylium ion intermediate which is 'attacked' by an electron pair from the bromobenzene. As an electron donating group, the bromine in bromobenzene is ortho/para directing and due to it's size, substitution in the ortho position is sterically hindered. Thus the product form the acylation is only the para isomer.

Both diketones were reduced via Wolff Kishner reaction⁹⁴ to give the complete spacer units **67** and **68**. Due to poor solubility, a reasonably large amont of solvent was required in order to dissolve the diketones. Additionally an excess of hydrazine is required to limit the formation of an azine side product.⁹² Unreduced diketone in addition to remaining bromobenzene and dibromobenzene from the Friedel Crafts step was easily separated by column chromatography using the low polarity solvent hexane.



Figure 3.2. Mechanism for the reduction of a ketone by Wolff Kishner reaction, featuring the intermediate hydrazone.

Reduction via the Wollf Kishner reaction mechanism (Figure 3.2) proceeds through the use of hydrazine to create a hydrazone intermediate. Addition of a base leads to the evolution of nitrogen and subsequent added acid yields the reduced alkyl materials.

⁹⁴L. Wolff. Justus Liebigs Ann. Chem. 1912, **394**, 86–108.

3.1.2 Synthesis of the Positive Arm

Scheme 3.2 shows the synthesis route to the positive arm. Introduction of the fluorine substituents was achived through the use of 1-bromo-2,3-diffuorobenzene unit which is widely available from chemical suppliers. Synthesis of the positive arm involved both low temperature lithiations and a selective Suzuki coupling.



Scheme 3.2. Synthesis of positive arm, 73 starting from 1-bromo-2,3-difluorobenzene.

1-bromo-2,3-difluorobenzene, 69 was converted to the boronic acid, 70 both via a Grignard and an aryllithium reagent. Multiple preparations via both methods achieved yields of 70–80 %.

Generation of boronic acids progresses through three steps as shown in Figure 3.3. First, generation of the aryl-metal intermediate, either a Grignard reagent or an aryl-lithium. Second, the addition of trimethyl borate results in the electrophilic borate trapping of the trialkylborate. Finally, quenching with aqueous acid causes hydrolysis of the labile boronate ester yielding the boronic acid, 70.95

⁹⁵D. G. Hall. "Structure, Properties, and Preparation of Boronic Acid Derivatives. Overview of Their Reactions and Applications". In: Preparation and Applications in Organic Synthesis and Medicine. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2005. 1–99.



Figure 3.3. Formation of a boronic acid via (a) generation of the organometallic intermediate, M = Mg or *n*-BuLi, (b) electrophilic borate trapping of trimethyl borate, (c) hydrolysis of the boronic ester to the boronic acid.⁹⁵

Preparation of the Grignard⁹⁶ method consisted of adding the aryl bromide to magnesium turnings in a ethereal solvent (THF). The creation of the organometallic proceeds via an oxidative insertion mechanism, where the Mg inserts between a new aryl-Br bond. The exact mechanism for this is not known, one possibility is illustrated in Figure 3.4⁹⁷



Figure 3.4. Oxidative insertion mechanism for preparation of a Grignard reagent where Mg is inserted into the new aryl-Br $bond^{95,97}$

An alternative method to the boronic acid is via a low temperature lithiation. The halogen metal exchange mechanism for this is shown in Figure 3.5. In theory the protons (H_{α}) alpha to the fluorine substituents can also be lithiated (via the ortho directed metallation mechanism, Figure 3.10). However, the bromine is significantly more labile than the protons so only the desired product is seen.^{97,98}



Figure 3.5. Lithiation via halogen metal exchange.

⁹⁶V. Grignard. C. R. Hebd. Seances Acad. Sci. 1900,

⁹⁷F. A. Carey and R. Giuliano. Organic Chemistry. 4th ed. McGraw-Hill Science/Engineering/Math, Jan. 2010.

⁹⁸J. Clayden et al. Organic Chemistry. Oxford University Press, Oxford, Sept. 2004.

3.1.2.1 Suzuki Reaction

The Suzuki reaction is a palladium catalysed cross-coupling, first reported by Suzuki & Miyaura in $1979^{99,100}$ It is one of a string of different transition metal-catalysed reactions used to create arylaryl bonds, others include the Heck,^{101,102} Negishi^{103,104} and Stille^{105,106} couplings. The Suzuki's advantages over the other cross-couplings include, wide availability of boronic acids, low costs, low toxisity and mild conditions. In the Suzuki reaction an aryl halide (or vinyl halide / pseudohalide) undergoes a palladium catalysed reaction with a nucleophillic alkyl-boron species such as a boronic acid or ester. All Suzuki couplings in this work used boronic acids, with tetrakistriphenylphosphine palladium(0).



Figure 3.6. Suzuki Reaction Mechanism, featuring oxidative addition, transmetallation and reductive elimination steps.

The mechanism for the Suzuki mechanism is shown in Figure 3.6. There are three key steps, oxidative addition, transmetallation and reductive elimination. In the oxidative addition step, two of the triphenylphosphine ligands are replaced by the aryl-halogen ($\mathbb{R}^1 \& X$) oxidising the palladium, $\mathbb{Pd}^0 \rightarrow \mathbb{Pd}^{II}$. Base present in the system removes a further ligand. In the transmetallation stage, the boronic acid is converted to a boronate under basic conditions, the OH and halogen leave the Pd as X^+ and $-\mathbb{B}(OH)_4$ with the \mathbb{R}^2 group binding to the palladium. Two triphenylphosphine ligands then replace the newly bonded $\mathbb{R}^{1-}\mathbb{R}^2$ product in the reductive elimination step, restoring the palladium $\mathbb{Pd}^{II} \rightarrow \mathbb{Pd}^0$.

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- ¹⁰⁰N. Miyaura and A. Suzuki. J. Chem. Soc., Chem. Commun. 1979, 866-2.
- ¹⁰¹R. F. Heck and J. P. Nolley. J. Org. Chem. 1972, **37**, 2320–2322.
- ¹⁰²H. A. Dieck and R. F. Heck. J. Am. Chem. Soc. 1974, **96**, 1133–1136.
- ¹⁰³S. Baba and E. Negishi. J. Am. Chem. Soc. 1976, **98**, 6729–6731.
- ¹⁰⁴E. Negishi, A. O. King, and N. Okukado. J. Org. Chem. 1977, 42, 1821–1823.
- ¹⁰⁵D. Milstein and J. K. Stille. J. Org. Chem. 1979, **44**, 1613–1618.

¹⁰⁶D. Milstein and J. K. Stille. J. Am. Chem. Soc. 1978, **100**, 3636–3638.

Protodeboronation Under Suzuki reaction conditions, some boronic acids can undergo a base catalysed protodeboronation, $Ar-B(OH)_2 + H_2O \longrightarrow Ar-H + B(OH)_3$.^{95,107–109} reducing the available boronic acid reagent and lowering yields. Alternative boron materials such as boronic esters and trifluoroborates are more stable. In the case of the work discussed here, boronic acids were sufficient and any protodeboronated materials was easily removed with the described purification methods. Additionally, in most cases the boronic acid was used in excess, thereby yields were not overly reduced.

Homo-coupling The palladium catalysed homo-coupling or self-coupling of aryl derivatives is well known.¹¹⁰ Self-coupling produces symmetrical aryl units and can happen through two main mechanisms, reductive and oxidative.^{111–113} The reductive mechanism involves electrophilic aryl derivatives such as aryl-halides or triflates in the presence of a reducing agent.¹¹⁴ In the second mechanism nucleophilic aryls such as boronic acids in conjunction with an oxidant give the symmetrical bi aryl in an oxidative process.¹¹² The oxidative coupling mechanism is important in normal Suzuki reaction conditions where the homo-coupled boronic acid side product is often seen.^{108,115,116} In some cases the homo-coupled material has been the targeted material.¹¹⁵

Biphenyl intermediate 72 was synthesised from a selective Suzuki coupling of bromoiodobenzene, 71 with boronic acid, 70 as shown in Figure 3.7 The selectivity in this reaction arrises from the fact that the iodine is a much better leaving group than bromine. The reactivity of the halogen leaving groups is in the order of $I > Br > Cl^{97,98}$ Bromoiodobenzene was used in excess to limit formation of the double coupled material, 74. In some preparations, an appreciable amount (14 %) of the homo-coupled boronic acid (75) was isolated.

¹⁰⁸E. M. Campi et al. J. Chem. Soc., Chem. Commun. 1994, 2395–1.

¹⁰⁷H. G. Kuivila and J. F. Reuwer Jr. Can. J. Chem. 1963, **41**, 3081–3090.

¹⁰⁹G. Noonan and A. G. Leach. Org. Biomol. Chem. 2015, **13**, 2555–2560.

¹¹⁰S. Kotha, K. Lahiri, and D. Kashinath. *Tetrahedron*, 2002, 58, 9633–9695.

¹¹¹C. Adamo et al. J. Am. Chem. Soc. 2006, **128**, 6829–6836.

¹¹²M. Moreno-Mañas, M. Pérez, and R. Pleixats. J. Org. Chem. 1996, **61**, 2346–2351.

¹¹³J. Hassan et al. Chem. Rev. 2002, **102**, 1359–1470.

¹¹⁴A. Jutand and A. Mosleh. J. Org. Chem. 1997, **62**, 261–274.

¹¹⁵Z. Z. Song and H. Wong. J. Org. Chem. 1994, **59**, 33–41.

¹¹⁶T. Gillmann and T. Weeber. Synlett, 1994, **1994**, 649–650.



Figure 3.7. Suzuki coupling of 71 and boronic acid 70 giving the (a) targeted single-coupled material, (b) double-coupled terphenyl and (c) homo-coupled biphenyl.

The final step to form the positive arm was the conversion of bromide, 72 to the boronic acid 73. This was carried out by a low temperature lithiation. The alternative Grignard method is possible, but relatively difficult to initiate. Some attempted preparations this material resulted in incomplete conversion to the boronic acid leaving some bromide remaining. This solid was not removed by the hexane stirring process, due to low solubility. Both the bromide and the boronic acid look similar on NMR so the bromide impurity can be difficult to detect. Figure 3.8 shows the ¹³C-NMR spectra of (a) the starting bromide, 72 and (b) the targeted boronic acid, 73. The carbon attached to the bromide shows a peak at 122 ppm. However, once bonded to the boron in the boronic acid this carbon no longer shows a visible signal. This additional bromide caused issues with later Suzuki couplings, where the boronic acid can couple to the bromide impurity in addition to the targeted coupling partner. This problem was solved in later lithiations by using a larger excess of *n*-BuLi to ensure the complete conversion to the boronic acid.



Figure 3.8. ¹³C-NMR spectra of (a) bromide, 72 and (b) boronic acid, 73. The C-Br peak is shown at 122 ppm, the same carbon when attached to boron is no longer visible.

3.1.3 Synthesis of the Negative Arm

Synthesis of the negative are began with preparation of the ketone material **78** by Friedel Crafts acylation⁹³ of bromobenzene, **62** and valeryl chloride. As with the previous acylations with bromobenzene, only the para substituted product is formed as the bromine is ortho-para directing, with the ortho position being sterically hindered. Wolff-Kishner reduction⁹⁴ of the ketone yieleded 1-bromo-4-pentylbenzene **79**. The heptyl analogue **80** was supplied by Kingston Chemicals Ltd. and was prepared via the same method.



Scheme 3.3. Synthesis of the negative arm units, 85, 86 and 87. Compounds 76 and 80 were supplied by Kingston Chemicals Ltd.

In addition to the alkyl aromatics, an alkoxy derivative was also required. This was prepared using a Williamson Ether Synthesis¹¹⁷ of 4-bromophenol with 1-bromobutane, giving the targeted material **81** in high yield, 96 %. The mechanism for the Williamson ether synthesis is shown in Figure 3.9.

¹¹⁷A. Williamson. Philos. Mag. 3, 1850, **37**, 350–356.
The reaction proceeds in the presence of a base (K_2CO_3) and an aprotic solvent (MEK). The base removes the proton from the phenol and the resulting alkoxide ion attacks the δ^+ carbon on the primary alkyl-halide, via an S_N 2 mechanism. The aprotic solvent is required so that nucleophilicity of the alkoxide ion isn't suppressed by solvation effects.⁹⁷



Figure 3.9. Williamson Ether Synthesis, $S_N 2$ mechanism.

Bromide materials **79**, **80** and **81** were all coupled to boronic acid, **76** via a Suzuki reactions generating the biphenyl intermediates **82**, **83** and **84**. The mechanisms and procedures were as described previously. However, the boronic acid was used in excess to ensure the conversion of all the bromide, simplifying the purification procedure. All three reactions were high yielding 76–89 %.

Boronic acids 85, 86 and 87 were prepared via lithiations of the biphenyls prepared in the previous step. Unlike previous lithiations which used the halogen metal exchange mechanism, these reactions used the directed ortho metallation mechanism shown in Figure 3.10 (a). This mechanism exploits the acidic proton ortho to a fluorine substituent. The electron withdrawing effect of the fluorine substituents leaves the proton electron deficient and thus a good leaving group in nucleophilic substitution. Additionally the lithium coordinates with the fluorine reinforcing the ortho direction of the mechanism. Conversion from the organometallic intermediate to the boronic acid progresses as previously discussed, by addition of an trialkylborate followed by quenching with acid. Boronation via a Grignard is not possible with these materials as, at the temperatures required for initiation the metal derivative is unstable and undergoes β -elimination of the FMgBr salt, creating a highly reactive aryne (b). The same issue occurs with lithiation, however, the more powerful nucleophile, *n*-BuLi can metallate at a much lower temperature (-78 °C) where the metal derivative is stable.⁹⁷



Figure 3.10. (a) Lithiation — Directed ortho metallation mechanism (b) Generation of aryne via β elimination of FMgBr.

3.1.4 Suzuki Coupling Reactions to Primary Target Materials

The final stages synthesis involved coupling the two arm units to the spacer group via consecutive Suzuki coupling reactions as shown in Scheme 3.4. All targets dimers have a common positive arm structure based on boronic acid, **73** so this was coupled first reducing the number of steps to complete the synthesis.



a = DME, H₂O, Na₂CO₃, Pd(PPh₃)₄

Scheme 3.4. Suzuki coupling of target materials 90-95, initially coupling the positive arm, 73 to the spacers, followed by a consecutive coupling to the various negative arms 85-87.

The symmetric nature of the two methylene spacer units complicates the reaction. Unlike the selective coupling to prepare 72, the spacer units 67 and 68 have no selectivity (I vs Br) to exploit, both halogens are identical. Additionally the methylene spacer separates the ends of the molecule so that steric effects are reduced. The combination of these effects are that a mixture of the targeted single coupled material and the double coupled dimer are produced, separation of which is achievable, but non-trivial. By controlling the stochiometery and using an excess of the spacer unit vs the boronic acid the amount of doubly coupled material can be reduced giving the mono-coupled system as the major product. The excess spacer can easily be recovered by chromatography and reused. Yields of 51 and 55 % were achieved for these reactions.

The subsequent Suzuki couplings with 88 and 89 were comparatively straightforward as only a single halogen site is now available. These reverted to the conventional method where an excess

of the boronic acid is employed. Some homo-coupled boronic acid material was easily isolated by chromatography. Yields for the final reactions were in the range 45-68 %.

Structure conformation by NMR and MS with purity via EA an HPLC. Table 3.1 shows a summary of the final compounds with yields for the final coupling and purity by HPLC.

F			— (CH ₂) _n –	F F R
Compound	n	R	Shape	Purity %
90	8	OC_4H_9	linear	98.2
91	8	$\mathrm{C}_{5}\mathrm{H}_{11}$	linear	99.0
92	8	$\mathrm{C}_{5}\mathrm{H}_{11}$	linear	96.9
93	9	$\mathrm{OC}_4\mathrm{H}_9$	bent	97.8
94	9	$\mathrm{C}_{5}\mathrm{H}_{11}$	bent	98.7
95	9	$\mathrm{C}_{5}\mathrm{H}_{11}$	bent	99.4

Table 3.1. Summary of primary target dimers showing purity % from HPLC.

4 Mesophase Behaviour I

The transitional properties of the six primary target materials were investigated using a combination of optical polarising microscopy (OPM), differential scanning calorimetry (DSC) and for some materials x-ray diffraction (XRD). For OPM, the images are generally taken on cooling from the isotropic phase on untreated slides unless otherwise specified. Full experimental procedures are detailed in Section 10.3.

4.1 Compound 90



Figure 4.1. Structure of target compound 90, transition temperatures (°C) on heating.

Compound 90 is a linear dimer with pentyl terminal chain. This material has both a nematic and a smectic A phase. The material is crystalline up to 96 °C where it melts into a smectic phase, continued heating till 228 °C yields the nematic phase which clears to isotropic at 245 °C. The smectic phase has a much greater width than the nematic, a range of 132 °C.





(b)



Figure 4.2. OPM textures of 90 on cooling from the isotropic phase [x200 magnification] (a) N at 235 °C, (b) N-SmA transition at 227 °C, (c) SmA at 222 °C, (d) SmA at 222 °C, showing dark areas in homeotropically aligned regions.

[H]

Figure 4.2 shows the textures seen on cooling the material from the isotopic phase. The nematic phase forms as droplets and develops into a typical marble type texture (a) as seen for nematics. Upon further cooling the nematic phase transitions (b) to the smectic phase, where a focal conic fan texture is developed (c). In the smectic phase the lack of Schlieren texture in the homeotropically aligned areas (d) means that a tilted smectic phase can be discounted and a SmA phase assigned.

DSC for compound 90 showed three transitions, the first at 97 °C where the material melts into the smectic phase, this has the largest enthalpy, expected upon changing from an ordered crystal to much less ordered liquid crystal. The second transition is from the smectic A to the nematic phase at 228 °C and has a much smaller enthalpy. The final transition from the nematic to isotropic phases occurs at 245 °C, with an unusually large enthalpy of 8.2 kJ mol⁻¹ (discussed later). Transitions on cooling were at the same temperatures with the exception of crystallisation, which happened ~ 30 °C below the melting point. Figure 4.3 shows the DSC curve, and Table 4.1 the data for compound 90.



Figure 4.3. DSC curve for compound 90, (--) 1st heat, (--) 2nd heat, (--) 2nd cool.

Table 4.1. DSC data for compound 90, transition temperatures and enthalpies taken from the 1st heating run.

Transition (°C)	C-	96	C A	228	N	245	T
$\Delta \mathbf{H} \ (kJ mol^{-1})$	Cr	32.7	SmA _c	2.0	IN	8.2	180

In addition to the two characterisation methods already detailed dimer, **90** was investigated by XRD. Figure 4.4 (a) shows the diffraction pattern and the 2D plot of intensity vs 2θ (b) for the smectic phase at 150 °C. The nematic phase could not be captured as it exceeds operating range (200 °C) of the XRD furnace. Table 4.2 lists intensities and calculated lengths found. The smectic phase of this material shows two intensities in the diffraction pattern. In the wide angle there is a diffuse intensity at $2\theta = 18.52^{\circ}$ that represents the lateral distance between mesogens, this is

calculated to be 4.79 Å. The diffuse shape of the peak is indicitive of the liquid crystal nature of the material. The small angle shows a sharp peak, with much greater intensity at $2\theta = 4.03^{\circ}$, d = 21.89 Å. The sharp, intense peak in the small angle usually points to a layered structure in this case smectic type system. There is no apparent tilt between the two intensities, thus a tilted smectic phase can be ruled out. Additionally, the wide angle scattering is too diffuse to correlate with the hexatic order of the smectic B phase.⁵⁶



Figure 4.4. XRD pattern of 90 in the SmA_c phase at 130 °C.



Figure 4.5. XRD plot of 90 in the SmA_c phase at 130 °C. The small peak to the left of the intense peak at $2\theta = 4.03$ is an artefact from the optics.

Table 4.2. XRD data for compound 90.

Phase	Temp (°C)	2θ (°)	d (Å)	Comments
SmA	120	4.03	21.89	smectic layer spacing d/l = 0.54
SIIIA _c	100	18.52	4.79	lateral distance between mesogens

The estimated all-trans length of compound 90 is $l \sim 40.51$ Å. The value of d/l in conventional calamitic smectics is approximately 1 and indicates monolayer type phase. Interdigitated smectics (Sm_d) have $d/l \sim 1.8$ this represents the slight overlap of mesogens giving a much larger layer spacing. In the case of 90, the value of d/l = 0.5 indicates a intercalated smectic A phase (Sm_d), as

depicted in Figure 4.6. In this system the non-equivalent mesogens interact and the flexibility of the terminal pentyl chain fills the void between the spacers. The mixing of the unlike mesogenic units is entropically favourable.^{43,45,56,118–121}



Figure 4.6. Schematic of the intercalated SmA phase of 90, the red ellipses are the positive mesogens and the blue the negative mesogens.

¹¹⁸J. L. Hogan, C. T. Imrie, and G. R. Luckhurst. *Liq. Cryst.* 1988, **3**, 645–650.

¹¹⁹A. E. Blatch and G. R. Luckhurst. *Liq. Cryst.* 2000, **27**, 775–787.

 $^{^{120}{\}rm G.}$ S. Attard et al. $Liq.~Cryst.~2006,~{\bf 16},~529{-}581.$

¹²¹C. T. Imrie. *Liq. Cryst.* 2011, **33**, 1449–1485.

4.2 Compound 91



Figure 4.7. Structure of target compound 91, transition temperatures (°C) on heating.

In compound 91 the terminal pentyl group on the negative arm has been replaced with a heptyl group. As with the previous dimer, 91 shows nematic and smectic phases identified by the characteristic textures seen in Figure 4.8. The nematic phase appears as droplets on cooling from the isotropic phase at 235 °C (a) and develops into Schlieren and marble textures. The transition to the smectic A phase occurs at 217 °C (b) and appears as a typical focal conic fan texture.





Figure 4.8. OPM textures of 91 on cooling from the isotropic phase [x200 magnification] (a) N at 232 °C, (b) N-SmA transition at 215 °C, (c) SmA at 210 °C, (d) SmA at 210° showing homeotropic area.

The slightly longer chain imparts a subtle difference to the transitional properties. Both the melting point and the phase stability have been slightly reduced, by 4 and 10 °C respectively. The lower melting point is a result of the greater flexibility granted by the longer chain. One might expect the slightly longer chain to increase liquid crystal phase stability due to the the combination of enhanced microphase segragation and strengthened interaction between the alkyl chains, however this is surpassed by the negative effect of flexibility that disrupts molecular packing.

Compound **91** showed similar behaviour on DSC as the previous linear material, the data on heating is shown in Table 4.3. The SmA-N transition has an enthalpy of 1.4 kJ mol⁻¹ and the T_{N-I} transition has a particularly large enthalpy of 7.2 kJ mol⁻¹.

Table 4.3. DSC data for compound 91, transition temperatures and enthalpies taken from the heating run.

Transition (°C)	Cm	92	Cros A	217	N	235	Ico
$\Delta \mathbf{H} \ (\mathbf{kJ mol^{-1}})$	Cr	32.5	SIIIA _c	1.4	IN	7.2	180

XRD experiments were not performed for compound **91**. However, based on the previous materials, would likely indicate a intercalated system with a $d/l \sim 0.5$ as shown in Figure 4.6. However, the additional length of the terminal chain would increase the likelihood of a monolayer type system as the terminal chain becomes too long to efficiently fill the void between spacers.

4.3 Compound 92



Figure 4.9. Structure of target compound 92, transition temperatures (°C) on heating.

Like the previously discussed materials, compound **92** is a linear dimer, but the terminal alkyl chain has been replaced by a butoxy group instead. This material also displays nematic and smectic mesophases and the typical textures can be seen in Figure 4.10. The addition of the alkoxy group has, as would be expected raised the melting point, and the T_{N-I} by 20–30 °C. The rise in melting point and nematic phase stability is a result of the more linear shape of the alkoxy systems, that allows for better molecular packing in addition to the oxygen partaking in the mesomeric effect strengthening lateral associations.





Figure 4.10. OPM textures of 92 on cooling from the isotropic phase [x200 magnification] (a) N at 270 °C, (b) N at 255 °C, (c) N-SmA transition at 250 °C, (d) SmA at 250°.

Like the both previous linear materials compound 92 has a much larger ΔH_{N-I} than ΔH_{SmA-N} . The T_{N-I} transition has an enthalpy of 8.1 kJ mol⁻¹, while the SmA-N transition has an enthalpy of 2.2 kJ mol⁻¹.

Table 4.4. DSC data for compound 92, transition temperatures and enthalpies taken from the heating run.

Transition (°C)	C.	106	C A	246	N	266	T
$\Delta \mathbf{H} \; (\mathrm{kJ} \mathrm{mol}^{-1})$	Cr	75.5	SmA	2.2	IN	8.1	Iso

XRD experiments were not performed for compound **91**. However, besed on previous materials in this series, would likely indicate a intercalated system with a $d/l \sim 0.5$, as shown in Figure 4.6. The terminal chain is sufficiently short to effectively fill void between the alkyl spacer groups.

4.4 Compound 93



Figure 4.11. Structure of target compound 93, transition temperatures (°C) on heating.

Compound **93** is the first of the bent dimers to be discussed. Compound **93** has a nine methylene long spacer combined with a pentyl terminal chain. The additional methylene group in the spacers confers a bent shape to the dimer. This has a great effect on the transitional properties of the material. Compound **93** has both nematic and smectic phases.



Figure 4.12. OPM textures of **93** on cooling from the isotropic phase [x200 magnification] (a) N at 188 °C, (b) N-SmC transition at 185 °C, (c) SmC at 182 °C, (d) SmC at 180 °C showing Schlieren texture in homeotropic region.

Figure 4.12 shows the OPM textures seen for this material in the nematic and smectic phases. The nematic phase (a) shows characteristic Schlieren and marble textures. On the transition to the smectic phase bayonets into each other (b), quickly converging into a fan type texture typical of smectics (c). The presence of Schlieren texture in the homeotropic areas after shearing (d) indicated the tilted smectic C phase. However, this assignment was later refined to a smectic C alternating phase, and will be discussed in following sections.

Figure 4.13 shows the DSC curves for compound **93**. The material melts into the smectic phase at 69 °C, transitions to the nematic at 180 °C before clearing at 188 °C. The much lower liquid crystal phase stability is a consequence of the poorer packing in the nematic phase due to the bent shape. The enthalpy of the smectic-nematic transition at 8.7 kJ mol⁻¹ is relatively large compared to that seen in the linear dimers previously discussed. Comparatively the nematic-isotropic transition enthalpy $(0.7 \text{ kJ mol}^{-1})$ is much smaller and comparable to that seen in conventional calamitic mesogens^{122,123} and other bent shaped dimers.⁵⁰



Figure 4.13. DSC curve for compound 93.

Compound **93** was subjected to XRD measurements in order to confirm the presence of the SmC phase and calculate the tilt angle. Figure 4.14 shows the diffraction patterns for the nematic (a) and smectic (b) phases and Figure 4.15 a plot of the same data. The nematic shows the characteristic highly diffuse scattering in the small and wide angle, where the wide angle represents the lateral distance between the molecules. The smectic phase has a high intensity peak in the small angle and diffuse scattering in the wide angle. The wide angle scattering is less diffuse and has a slightly smaller d than that seen in the nematic phase, this is expected and a result of the greater order of the smectic phase. The highly intense small angle scattering at 4.35 2θ (easily seen in Figure 4.15 is a result of the layered structure of the phase. There initially appears to be a tilt of the wide angle scattering appears to be approximately 16° . However, this is not likely to be accurate as the small

¹²²P. G. De Gennes. Mol. Cryst. Liq. Cryst. 1984, **115**, 11–22.

¹²³S. Chandrasekhar. Liquid Crystals. 2nd ed. Vol. 3. Cambridge University Press, Cambridge, 1992.

angle is not particularly well resolved and as will be discussed later the anticlinic smectic C phase should show no tilt on XRD. Additionally the apparent appearance of tilt could be a result of poor alignment of the sample with respect to the magnetic field.



Figure 4.14. XRD patterns of 93 in (a) the N phase at 195 °C and (b) the SmC phase at 185 °C.



Figure 4.15. XRD plot of 93 in N and SmC phases °C.

Table 4.5. XRD data for compound 93.

Phase	Temp (°C)	2θ (°)	d (Å)	Comments
Ν	195	4.46	19.81	
		18.01	4.92	lateral distance between mesogens
SmC_{ca}	185	4.35	20.30	smectic layer spacing $d/l = 0.50$
cu		18.64	4.76	lateral distance between mesogens

The all-trans length of **90**, (as measured in Chem3D, MM2 minimised structure) l = 40.3 Å. In the smectic phase the small angle scattering has d/l=0.5, this indicates an intercalated smectic C phase (SmC_c). The bent dimer adopts a different arrangement to the previously discussed linear dimers. The SmC_{ca} phase is shown in Figure 4.16. This system is an alternating/anticlinic phase. Locally,

within a layer there is a tilt angle, however the alteration through the layers means macroscopically there is zero effective tilt angle — this might account for the inconclusive tilt in the XRD.



Figure 4.16. Schematic of the intercalated, alternating SmC phase of 93, the red ellipses are the positive mesogens and the blue the negative mesogens.

Assignment of the anticlinic phase was subsequently confirmed by OPM measurements. The presence of $s = \pm 1/2$ singularities in the Schlieren texture have previously been reported to indicate a anticlinic type phases.^{86,124–126} Figure 4.17 shows the presence of both $s = \pm 1$ and $s = \pm 1/2$ defects in the Schlieren texture of the smectic phase. The $s = \pm 1/2$ singularities arise from screw dislocations or dispirations where there is no discontinuity in the tilt director.¹²⁴



Figure 4.17. OPM of **93**, showing presence of both $s = \pm 1$ and $s = \pm 1/2$ defects in the Schlieren texture of the smectic phase. Taken on cooling from the isotropic phase [x400 magnification] at 180 °C.

¹²⁴Y. Takanishi et al. J. Mater. Chem. 1992, **2**, 71–3.

¹²⁵J. Watanabe, H. Komura, and T. Niiori. *Liq. Cryst.* 1993, **13**, 455–465.

¹²⁶J. Watanabe et al. Progress in Polymer Science, 1997, **22**, 1053–1087.

4.5 Compound 94



Figure 4.18. Structure of target compound 94, transition temperatures (°C) on heating.

As with the linear dimers, replacement of the pentyl chain with the longer heptyl chain in dimer, **94** has a relatively small effect on the mesophase properties. The material has nematic and smectic C alternating phases, which were identified based on the textures shown in Figure 4.19.



Figure 4.19. OPM textures of 94 on cooling from the isotropic phase [x200 magnification] (a) N at 180 °C, (b) N-SmA transition at 176 °C, (c) SmC at 170 °C, (d) SmC at 160 °C showing $S = \pm 1/2$ defects.

The nematic phase exhibits a Schlieren texture (a). At the transition, the smectic phase displays bayonet type growth (b) stabilising onto a focal conic fan texture (c). On shearing the smectic

phase has a Schlieren texture (d) in the homeotropic areas usually associated with the SmC phase. However, the appearance of $S = \pm 1/2$ defects suggests an alternating/anticlinic type phase.

Table 4.6. DSC data for compound 94, transition temperatures and enthalpies taken from the heating run.

Transition (°C)	C	70	a a	172	NT	179	т
$\Delta H \ (kJ \ mol^{-1})$	Cr	12.9	SmC_{ca}	8.4	IN	0.6	ISO

Table 4.6 shows the DSC data on heating for this material. **94** has a lower melting point (70 °C) and LC phase stability (178 °C) than the equivalent linear dimer. As expected the slightly longer terminal chain confers lower melting point and T_{N-I} than than the shorter chain in **93**. Both **93** and **94** have slightly narrower nematic phase ranges than the respective linear dimers. The enthalpy values for the liquid crystal transitions are comparable to the previous bent dimer, and conventional calamitics.

XRD was performed on this material, and showed similar behaviour as the previous bent dimer. The XRD data is summarised in the Table 4.7 below. The layer spacing of d/l = 0.5 indicates an intercalated system. There is no tilt in the XRD pattern. The smectic phase is assigned as SmC_{ca} based on the combination of a small angle where d/l = 0.5 and the presence of $S = \pm 1/2$ singularities in the Schlieren texture.

Table 4.7. XRD data for compound 94.

Phase	Temp (°C)	2θ (°)	d (Å)	Comments
N	105	4.46	19.81	
IN	195	18.01	4.92	lateral distance between mesogens
SmC	185	4.35	20.30	smectic layer spacing $d/l=0.5$
SIIIC _{ca}	160	18.64	4.76	lateral distance between mesogens

4.6 Compound 95



Figure 4.20. Structure of target compound 95, transition temperatures (°C) on heating.

Compound 95 is the bent analogue of 92, the terminal chain is a butoxy group. This material, like those previously discussed has both a nematic and smectic phase. The nematic phase appears at 210 °C upon cooling from the isotropic liquid, and the Schlieren texture can be seen in Figure 4.2a. The nematic-smectic transition occurs at 193 °C, this phase was was assigned a smectic C based on the focal conic texture (c) combined with the presence of Schlieren texture in homeotropic aligned areas (d). No evidence of $S = \pm 1/2$ defects was found.



Figure 4.21. OPM textures of 95 on cooling from the isotropic phase [x200 magnification] (a) N at 202 °C, (b) N-SmC transition at 195 °C, (c) SmC at 190 °C, (d) SmC at 179 °C showing Schlieren texture.

As with the other bent systems, the melting point and phase stability is lower than that seen in the linear dimers. And compared with the other bent dimers the alkoxy group has raised the melting point and T_{N-I} due to the additional linearity of the group. Interestingly, this material has a slightly wider nematic phase stability than the other bent dimers, most likely due to the better molecular packing in the nematic phase.

Table 4.8. DSC data for compound 95, transition temperatures and enthalpies taken from the heating run.

Transition (°C)	C.	80	C C	193	N	210	T
$\Delta H \ (kJ \ mol^{-1})$	Cr	13.9	SmC_{ca}	7.6	IN	0.9	ISO

XRD was performed on this material, and showed similar behaviour as the two previously discussed bent dimers. The XRD data is summarised in the Table 4.9 below. The layer spacing of d/l = 0.5indicates an intercalated system. There is no tilt in the XRD pattern. The smectic phase is assigned as SmC_{ca} based on the combination of Schlieren texture, a small angle intensity where d/l = 0.5 and previous materials in this series. However, $S = \pm 1/2$ singularities in the Schlieren could be used to confirm the anticlinic nature of the phase, however these were not located.

Table 4.9. XRD data for compound 95.

Phase	Temp (°C)	2θ (°)	d (Å)	Comments
N	105	4.46	19.81	
IN	195	18.01	4.92	lateral distance between mesogens
SmC	195	4.35	20.30	smectic layer spacing d/l = 0.5
SmU _{ca}	100	18.64	4.76	lateral distance between mesogens

4.7 Mesophase I Overview & Comparisons

The preceding sections have detailed the transitional properties of each target material individually. This section aims to look at the materials comparatively and identify any trends. Table 4.10 and Figure 4.22 give and overview of the transitional properties for all target dimers **90–95**. All the dimers have small nematic ranges with much wider smectic phases below.

 Table 4.10. Overview of the primary target materials with transition temperatures on heating measured via DSC.

	F—	F			R
Compound	n	R	Shape	Transition Temperatures (°C)	$\Delta H_{N-I} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
90	8	$\mathrm{C}_{5}\mathrm{H}_{11}$	linear	Cr 96 $\rm SmA_c$ 228 N 245 Iso	8.3
91	8	$\mathrm{C_7H_{15}}$	linear	Cr 92 SmA _c 217 N 235 Iso	7.2
92	8	$\mathrm{OC}_4\mathrm{H}_9$	linear	Cr 106 SmA _c 246 N 266 Iso	8.1
93	9	$\mathrm{C}_{5}\mathrm{H}_{11}$	bent	$\rm Cr~77~SmC_{ca}$ 180 N 188 Iso	1.5
94	9	$\mathrm{C_7H_{15}}$	bent	$\rm Cr~70~SmC_{ca}$ 172 N 179 Iso	0.6
95	9	$\mathrm{OC}_4\mathrm{H}_9$	bent	$\rm Cr~80~SmC_{ca}$ 193 N 210 Iso	0.9



Figure 4.22. Overview of the transition temperatures for primary target materials, chart form, transition temperatures on heating as measured by DSC.

The main difference depends upon the parity of the spacer. Even spaced dimers (90, 91 & 92) with a linear shape exhibit an untilted smectic A phase. On the other hand, the bent shape of the odd dimers (93, 94 & 95) results in anticlinic smectic C phases. Both smectic types are intercalated, based on XRD evidence showing a smectic layer spacing of approximately d/l=0.5. Some of the SmC_{ca} phases show inconclusive evidence of tilt on XRD and so were confirmed using OPM, with the presence of $S = \pm 1/2$ singularities in the defect texture confirming the anticlinic phase. None of the bent dimers displayed evidence of an N_x phase below the conventional uniaxial nematic (N_u) . The bent dimers have lower melting & clearing points with narrower smectic & nematic phase stability. The lower melting points are a result of the additional flexibility of the chain granted by the extra methylene group combined with the less efficient shape for molecular packing.

One of the key differences between the linear and bent dimers is the enthalpy for the nematic-isotropic phase transition. These are listed for the target materials in Table 4.10. For the bent dimers, $\Delta H_{\rm N-I} = 0.9-1.5 \text{ kJ mol}^{-1}$, this is within the range normally seen for conventional calamitic materials.^{122,123} In the case of the linear dimers, the enthalpies are much larger, $\Delta H_{\rm N-I} > 7$. This is unusual for a nematic-isotropic transition, but has previously been reported for linear dimer materials. A possible reasoning behind this difference was discussed in work by C. Imrie⁴³. Essentially, in the isotropic phase both even and odd parity spacers have linear and bent conformers, for the even spacer approximately 50 % are linear whereas for the odd spacer only 10 % are in the linear form. At the isotropic-nematic transition for even-spaced dimers many of the bent conformers are converted to the linear form, enhancing the orientational order of the phase giving a larger transition enthalpy. Conversely for the odd spaced dimers, the orientational order of the nematic phase os insufficient to overcome the majority bent conformers into linear. Hence, there is no enhancement of the orientational order of the nematic phase, or the associated enthalpy of the transition.⁴³

More subtle differences are seen when the spacer length is fixed and the length and structure of the terminal chain is varied. Comparing the pentyl (90 & 93) and heptyl (91 & 94) systems, the longer chained heptyl has the lower melting point and $T_{\text{N-I}}$. Additional flexibility granted by the longer chain serves to lower the m.p. and reduce packing efficiency. The two butoxy materials (92 & 95) have higher transition temperatures when compared to the alkyl analogues. This is a result of the Ar–O–R bond angle, which is smaller than Ar–CH₂–R, giving the structure a more linear shape, thus allowing better packing and a higher m.p.

5 Aims II

5.1 Lower Melting Points and Broader Nematic Phases

The target materials synthesised in the previous section all had high melting points, and were mostly smectic in character, with very narrow ranged nematic phases. Further materials with greater nematic character were sought. It was decided to vary the length of the mesogen on either side of the spacer group. Three additional systems were synthesised and investigated. The additional targets all had the same terminal pentyl chain with both linear and bent dimers being investigated. The three systems differ only in the length of the mesogenic cores. Materials **97** and **98** removed one phenyl from the negative arm, **101** and **102** removed a phenyl from the positive arm and **103** and **104** removed a phenyl from both sides of the spacer. The structures of the secondary target materials are shown in Figure 5.1.



Figure 5.1. Structures of the secondary target materials — variation of the core length.

6 Synthetic Discussion II

Synthesis of the secondary target materials proceeded much like the primary targets and made use of many of the same intermediates and procedures as described by the following schemes.

6.1 Schemes



a = DME, H₂O, Na₂CO₃, Pd(PPh₃)₄

Scheme 6.1. Synthetic route to secondary target materials, 97 & 98. Boronic acid, 96 was supplied by Kingston Chemicals Ltd.

Compounds 97 and 98 were prepared jointly with MChem project student C. Holmes. The synthetic scheme is shown in Scheme 6.1 These two targets were synthesised using intermediate materials 88 and 89 that were previously prepared in the synthesis of the primary target dimers. These intermediates are the spacer groups with the positive mesogen coupled to them. These were subjected to a Suzuki style cross coupling reaction with boronic acid 96 (supplied by Kingston Chemicals Ltd.). The boronic acid was used in 50% excess to ensure the complete reaction of the bromide intermediate, streamlining the purification steps. This gives the two target materials 97 and 98. The yields for the two couplings were 67 % for the linear dimer and 64 % for the bent. However HPLC revealed that the purity for the linear system, 97 was only 89 % with a single impurity constituting 9.4 % of the sample with a retention time of 6.5 min on HPLC (Figure 6.1a), this was subsequently identified by NMR (Figure 6.2) and MS (1:1 isotope distribution for Br) as compound 89. This should have all been reacted in the final step as the boronic acid 96 was used in excess. However, this wasn't the case and the pure material was unable to be isolated by column chromatography. This low purity has an effect on the mesomorphic properties of the dimer and this will be discussed in later sections. Purity of the bent dimer was acceptable at 99.0 %.



Figure 6.1. HPLC trace of target dimer, 97, (a) the main impurity at t=6.5 min, 9.4 % and (b) the target at t=10.1 min, 89 %.



Figure 6.2. ¹H-NMR (a) bromide, 88 and (b) compound 97 showing presence of the bromide in the target material.



Scheme 6.2. Synthetic route to secondary target materials, 101, 102, 103 and 104. Material 96 was supplied by Kingston Chemicals Ltd.

Scheme 6.2 shows the synthetic route to preparing secondary target dimers 101, 102, 103 and 104. Synthesis began by reusing the previously prepared spacer intermediates, 67 and 68 and coupling them with boronic acid, 70. Like the previous couplings to the symmetrical spacers, careful control of the stoichiometry, allowed isolation of the singly coupled products 99 and 100 in good yields. Following the coupling of the arms the final step was to couple the negative arms to give the targeted structures. Boronic acid 85 was used in excess for the five ring systems, yielding compounds 101 and 102 in good yields, 73–78 % and purity 97.0–99.3 %.

Using the same procedure compound 96 was used to form the four ring targets 103 and 104. Though the yields for these were significantly lower at 43 % and 45 %. The four ring bent dimer, 104 melted at 31 °C and then doesn't quickly crystallise unless cooled to -14 °C. Therefore the recrystallisation step was skipped, giving a purity of 99.4 %.

All targets with the exception of **97** were obtained with good purity, verified by HPLC and EA. Table 6.1 summarises the synthesised secondary targets with their purity values by HPLC.

Compound	n	Shape	Purity %
F-	- </td <td>)(CH₂)n</td> <td>F C₅H₁₁</td>)(CH ₂)n	F C ₅ H ₁₁
97	8	linear	89.0
98	9	bent	99.0
F		(CH ₂) _n	
101	8	linear	97.0
102	9	bent	99.3
F-		(CH ₂) _n	F
103	8	linear	98.3
104	9	bent	99.4

Table 6.1. Summary of secondary target dimers showing purity % from HPLC.

7 Mesophase Behaviour II

The mesophase behaviour of the secondary target materials was investigated in a similar fashion to the first targets, using a combination of OPM and DSC. Only in the case of 102 was XRD required and was used to confirm the presence of the N_x phase. As expected the change in core length has a great influence on the transitional properties and this will be discussed in the following sections.

7.1 Compound 97



Figure 7.1. Structure of secondary target compound 97, transition temperatures (°C) on heating.

The structure of compound **97** is shown above, it is a linear system with pentyl terminal chain, featuring only two aromatic rings on the negative side. The change in core structure has, as expected had a significant influence of the transitional properties. **97** has a nematic and smectic phase, illustrated in the OPM images in Figure 7.2. The nematic phase is identified by Schlieren texture (a) which transitions (b) to a smectic A phase on cooling. The smectic phase displays typical focal conic fans, and in homeotropic areas, a pseudo-isotropic texture.



Figure 7.2. OPM textures of 101 on cooling from the isotropic phase [x200 magnification] (a) Schlieren of the nematic phase at 175 °C, (b) fan texture of the smectic phase at 140 °C.

Figure 7.3 shows the DSC data on heating for 97. As detailed in the synthesis section the purity of 97 is only 89 % with the major impurity being the intermediate bromide 88. This impurity has a substantial impact on the properties. The material melts into a smectic A phase at 50 °C, this is lower than expected, when compared with other materials and is likely a result of the 88 impurity. Further heating, results in the transition to the nematic phase at 137 °C, and then to the isotropic at 162 °C. As with the previous linear systems, the ΔH_{N-I} at 6.1 kJ mol⁻¹ is high compared to conventional calamitics.



Figure 7.3. DSC curve for compound 97, (—) 1st heat, (—) 1st cool.

XRD was not performed for this material. However, based on previous materials, the OPM textures and the linear shape of the molecule, a conventional nematic should be confirmed where the XRD scattering is diffuse in both the small and wide angle regions. In smectic phase, the wide angle scattering should remain diffuse, while in the small angle region there should be a sharp intensity indicating the layered structure. Like the previous linear dimers, the smectic phase is mostly likely an intercalated phase and should show a $d/l \sim 0.5$. If correctly assigned as SmA, the diffraction pattern should show no tilt.

7.2 Compound 98



Figure 7.4. Structure of secondary target compound 98, transition temperatures (°C) on heating.

Compound 98 is the bent analogue of 97. This material melts directly into a smectic phase, and then clears to the isotropic. On cooling, a short-lived nematic phase can be seen, as evidenced by the Schlieren texture seen in Figure 7.2(a). The nematic rapidly transitions to a smectic phase displaying a focal conic fan texture (b) that, after shearing develops Schlieren (c) pointing to a smectic C phase. (d) shows an area of Schlieren in the smectic that has $S = \pm 1/2$ singularities which indicate an alternating type phase.



Figure 7.5. OPM textures of **97** on cooling from the isotropic phase [x200 magnification] (a) Iso-N-SmC transition at 102 °C, (b) fan texture at 102 °C, (c) sheared sample at 98 °C, (d) SmC schlieren at 85 °C.



Figure 7.6. DSC curve for compound 98, (—) 1st heat, (—) 1st cool.

The DSC data on heating is shown in Figure 7.6. The material melts into the smectic phase at 67 °C and then clears to the isotropic at 102 °C. The $\Delta H_{SmC_{alt}-I}$ at 9.4 kJ mol⁻¹ is significantly higher than the ΔH_{N-I} seen for the other bent target materials and this is due to the higher order of the smectic phase.

XRD was not performed for this material. However, based on previous materials and the OPM evidence of an alternating SmC phase, there should be no tilt, and a high intensity sharp peak in the small angle, with diffuse wide angle scattering. The small angle XRD peak is likely to show a $d/l \sim 0.5$ which would be typical for an intercalated type phase.

7.3 Compound **101**



Figure 7.7. Structure of secondary target compound 101, transition temperatures (°C) on heating.

Compound 101 is a linear dimer based on 90, but where one of the aromatic rings on the positive arm has been removed. This material has a wide range nematic phase, and a lower temperature phase. Figure 7.8 shows OPM textures seen on cooling from the isotropic. The Schlieren texture (a) of the nematic phase forms as droplets, which when further cooled develops additional disinclination line like features (b) (possibly a surface effect). On transition to the lower phase an atypical texture develops (c) which upon shearing aligns (d) to a more smectic like texture.



Figure 7.8. OPM textures of 101 on cooling from the isotropic phase [x200 magnification] (a) 166 °C, Schlieren of the nematic phase, (b) 85 °C, disinclination lines prior to phase transiton, (c) 82 °C, fan-type texture of the lower phase, (d) 82 °C, lower phase after shearing.

(d)

(C)



Figure 7.9. Additional OPM textures of 101 on cooling from the isotropic phase [x200 magnification] (a) 81 °C, focal conic fans, (b-e) 81 °C, blocky texture, (f) 83 °C, smoother texture, aligned.

Due to the atypical looking smectic texture seen in Figure 7.8 (c), further OPM studies were carried out. Figure 7.9 shows some of the textures seen for a single slide preparation of **101**. In (a) a more usual focal conic fan type texture is observed as conventionally seen for smectics. (b) shows elongated ellipsoid shaped defects. Images (c)-(e) illustrate the blocky type texture seen in different areas of the slide. This texture has previously been seen in the N_x phase.^{34–36,127,128} The final image (f) is an area that more uniformly aligned and so adopts a smoother, marble like texture. No homeotropic areas were found and so a tilted smectic could not be ruled out — although based on the linear shape and previous materials a SmA is expected. Finally the cell was filled into both 2 µm and 6 µm planar cells where the lower phase showed only a uniform aligned texture, no rope type texture was exhibited. This phase was preliminarily assigned as a SmA phase, though XRD was required to confirm this and will be detailed later.



Figure 7.10. DSC curve for compound 101, (—) 1^{st} heat, (—) 1^{st} cool. Inset: expansion showing the very small N-SmA transition peaks ((—) 2^{nd} heat).

DSC was carried out and the curves are show in in Figure 7.10. 101 melts directly into the nematic phase at 47 °C, and is stable up to 166 °C where it clears into the isotropic phase. Like other linear dimers the ΔH_{N-I} is much larger than that seen in conventional calamitics. On cooling there is a nematic-monotropic phase transition at 85 °C, the enthalpy of which is very small — much lower than that seen for the other linear dimers (N-SmA transition). This small enthalpy could be the result of the broad nematic phase range, which can result in small first order or even second order N-SmA transition. This has been explained as a result of coupling between the translational and orientation order and is in accord with the McMillan molecular field theory.^{129–133} Combined with the

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¹³²J. Thoen, G. Cordoyiannis, and C. Glorieux. *Liq. Cryst.* 2009, **36**, 669–684.

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OPM data this appeared to be an unusual looking smectic phase. The Sm-N transition doesn't show on the first heating curve due to the large enthalpy of melting dwarfing the very small transition. However, it can be found on the second heat by cooling past the transition and then heating before allowing crystallisation.

Figure 7.11 shows the x-ray diffraction patterns seen for this material in the nematic (a) and lower temperature phase (b). The right hand side of each pattern has the data from an empty capillary subtracted, to remove an artifact in the small angle due to beam leakage around the beamstop.



Figure 7.11. XRD scattering patterns of 101, (a) nematic phase at 100 °C (b) SmA_c phase at 83 °C. Where, H is the capillary and B the field direction.

Figure 7.12 shows the 2θ plots of the subtracted data described above. The nematic phase (\circ) shows the typical diffuse, low intensity scattering in both the wide and small angle regions and is representative of the diffuse nature of the phase. On the other hand the low temperature phase (\circ) shows a sharp, high intensity peak in the small angle, indicating the layered structure and so confirming a smectic phase. The lack of tilt, combined with the absence of evidence of a schlieren texture discounts a smectic C phase and allows the assignment of a smectic A phase.

Goodby et al. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Feb. 2014. 1–32.



Figure 7.12. XRD 2θ plot for 101 in the N (\circ) and SmA_c (\Box) phases, based on the data with subtracted background.



Figure 7.13. MM2 minimised structure of 101 showing the approximate length of the molecule.

Figure 7.13 shows the MM2 minimised structure of 101, with the approximate length of the molecule being 35.42 Å. Table 7.1 lists the XRD data for the two phases. For the nematic phase, the diffuse peak in the wide angle region at $2\theta = 18.11^{\circ}$ theta represents the lateral distance between the molecules and is equal to 4.90 Å. On transition to the smectic A phase there is a reduction in this lateral distance and this is explained the higher order of the smectic phase. In the small angle region, sharp intensity at $2\theta = 18.11$ represents a smectic layer spacing of 18.97 Å which is approximately half the molecular length suggesting an intercalated phase where d/l = 0.54.

Table 7.1. XRD data for compound 101.

Phase	Temp (°C)	2θ (°)	d (Å)	Comments
N	85	4.95 18.11	$17.87 \\ 4.90$	lateral distance between mesogens
$\mathrm{SmA}_{\mathrm{c}}$	45	$4.66 \\ 19.20$	$18.97 \\ 4.62$	smectic layer spacing, $d/l = 0.54$ lateral distance between mesogens
7.4 Compound 102



Figure 7.14. Structure of secondary target compound 102, transition temperatures (°C) on heating.

Compound 102 is the bent anologue of 101. This material has both a conventional uniaxial nematic phase and at a lower temperature, a more ordered nematic phase (N_x). Figure 7.15 shows the optical textures seen on OPM. The N_u phase shows the characteristic, Schlieren and marble textures, though only $S = \pm 1/2$ singularities are observed (a). At the N-N_x transition, a block-like texture appears (b). With further cooling this develops (c) into the rope texture (d) typically seen for the N_x phase. Figure 7.16 shows 102 in a planar cell. Under planar alignment the characteristic rope texture is more clearly seen.





Figure 7.15. OPM textures of 102 on cooling from the isotropic phase [x200 magnification]. (a) nematic phase at 66 °C, (b) blocky texture at N-N_x transition 65 °C, (c) N_x phase at 64 °C, (d) N_x in a different area at 57 °C.



Figure 7.16. Rope texture 102's N_x phase in a planar aligned cell, seen on cooling from the isotropic phase at 45 °C, (a) [x100] (b) [x400] magnification.

The DSC curves for compound 102 are shown in Figure 7.17. The material melts into the N_x phase at 45 °C, before transitioning to the conventional, uniaxial nematic at 66 °C and then clearing to the isotropic at 97 °C. The ΔH_{N-I} is at ~0.4 kJ mol⁻¹ much smaller than that seen for the linear analogue. Of importance to note is the enthalpy of the N-N_x transition. It is very small at only 0.1 kJ mol⁻¹, though this is characteristic for this type of transition. Additionally the unusual peakshape appears to have both first and second order character, previously reported in other dimer materials.³⁶ On cooling from the N_x phase, 102 can be super-cooled well below the melting point before crystallisation occurs.



Figure 7.17. DSC curve for compound 102, (-) 1st heat, (-) 1st cool. Inset: expansion showing the N_x transition peaks.

Figure 7.18 shows the XRD scattering patterns for 102 in the (a) nematic and (b) N_x phases. While Figure 7.19 shows the MM2 minimised molecular structure in the all-trans conformer. The approximate length of the molecule is 35 Å.



Figure 7.18. XRD scattering patterns of 102, (a) nematic phase at 85 °C (b) N_x phase at 45 degrees C. Where, H is the capillary and B the field direction.



Figure 7.19. MM2 minimised structure of 102 showing the approximate length of the molecule.

Figure 7.20 shows (a) the 2θ and (b) the χ plots for the diffraction patterns above. The nematic phase shows a characteristic diffraction pattern with diffuse small and wide angle scattering. The diffuse nature of scattering discounts any ordered layer structure and thus any smectic character. The wide angle scattering has a maxima at $2\theta = 18.64^{\circ}$ which is equivalent to a d-spacing of d = 4.76 Å, this corresponds to the lateral distance between mesogens. The intensity observed in the small angle region, $2\theta = 4.96^{\circ}$ gives a d = 17.81 Å, which is roughly half the length of the molecule and so indicates an molecular overlap of approximately 50 %.



Figure 7.20. XRD (a) 2θ and (b) χ plots for 102, in the N at 85 °C (\circ) and N_x phase at 45 °C (\Box). Solid lines are curves fitted in OriginPro.

Of more interest is the N_x phase, which shows similar diffuse scattering behaviour, so a smectic phase can immediately be ruled out and a nematic type phase confirmed. However, there are some key differences, which point to a different type of nematic. The 2θ plot in Figure 7.20 (a) shows that the N_x phase has higher intensity than the N phase, additionally the ratio between small and wide angle intensities is greater in the N_x , this is suggestive of longer range order than the standard nematic. In the wide angle, the peak maxima is at $2\theta = 17.58^{\circ}$ which gives a d-spacing of d = 4.57 Å. This is smaller than that of conventional nematic phase and is due to the molecules being more tightly packed in the N_x phase. When comparing the relative widths of the wide angle scattering, one can see that the N_x phase has less diffuse scattering, suggestive of a more ordered phase than the N. The χ plot of the wide angle scattering in Figure 7.20 (b) shows that the scattering for the N_x in the χ direction is more diffuse. This could be interpreted as (1) reduced order of the director as it twists through the bulk (N_{TB} model).⁵⁰ or (2) misalignment, consistent with the possible domain formation.¹²⁷ Additionally, from the χ plot it can be seen that there is approximately 9° tilt in the wide angle scattering of the N_x phase, the presence of tilt in the N_x phase has been reported previously with some dimer systems³⁴ and has been attributed to surface effects from the capillary.⁵⁰ Table 7.2 shows an overview of the data discussed above.

Table 7.2. XRD data for compound 102.

Phase	Temp (°C)	2θ (°)	d (Å)	Comments
Ν	85	4.96	17.81	
27		$18.64 \\ 5.03$	4.76 19.44	lateral distance between mesogens
N_x	45	17.58	4.57	lateral distance between mesogens

7.5 Compound 103



Figure 7.21. Structure of secondary target compound 103, transition temperatures (°C) on heating.

Material 103 has a phenyl unit less from both sides of the spacer, giving a linear four ring system. This had a nematic phase and a monotropic smectic phase. Figure 7.22 shows some of the textures seen in this material. The nematic phase exhibited both Schlieren (a) and marble textures (b). On transition to the monotropic smectic phase (c) & (d) elongated ellipsoid shaped defects are seen.





Figure 7.22. OPM textures of **103** on cooling from the isotropic phase [x200 magnification] (a) Iso-N transition at 76 °C, (b) N phase at 75 °C, (c) Sm phase at 27 °C, (d) Sm phase at 27 °C.

Figure 7.23 shows the DSC data for compound 103. The material melts at 55 °C directly in to the nematic phase, before clearing at 73 °C. The smectic phase is monotropic and only appears on cooling, where it appears at 30 °C, with a very small N-SmA enthalpy of 0.2 kJ mol⁻¹. As discussed for previous materials, this could be a result of the relatively broad nematic phase range (on cooling).



Figure 7.23. DSC curve for compound 103, (—) 1^{st} heat, (—) 1^{st} cool.

XRD was not performed for this material. However, based on the OPM textures and the linear nature of the material the XRD should show the typical diffuse scattering for the nematic phase. The lower phase if smectic, would show a sharp peak in the small angle region, with a d/l = 0.5 indicating an intercalated system. Absence of tilt in the diffraction pattern would confirm the smectic A phase.

7.6 Compound 104



Figure 7.24. Structure of secondary target compound 104, transition temperatures (°C) on heating.

Compound 104 is the bent analogue of the previous material. OPM was more difficult in this case as the transition temperatures were much lower and a monotropic phase was seen only significantly below room temperature. Figure 7.25 shows the texture seen on cooling from the isotopic phase. The unidentified phase (LC_x) had very small domains which were difficult to see clearly even at x400 magnification. Image (a) is texture seen at the transition from the iso phase, with (b) and (c) showing the development of the texture with further cooling. (d) is the same area at a cooler temperature (-8 °C).



Figure 7.25. OPM textures of 104 on cooling from the isotropic phase into the unknown LC phase [x400 magnification] (a) at 0 °C, (b) at -2 °C, (c) at -2 °C, [x200 magnification], (d) at -8 °C.

Figure 7.26 shows the DSC curves for 104. The material melts directly into the isotropic phase at 31 degrees C. The monotropic phase appears at just 2 °C on cooling, where the I-N enthalpy is 3.4 kJ mol⁻¹. Crystallisation occurs at -13 °C.



Figure 7.26. DSC curve for compound 104, (--) 1st heat, (--) 2nd heat, (--) 1st cool.

XRD was not performed for this material. Due to the very low transition temperature of the monotropic phase from the isotropic of 2 °C. However, based on the smectic like OPM textures and the bent nature of the material it is likely a SmC alternating phase. XRD should show the typical sharpe small angle peak combined with diffuse wide angle scattering. A d/l = 0.5 would indicate an intercalated system. Absence of tilt would not confirm a smectic A phase as tilt is also not seen in the anticlinic smectic C phase. Based on the previously discussed bent dimers this materials is most likely to exhibit a SmC alt phase.

7.7 Mesophase II Overview & Comparisons

Table 7.3. Transition temperatures of the secondary target materials on 2^{nd} heating (mp from 1^{st} heat) with enthalpy for the nematic-isotropic transition.



 $^{\dagger}\Delta H_{\text{I-N}}, \,^{\ddagger}\Delta H_{\text{I-LC}}, \text{ both on cooling.}$

Table 7.3 gives an overview of the transitional properties for all secondary target dimers (97–104). All materials show enantiotropic liquid crystal phases, with the the exception of 104 which exhibits only a monotropic phase. Like the primary target materials, the trend of linear dimers having a much larger T_{N-I} follows here also. Figure 7.27 shows the transition temperatures in graph form. In addition to the six secondary materials the pentyl compounds 90 and 93 from the primary targets are included as a comparison. From this graph one can clearly see the trend between overall mesogenic core length and the transition temperatures, materials with shorter cores have significantly lower melting and clearing points than the longer analogues. One exception to this is compound 98, which has a slightly higher mp than the analogous 93. As mentioned in earlier sections, the bent systems have lower melting and clearing points. For the melting point this could be explained by the molecules having poorer packing due to their bent shape. This is supported by the enthalpy of the melting transition which is significantly lower for the bent dimers.

Compounds 97 and 98 do not appear to fit the pattern, as the T_{mp} of the linear dimer (97) is expected to be ~ 20 °C higher than the bent analogue (98) and this is not the case. Additionally it was expected that the T_{mp} of 98 would be lower than the analogous primary target, compound **93**. This is almost certainly a result of the bromide impurity present within the sample, lowering the transition temperatures.



Figure 7.27. Overview of the transition temperatures for secondary target materials, chart form, transition temperatures on heating as measured by DSC, primary targets 90 and 93 are included for comparison.

When compared with the six aryl ring primary target materials (90 and 93), compounds 97 and 98 have substantially lower T_{N-I} and smaller overall liquid crystal phase ranges. This is a result of the reduced length-breadth ratio for the shorter materials. Comparison of linear compound 97 with the bent anologue 98, shows that the linear system has a much broader nematic phase range, whereas the bent material has only a very small nematic phase of less than 1 °C. This follows the trend that was seen with the primary targets, albeit to more extreme degree. In general, the five ring compounds 97 and 98 behave very similarly to the primary targets, with just lower transition temperatures and ranges.

Comparatively, much greater differences are seen when moving to compounds 101 and 102 where the aryl ring is removed from the alternate side of the spacer, the positive arm. In both of these systems the smectic phases are greatly suppressed, indeed a smectic phase is not exhibited at all by 102 and a N_x phase is displayed. Replacing the smectic character are much broader nematic phases, particularly in the linear dimer, 101 where the nematic is present over ~ 80 °C. Despite these substantial differences, the T_{N-I} remains similar between the five ring materials, 97/98 and 101/102. The huge reduction in smectic tendency suggests that the materials are not able to efficiently pack into a layered structure as a result of their shape and so adopt a nematic phase structure instead.

In the next set of materials compounds 103 and 104, where an aryl group has been removed form both sides of the spacer, there is a substantial decline in liquid crystal phase character. In both systems, bent and linear the melting points have been further reduced when compared with the six and five ring materials. Though at much lower temperatures, the range of the nematic phase in the linear dimer 103 is similar to that seen in the primary target material 90. In comparison the bent dimer only displays a single monotropic phase (unassigned). The lower transition temperatures and liquid crystal phase stability can be attributed to the smaller length-breadth ratio in the shorter dimers.

7.8 Mixtures

A series of mixtures of the bent dimer (102) doped with the linear dimer (101) were created and the mesophase behaviour investigated. The mixture compositions and transition temperatures are listed in Table 7.4. The transitional data for the four mixtures was obtained solely by OPM.

Mixture	Composition w/w $\%$		Transition Tomporatures (°C)	
Mixture	linear (101)	bent (102)	Transition Temperatures (C)	
bent (102)	0	100	Cr 45 $\rm N_x$ 66 N 97 Iso	
Mixture A	20	80	Cr 43 $\rm N_x$ 52 N 116 Iso	
Mixture B	40	60	Cr 51 (N _x 35) N 131 Iso	
Mixture C	60	40	Cr 55 (N $_{\rm x}$ 20) N 144 Iso	
Mixture D	80	20	Cr 75 (SmA 53) N 155 Iso	
linear (101)	100	0	Cr 79 SmA 85 N 162 Iso	

Table 7.4. Dimer Mixture composition & transition temperatures. Mixtures of bent dimer (109) doped withlinear dimer 101.

Figure 7.28 below shows phase diagrams for both heating (a) and cooling (b) for the mixtures above — the heating diagram (a) will be de discussed first. Firstly there is a linear relationship for the nematic-isotropic transition temperature, which suggests the two dimers are compatible and mix well. Mixture A is the only mixture that maintains an enantiotropic N_x phase albeit at a lower temperature and narrower than the pure bent dimer 102. Mixtures B, C and D show no N_x phase on heating and melt directly to the nematic phase, with increasing melting point as larger amounts of the linear dimer (101) are present. On heating the smectic A phase is only seen for the pure linear dimer and is not present in any of the other mixtures.



Figure 7.28. Phase diagram of mixtures between the linear (101) and bent (102) dimers. (a) on heating, (b) on cooling.

On cooling (Figure 7.28 (b)), mixtures B and C exhibit monotropic N_x phases where the N-N_x transition temperature falls with increasing linear dimer presence, mixture D shows no N_x phase. Mixture D displays a monotropic SmA phase that is at a lower temperature and narrower than the SmA of the pure material on cooling. None of the other mixtures with larger w/w % of bent material exhibited a monotropic smectic phase. The results overall show that the N_x phase while enantiotropic in mixtures of up to 20% linear dimer the phase is destabilised by the addition of linear shaped materials. Additionally the phase stability of the SmA phase in the linear dimer is quite quickly reduced suggesting that bent material disrupts the smectic layer packing.

8 Electro-Optic Studies

Both the linear dimer 101 and the bent form 102 were selected for further investigation into their electro-optic properties. This was due to the wide nematic phase stability and relatively low melting point of these systems, compared to all of the other dimers synthesised. Comparison between the two was likely to show significantly different electro-optic properties as they did for the transitional properties. In addition the voltage/frequency response of the same mixtures discussed earlier was investigated. A number of different electro-optical properties were investigated including birefringence, voltage/frequency response and switching times. The results from these measurements will be discussed in the following sections. The diffuoroterphenyl monomer, MTC5 (105) was used as a non-dimer comparison.



Figure 8.1. Selected materials for electro-optic investigation, the linear, 101 and bent, 102. The monomer 2',3'-diffuoro-4,4''-dipentyl-1,1',4',1''-terphenyl (MTC5 (105) is included for comparison.)

8.1 Birefringence / Optical Ansiotropy

Figure 8.2 shows the temperature dependence on Δn for the two studied materials with MTC5 included for comparison. All Δn measurements were taken via the Berek compensator method previously discussed. As expected for all materials tested the birefringence falls as the temperature approaches T_{N-I}. For the linear system the higher Δn versus MTC5 can be expected due to the additional aromatic rings in the system (though the lack of conjugation linking the mesogens together is limiting. Additionally the longer shape gives a greater length-breadth ratio. As temperature falls and the nematic transitions into the smectic phase Δn continues to rise at a similar rate. Only upon crystallisation does this changes, where Δn falls rapidly.



Figure 8.2. Birefringence of the linear dimer, 101 (\circ), bent dimer, 102 (\circ) and the monomer MTC5 (\diamond) for comparison. Mesurments via Berek compensator.

In comparison, the bent dimer has significantly lower Δn than both MTC5 and the linear dimer. This can be explained based on the molecular shape. In the bent dimer one mesogen is off axis compared to the other, thus it contributes less to n_e and more to n_o giving a lower overall Δn . Previous research by Meyer, Luchurst & Dozov on the cyano-biphenyl dimer, CB7CB has shown that at the N-N_x transition there is a slight jump, followed by a rapidly fall in Δn as the temperature drops further into the N_x phase.¹³⁴ The same effect could not be verified with the studied bent dimer as measurements of Δn , in the N_x phase using the Berek compensator method proved difficult. In the Meyer investigation an almost uniform alignment was achieved in the N_x phase, that method employed a very thin cell (1.6 µm). Despite attempts switching from a 5 µm to a 2 µm planar cell a uniform alignment was not successfully achieved and only a rope texture was seen. This meant that at a temperature a few degrees below T_{N-Nx} reliable measurements with the Berek became impossible as the rope texture developed fully.

¹³⁴C. Meyer, G. R. Luckhurst, and I. Dozov. J. Mater. Chem. C, 2014, 3, 318–328.

8.2 Voltage Response

In order to investigate the voltage response for the pure materials and the mixtures they were filled into electro-optic cells with a twisted geometry forming a simple TN device which in the off state transmits light. In general data was collected at 92 °C where both pure dimers and mixtures were in the nematic phase. Both dimers are positive dielectrics (at 1 kHz) so reorient with the field on application of a voltage giving the dark state. By slowly ramping up the applied voltage the threshold value can be found. Approximate threshold voltages were determined via joint observation of a colour/brightness change on OPM and a fall in the transmission recorded by the photodiode. Table 8.1 lists these values for both the pure materials and the mixtures, the same data is shown in Figure 8.3 and shows that increasing the concentration of the linear dimer increases the threshold voltage linear relationship. Full procedures for the voltage & frequency response are detailed in Section 10.4.3.

Mixture	Composition $w/w \%$ linear (101) bent (102)		V_{th} (V _{RMS})
bent (102)	0	100	2.2
Mixture A	20	80	3.0
Mixture B	40	60	3.5
Mixture C	60	40	4.4
Mixture D	80	20	5.4
linear (101)	100	0	6.8

Table 8.1. Threshold voltages for dimer mixtures, with a 1 kHz applied field.



Figure 8.3. Threshold voltages of the pure dimers and mixtures at 90 °C. Applied voltage is fixed at 1 kHz frequency.



Figure 8.4. Voltage response of the bent dimer (102) at different temperatures 92 °C (\bullet), 82 °C (\bullet) and 72 °C (\circ). Applied voltage is fixed at 1 kHz frequency.

Figure 8.4 shows the temperature dependence of the voltage response for the bent dimer. The data shows that higher temperatures lead to a lower Vth. This is a result of the materials lower rotational viscosity at higher temperatures, though countering this is the reduction in $\Delta \varepsilon$. Additionally, it can be seen that at 92 °C, the Transmission in the light, off state is lower. This is because this temperature is close to the T_{N-I}, where the order parameter is lower, hence the reduced Δn and lower transmission. At a sufficiently voltage above the V_{th} a good dark state is achieved at all three temperatures. Due to the temperature dependence of V_{th} (and relaxation frequency) the measurements for both dimers were carried out at the same temperature, 92 °C (0.95x T_{N-I} of 102). At this temperature both materials are in the nematic phase. However, an issue is that the bent dimer is close the T_{N-I} and the linear dimer is close to T_{N-SmA} and consequently far from T_{N-I}.



Figure 8.5. Voltage response of the bent (\bullet) & linear (\bullet) dimers at 92 °C and 1 kHz frequency of applied voltage.

The voltage response of transmission for both dimers is shown in Figure 8.5, both materials are at the same temperature (92 °C). As previously mentioned the bent dimer has a lower intensity bright state, but also has a significantly lower threshold voltage, V_{th} (~ 2.2 V_{RMS}) that the linear dimer (~ 6.8 V_{RMS}). The bent dimer also has a much sharper voltage profile, with the full dark state achieved within ~ 1 V_{RMS} of the V_{th} . Conversely, the linear dimer barely reached the same dark state at 10.6 V_{RMS}, 4 V_{RMS} above V_{th} . The dimers were mixed together and the measured data is shown in Figure 8.6. This shows that it only takes a relatively small amount of linear material in a majority (80 %) bent mixture to achieve the maximum transmission state



• bent + 80% bent • 60% bent • 40% bent × 20% bent • linear

Figure 8.6. Voltage response; bent & linear dimer mixtures at 92 °C and 1 kHz frequency.

20 % w/w addition of the negative dielectric diffuoroterphenyl monomer (MTC5) to the dimers lowers the $\Delta \varepsilon$ of the mixture. Threshold voltage is related $\Delta \varepsilon$, so lowering of $\Delta \varepsilon$ leads to an increase in the V_{th} of the mixtures and this is shown in Figure 8.7. The bent mixture with MTC5 has a higher T_{N-I} and as result the mixture now gives higher transmission in the light state (order parameter is greater at this temperature).



Figure 8.7. Voltage response of the bent (•), bent + 20 % MTC5 (\circ), linear (•) and linear + 20 % MTC5 (\circ) dimers.

8.2.1 Conventional Voltage Switching

In an electro-optic device, the time taken for the liquid crystals switch orientations is a critical property for high performance devices. Therefore it was decided to measure the response times for the turn-on $(t_{\rm on})$ and turn-off $(t_{\rm off})$ process for dimer materials 101 and 102. The turn on process occurs on application of a voltage giving the dark state, while the turn-off process occurs when the applied field is removed and the molecules relax back the planar state and the transmissive state. Table 8.2 lists the recorded response times for the dimer mixture. The turn-on process for the bent dimer (102) is quicker than the linear (101) but when looking at the whole set of mixtures there doesn't appear to be a trend in the turn-on response time. For the turn off process it can be seen that mixtures with greater bent dimer content have much longer switch-off times, with the pure linear material's response time (4.8 ms) being ~ 18× faster than the bent dimers (84 ms). For the majority of the mixtures the turn-on time is faster than the turn-off time, and this is expected as the turn off switching is a relaxation process and not voltage driven. Consequently, the faster turn-off than turn-on times for the linear dimer and the 20% bent mixture is particularly surprising. This property could be a result of particularly strong surface anchoring combined with a high bend elastic constant.

Mixture	Composition linear (101)	$\operatorname{pn} w/w \%$ bent (102)	$t_{\rm on} \ ({\rm ms})$	$t_{\rm off} \ ({\rm ms})$
bent (102)	0	100	8.3	84.0
Mixture A	20	80	15.6	45.2
Mixture B	40	60	10.4	22.2
Mixture C	60	40	9.4	13.0
Mixture D	80	20	12.7	6.2
linear (101)	100	0	20.0	4.8

Table 8.2. Voltage switching times for dimer mixtures. With 10 V_{RMS}, 1 kHz applied field.

8.3 Frequency Response

In addition to the voltage response, the frequency response of the materials was investigated to assess viability for DFLC applications. A 10 V_{RMS} , 1 kHz field was applied across a normally transmissive TN cell to give the dark state. The frequency of the applied field is then ramped from 1 kHz up to 5 MHz where the materials has fully reorientated back to the light state. The frequency response, like the voltage is affected by the temperature of the liquid crystal material. This is shown in Figure 8.8 which displays the transmission of bent liquid crystal dimer with varying frequency of the applied field, at a number of diffrent temperatures. At higher temperatures, the dielectric relaxation occurs at a higher frequency, hence the crossover frequency is also greater. This results in the turn-off process (reorientation back to homogeneous) happening only when the frequency of the applied field is higher. As before the transmission of the dimer in the off-state at higher temperature is lower.



Figure 8.8. Frequency response of the bent dimer (102) at different temperatures 92 °C (\bullet), 82 °C (\bullet) and 72 °C (\circ). Applied field is fixed at 10 V_{RMS}.

The graph displayed in Figure 8.9 shows the frequency response of both linear and bent dimers (at 92 °C). As with the voltage response, the parity of the spacer group has a substantial effect on frequency response. The linear dimer begins to switch at a much lower frequency and is reaches it's highest transmissive state at 12 kHz. On the other hand, the bent dimer doesn't reach it's max transmission state till 700 kHz, though it does have a much sharper response. This data indicates the linear dimer has a much lower crossover frequency. The bent-linear dimer mixture were also subjected to a frequency response investigation and the response curves are shown in Figure 8.10.



Figure 8.9. Frequency response of the bent (•) & linear (•) dimers at 92 °C and 10 V_{RMS}.



Figure 8.10. Frequency response of the bent & linear dimer mixtures at 92 $^\circ C$ and 10 V_{RMS}.

Figure 8.11 shows the frequency response of the dimers mixted with 20 % MTC5. The expected behaviour is that upon addition of a negative dielectric (MTC5) the crossover frequency of the mixture should fall because of the greater content of negative $\Delta \varepsilon$ material. The mixture containing bent dimer and MTC5 follows the expected behaviour and has a slightly lower apparent crossover frequency than the pure dimer, **102**. Conversely the linear-MTC5 mixture, behaves differently and exhibits a higher apparent crossover than the pure material.



Figure 8.11. Frequency response of the bent (•), bent + 20 % MTC5 (•), linear (•) and linear + 20 % MTC5 (•) dimers.

8.3.1 Dual Frequency Switching

Table 8.3 lists the response times for materials when using the dual frequency switching. In this regime the turn-off process doesn't occur on the removal of the field but on switching from the low frequency ($f_{\rm L} = 1$ kHz) to a high frequency ($f_{\rm H}$). This high frequency is different for the various mixtures and is chosen to be triple the frequency when the material had fully switched based on the data from Figure 8.10 in the previous section. The turn-on process listed here occurs when the applied field is switched from the high frequency back to the original low frequency.

Table 8.3. Dual frequency switching times for dimer mixtures. With 10 V_{RMS}, 1 kHz applied field t-off=1 kHz- $f_{\rm H}$, t-on= $f_{\rm H}$ – 1 kHz.

Mixture	Composition w/w $\%$		$f_{\rm H}$ (kHz)	$t_{\rm on} \ ({\rm ms})$	t_{off} (ms)	
	linear (101)	bent (102)	J II ()	011 ()		
bent (102)	0	100	3600	6.8	71.0	
Mixture A	20	80	2100	12.6	43.6	
Mixture B	40	60	1500	9.2	25.2	
Mixture C	60	40	600	8.5	10.1	
Mixture D	80	20	240	12.6	5.4	
linear (101)	100	0	90	21.0	3.8	

Figure 8.12 below displays the switching times for the bent & linear dimers and the binary mixtures. In general it can be seen that the response times for the dual frequency switching regime is slightly quicker than for conventional voltage switching, though the difference is minimal. This could be attributed to the relatively small voltage used to switch the materials due equipment limitations. Application of larger voltages could improve the response times greatly and make the benefit of the dual frequency regime more apparent as the higher voltage would increase the speed of the turn off process. The graph also highlights the unusual behaviour of **101** and mixture D, whose turn off times are faster than the turn-on times both with conventional and dual frequency switching.



Figure 8.12. Switching times for conventional (solid points) and dual frequency (open points) switching.

9 Conclusions & Outlook

A series of asymmetric terphenyl dimers (90–95) featuring terminal and lateral fluorine substitution were synthesised and investigated. Both odd and even lengthed methylene spacers were chosen and the terminal alkyl chain was varied. Synthesis proceeded through the use of conventional synthetic reactions making wide use of low temperature lithiations and Suzuki cross-coupling reactions. The final targets were obtained in high purity and the mesophase behaviour of the materials was characterised by a combination of OPM, DSC and XRD.

It was found that the even parity, linear dimers have higher melting points, greater nematic character and a much larger nematic-isotropic transition enthalpy than the bent analogues. Additionally while the linear materials exhibit smectic A phases the bent generally show the tilted phase, smectic C. In both cases XRD evidence suggest intercalated smectic phases, where differing mesogenic cores form the layers. These materials were found to have high melting points and narrow nematic phases.

Further materials (97-104) were designed to enhance the nematic character and this was largely successful in materials 101 and 102. These compounds featured a biphenyl positive arm and a terphenyl negative arm. The linear dimer 101 exhibited a broad nematic phase and a relatively narrow smectic A phase. The bent dimer 102 showed a conventional nematic phase and uniquely in this work, a N_x phase. The N_x was confirmed through the appearance of rope textures in the OPM and on XRD a less diffuse intensity in the wide angle region. The lower temperature phase of the linear dimer compound 101 showed a particularly wide range of optical textures some of which are thought to be characteristic of the Nx phase. This highlighted the importance of XRD and it's use as a powerful tool for the characterisation of liquid crystals.

Compounds 101 and 102 mixed together to generate a phase diagram, which showed that the SmA phase is very quickly disrupted by the presence of bent dimer in the mixture. Likewise the N_x phase was destabilized by additions of linear material. Despite this the Nx phase was stable in mixtures of bent dimer featuring up to a 20 % w/w doping of linear dimer.

The same two materials were used in some electro-optic investigations to find birefringence, voltage and frequency response. The linear dimer, **101** has the higher birefringence of the two materials. Twisted-nematic cells were used to to characterise the voltage/frequency response threshold voltages, where the bent dimer (**102**) has the lower V_{th} and a steeper voltage-transmission response. Approximate switching times were measured and it was found that the bent dimer behaves in the conventional manner with fast turn-on times and slower turn off times, Whereas the linear dimer exhibits faster turn-off than turn-on times. This is a surprising result as conventionally turn-off times are relaxation processes and therefore always slower. The frequency response investigation revealed that the linear material has a much lower crossover frequency making it more suitable for dual frequency applications. However, possibly due the size of the materials and the resulting high viscosity the switching times are relatively slow limiting the effectiveness. To fully characterise the electro-optic properties of these materials they require significant further investigation by collaborators, particularly the linear systems. While much of current research is targeting bent dimer systems and the N_x phase, the linear materials also exhibit some unusual properties and present the opportunity for further investigation.

While the linear materials has a reasonably low crossover frequency this could be improved in further materials such as 106 in Figure 9.1. The ester linking group and the terminal cyano will generate a material with higher positive $\Delta \varepsilon$ while the alkyne linkage maintains nematic character and reduces viscosity versus an aryl ring. The lower large $\Delta \varepsilon$ could reduce switching times in the low frequency regime.



Figure 9.1. Proposed future dimer for DFLC.

10 Experimental

10.1 General Information and Characterisation Methods

Starting Materials Starting materials were purchased from Sigma Aldrich, Alfa Asar, VWR, Fluorochem, Apollo Scientific or Tokyo Chemical Industries(TCI). All were used as purchased, without further purification. 1-bromo-4-heptylbenzene, **80**, (2,3-difluorophenyl)boronic acid, **76** and (2,3-difluoro-4-pentylphenyl)boronic acid, **96** were sourced from Kingston Chemicals Ltd.

TLC Thin layer chromatography (TLC) was carried out using Merck aluminium backed silica gel plates (60 F_{254}).

Column Chromatography All purification by column chromatography utilised Merck Geduran Si 60 (40–63 µm) silica gel.

mp / bp Melting points (mp) were found via OPM and are recorded as onset temperatures. Boiling points (bp) are listed as ranges with units of hectopascal (hPa).

NMR ¹H-NMR 400 MHz, ¹³C-NMR 101 MHz and ¹⁹F-NMR 377 MHz were recorded on a Jeol JNM ECP400 spectrometer. All NMR spectra were carried out in solution using deuterated chloroform (CDCl₃) unless otherwise specified. Chemical shifts, δ are quoted in ppm downfield from TMS ($\delta = 0.00$), coupling constants, J are in Hz and splitting patterns are defined as listed below. In some cases the recorded 13 C NMR data has too few signals, this due to very weak signals, or signal overlap. This is particularly apparent for quaternary carbons that split with fluorine and the carbon bonded to boron in the boronic acid materials.

\mathbf{S}	singlet	\mathbf{q}	quartet
\mathbf{bs}	broad singlet	quin	quintet
d	doublet	\mathbf{sext}	sextet
\mathbf{t}	triplet	\mathbf{m}	multiplet

MS Mass spectropetry data was obtained using a Perkin Elmer Auto System XL GC & Turbo Mass Mass Spectrometer or in the case of MALDI a Bruker Autoflex Speed.

HPLC Purity of final compounds was confirmed in part by high performance liquid chromatography. The HPLC systems used were either Merck-Hitachi (T6300 column thermostat, D-6000 interface, L-4000 detector, L-6200A Inteligent pump) or Gilson (Gilson 321 pump, Agilent/HP1100 detector, Phenomex LUNA 18(2) reverse phase column with Unipoint software). All HPLC was performed using 80:20 acetonitrile-dichloromethane at 1 ml/min unless otherwise specified.

EA Additional purity conformation by elemental analysis was carried out using a Fisons EA-1108 CHN elemental analyser.

10.2 Synthetic Procedures

10.2.1 1,8-bis(4-bromophenyl)octane-1,8-dione — 65



Suberoyl chloride, **63** (25.33 g, 0.12 mol) in bromobenzene, **62** (100 mL) was added dropwise to a stirred mixture of aluminium chloride (34.67 g, 0.26. mol) in bromobenzene, **62** (200 mL) while under nitrogen. The temperature was maintained at <25 °C overnight. The reaction mixture was poured slowly into an excess mixture of ice and 36% (HCl). The product was extracted into dichloromethane DCM before being washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The crude product was recrystalised in ethanol (EtOH) / ethyl acetate (EtOAc) to yield the white solid ketone, **65**.^{91,92}

Yield 41.81 g, 76 %

mp 118–119 °C. (Lit. m.p. 151 °C).⁹¹

 $\pmb{\delta_{H}} \quad 1.42(4\mathrm{H,\ m}),\ 1.74(4\mathrm{H,\ quint},\ J{=}7.3),\ 2.93(4\mathrm{H,\ t},\ J{=}7.3),\ 7.60(4\mathrm{H,\ d},\ J{=}8.7),\ 7.81(4\mathrm{H,\ d},\ J{=}8.7).$

 $\boldsymbol{\delta_C} \quad 24.00,\, 29.10,\, 38.44,\, 127.78,\, 129.61,\, 131.86,\, 135.82,\, 200.13.$

MS m/z 448.1 (M^+).

10.2.2 1,8-bis(4-bromophenyl)octane — 67



Ketone, **65** (41.80 g, 0.092 mol) in DEG (300 ml) was heated to form a solution. Hydrazine monohydrate (27.63 g, 0.55 mol) was added all at once. The mixture was heated to 160 °C and stirred for 2 h. The solution was allowed to cool to room temperature overnight. The mixture was again heated to form a solution before adding potassium hydroxide (30.97 g, 0.55 mol) all at once. The mixture was heated to 180 °C for 3 h. After cooling slightly the solution was poured into an excess mixture of ice and 36% HCl. The product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The crude product purified by column chromatography (silica gel, hexane) and recrystalised from EtOH / EtOAc, yielding a white solid, **67**^{91,92}.

Yield 30.98 g, 79 %

mp 57–61 °C. (Lit. m.p. 67 °C).^{91,92}

 $\delta_{H} \quad 1.22 - 1.35(8\text{H, m}), \ 1.53 - 1.62(4\text{H, m}), \ 2.54(4\text{H, t}, \ J = 7.6), \ 7.04(4\text{H, d}, \ J = 8.4), \ 7.38(4\text{H, d}, \ J = 8.4).$

 δ_C 29.22, 29.45, 31.39, 35.42, 119.35, 130.27, 131.35, 141.87.

MS m/z 424.2 (M^+) .

10.2.3 1,9-bis(4-bromophenyl)nonane-1,9-dione — 66



Azelaoyl chloride, **64** (28.46 g, 0.13 mol) in bromobenzene, **62** (100 mL) was added dropwise to a stirred mixture of aluminium chloride (36.97 g, 0.28. mol) in bromobenzene, **62** (200 mL) while under nitrogen. The temperature was maintained at <25 °C overnight. The reaction mixture was poured slowly into an excess mixture of ice and 36% HCl. The product was extracted into DCM before being washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The crude product was recrystalised in EtOH / EtOAc to yield the white solid ketone, **66**.^{91,92}

Yield 45.08 g, 77 %

mp 131–133 °C. (Lit. m.p. 132 °C).⁹¹

$$\begin{split} \delta_{H} \quad 1.33-1.44(6\mathrm{H,\,m}), \ 1.72(4\mathrm{H,\,quin}, \ J{=}7.2), \ 2.92(4\mathrm{H,\,t}, \ J{=}7.3), \ 7.60(4\mathrm{H,\,d}, \ J{=}8.6), \ 7.81(4\mathrm{H,\,d}, \ J{=}8.7). \end{split}$$

 δ_C 24.21, 29.20, 29.38, 38.60, 128.14, 129.69, 131.97, 135.81, 199.49.

MS m/z 466.20 (M^+) .

10.2.4 1,9-bis(4-bromophenyl)nonane — 68



Ketone, **66** (18.64 g, 0.04 mol) in DEG (200 ml) was heated to form a solution. Hydrazine monohydrate (12.01 g, 0.24 mol) was added all at once. The mixture was heated to 160 °C and stirred for 2 h. The solution was allowed to cool to room temperature overnight. The mixture was again heated to form a solution before adding potassium hydroxide (13.46 g, 0.24 mol) all at once. The mixture was heated to 180 °C for 3 h. After cooling slightly the solution was poured into an excess mixture of ice and 36% HCl acid. The product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The crude product purified by column chromatography (silica gel, hexane) and recrystalised from EtOH / EtOAc, yielding a white solid, **68**^{91,92}

Yield 14.13 g, 81 %

mp 25–28 °C. (Lit. m.p. 32 °C).^{91,92}

$$\begin{split} \delta_{H} \quad 1.22-1.35(10\mathrm{H,\,m}), \, 1.57(4\mathrm{H,\,quin},\,J{=}6.9), \, 2.54(4\mathrm{H,\,t},\,J{=}7.6), \, 7.04(4\mathrm{H,\,d},\,J{=}8.4), \, 7.38(4\mathrm{H,\,d},\,J{=}8.4). \end{split}$$

 δ_C 29.23, 29.51, 29.53, 31.40, 35.43, 119.33, 130.27, 131.34, 141.90.

MS m/z 438.2 (M^+) .

10.2.5 (3,4-difluorophenyl)boronic acid — 70



1,2-Dibromoethane (6 drops), was added to a stirred mixture of magnesium (3.91 g, 0.16 mol), in THF (60 ml). **69** (38.60 g, 0.20 mol) was dissolved in tetrahydrofuran THF (180 ml). Approximately $^{1}/_{3}$ of the solution was added quickly to the magnesium / THF mixture and heated to initiate the reaction. Once initiated, the remaining solution was added dropwise to maintain reflux. The mixture was stirred at reflux for 30 min. After cooling to room temperature the reaction was cooled to -78 °C and trimethyl borate (31.18 g, 0.30 mol) was added dropwise keeping the temperature below -60 °C. The mixture was allowed to warm to room temperature overnight. 10 % HCl acid was added and the solution stirred for 1 h. The product was extracted into ether and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was stirred in hexane for 1 h (water added to hydrolyse anhydride). A white solid was filtered off yielding, **70**.

Yield 21.95 g, 70 %

 δ_H (DMSO-d₆) 7.37(1H, t, J=11.1, 8.1, ArH), 7.61(1H, m, ArH), 7.69(1H, ddd, J=11.6, 8.8, 1.4, ArH), 8.35(2H, bs, B(OH)₂).

 δ_F (DMSO-d₆) -140.40(1F, dt, J=20.8, 11.7), -136.67(1F, ddd, J=24.7, 13.4, 5.1).

 $\delta_{C} (\mathsf{DMSO-d_6}) \quad 117.38 (\mathrm{d}, J = 15.74), 122.88 (\mathrm{d}, J = 14.4), 131.88 (\mathrm{dd}, J = 6.5, 3.5), 149.72 (\mathrm{dd}, J = 245.5, 12.1), 151.48 (\mathrm{dd}, J = 248.2, 12.5).$

10.2.6 4'-bromo-3,4-difluorobiphenyl — 72



Bromoiodobenzene **71** (33.95 g, 0.12 mmol), was added to sodium carbonate (Na₂CO₃) (38.16 g, 0.36 mmol) in water (70 mL) and DME (450 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.69 g, 0.6 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid **70** (18.95 g, 0.12 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into ether and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane) and recrystallized in EtOH yielding a colourless solid **72**.

Yield 25.36 g, 77 %

mp 42.2 °C.

 δ_H 7.18-7.28(2H, m), 7.34(1H, ddd, J=9.7, 6.9, 1.7), 7.38(2H, d, J=8.6), 7.57(2H, d, J=8.7).

 δ_F -139.37(1F, tt, J=13.4, 8.1), -137.01(1F, ddd, J=19.2, 11.1, 7.4).

$$\begin{split} & \delta_{\pmb{C}} \quad 116.32 (\mathrm{dd}, \ J = 18.0, \ 5.3), \ 118.58 (\mathrm{d}, \ J = 17.5), \ 122.10, \ 124.01 (\mathrm{m}), \ 129.45, \ 132.43, \ 137.04 (\mathrm{m}), \\ & 137.69, \ 149.84 (\mathrm{dd}, \ J = 246.83, \ 12.9), \ 150.34 (\mathrm{dd}, \ J = 254.4, \ 12.7). \end{split}$$

MS m/z 270.1 (M^+) .

10.2.7 (3',4'-difluoro-[1,1'-biphenyl]-4-yl)boronic acid — 73



Compound 72 (25.03 g, 0.093 mol) in THF (200 mL) and under nitrogen was cooled to -78 °C. *n*-BuLi (2.5 M, 40.92 mL, 0.10 mol) was added dropwise ensuring that the temperature was below -60 °C. After complete addition of *n*-BuLi the reaction was stirred for 1 h at -78 °C. Trimethyl borate (14.5 g, 0.14 mol) was added dropwise while ensuring that the temperature was below -60 °C. The reaction was stirred for 1 h at -78 °C before being allowed to warm to room temperature overnight. 10 % HCl acid was added and the solution stirred for 1 h. The product was extracted into ether and washed with water and brine. The organic extract was dried over MgSO₄, filtered and the solvent was removed. The crude product was stirred in hexane for 1 h (water added to hydrolyse anhydride). Solid white powder filtered off yielding boronic acid, 73.

Yield 17.45 g, 80 %

 δ_H (DMSO-d₆) 7.49-7.60(2H, m, ArH), 7.55(2H, d, J=7.6, ArH), 7.81(1H, ddm, J=12.0, 7.9, ArH), 7.88(2H, d, J=7.6, ArH), 8.15(2H, bs, B(OH)₂).

 δ_F (DMSO-d₆) -140.58--140.4(1F, m), -138.06(1F, dt, J=20.7, 10.1).

 δ_C (DMSO-d₆) 116.27(dd, J=17.59, 4.68), 118.46(d, J=17.1), 124.02, 126.28, 135.38, 138.3(m), 139.87, 149.71(dd, J=245.9, 12.5), 150.35(dd, J=245.36, 12.60).

10.2.8 1-(4-bromophenyl)pentan-1-one — 78



Bromobenzene, 62 (105.98 g, 0.675 mol) was added to a cooled (5 °C) mixture of aluminium chloride (66.00 g, 0.495 mol) in DCM (200 ml). Valeryl chloride (54.26 g, 0.45 mol) was added dropwise. The mixture was allowed to warm to room temperature overnight. The mixture was poured slowly into an excess mixture of ice and 36% HCL acid. The product was extracted into DCM before being washed with water. The organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The product was distilled (140–150 °C, 20 hPa) to yield an orange/yellow solid, 78³⁰.

Yield 60.02 g, 55.31 %

bp 140–150 °C, 20 hPa (Lit. b.p. 180–184 °C, 27 hPa).³⁰

$$\begin{split} &\delta_{H} \quad 0.94 \; (3\mathrm{H, t}, \, J{=}7.3, \, \mathrm{CH}_3), \, 1.39 \; (2\mathrm{H, sext}, \, J{=}7.4, \, \mathrm{CH}_2), \, 1.70 \; (2\mathrm{H, quin}, \, J{=}7.5, \, \mathrm{CH}_2), \, 2.92 \; (2\mathrm{H, t}, \, J{=}7.3, \, \mathrm{CH}_2), \, 7.58 \; (2\mathrm{H, d}, \, J{=}8.4, \, \mathrm{ArH}), \, 7.81 \; (2\mathrm{H, d}, \, J{=}8.5, \, \mathrm{ArH}). \end{split}$$

 δ_C 14.02, 22.53, 26.44, 38.38, 128.08, 129.69, 131.94, 135.86, 199.57.

MS m/z 242 (M^+) , 240 (M^+) .

10.2.9 1-bromo-4-pentylbenzene — 79



Compound 78 (55.46 g, 0.23 mol) in DEG (300 ml) was heated to form a solution. Hydrazine monohydrate (34.50 g, 0.69 mol) was added all at once. The mixture was heated to 130 °C and stirred for 3 h. The temperature was raised to 180 °C and the excess hydrazine monohydrate was distilled out. The solution was allowed to cool to room temperature overnight. The mixture was again heated to form a solution before adding potassium hydroxide (38.71 g, 0.69 mol) all at once. The mixture was heated to 180 °C for 3 h. After cooling slightly the solution was poured into an excess mixture of ice and 36% HCl acid. The product was extracted into DCM and washed with lots of water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The crude product was distilled (120–130 °C, 20 hPa) yielding an colourless oil, 79.³⁰

Yield 36.20 g, 69 %

bp 120–130 °C, 20 hPa (Lit. b.p. 145–148 °C, 27 hPa).³⁰

$$\begin{split} & \delta_{H} \quad 0.94(3\mathrm{H,\,t},\,J{=}6.9,\,\mathrm{CH}_{3}),\, 1.28{-}1.43(4\mathrm{H,\,m},\,\mathrm{CH}_{2}{-}\mathrm{CH}_{2}),\, 1.63(2\mathrm{H,\,quin},\,J{=}7.5,\,\mathrm{CH}_{2}),\, 2.59(2\mathrm{H},\,\mathrm{t},\,J{=}7.7,\,\mathrm{CH}_{2}),\, 7.08(2\mathrm{H,\,d},\,J{=}8.2,\,\mathrm{ArH}),\, 7.43(2\mathrm{H,\,d},\,J{=}8.3,\,\mathrm{ArH}). \end{split}$$

 δ_C 14.18, 22.68, 31.18, 31.54, 35.48, 119.41, 130.31, 131.39, 141.95.

MS m/z 228.1(M^+), 226.1(M^+).

10.2.10 2,3-difluoro-4'-pentylbiphenyl — 82



Bromide **79** (18.25 g, 0.08 mmol), was added to Na₂CO₃ (25.44 g, 0.24 mmol) in water (80 mL) and DME (180 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.46 g, 0.4 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid **76** (18.95 g, 0.12 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into ether and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane) yielding a colourless oil **82**³⁰.

Yield 16.53 g, 79 %

$$\begin{split} & \delta_{H} \quad 0.92(3\mathrm{H, t}, \, J{=}6.8, \, \mathrm{CH_3}), \, 1.23{-}1.44(4\mathrm{H, m}, \, 2{\times}\mathrm{CH_2}), \, 1.67(2\mathrm{H, quin}, \, J{=}7.3, \, \mathrm{CH_2}), \, 2.66(2\mathrm{H, t}, \, J{=}7.8, \, \mathrm{CH_2}{-}\mathrm{Ar}), \, 7.08{-}7.22(3\mathrm{H, m}, \, \mathrm{ArH}), \, 7.28(2\mathrm{H, d}, \, J{=}8.1, \, \mathrm{ArH}), \, 7.47(2\mathrm{H, dd}, \, J{=}8.1, \, 1.5). \end{split}$$

 δ_F -143.74(1F, d, J=20.1), -138.04(1F, dt, J=20.6, 6.4).

 δ_{C} 14.14, 22.66, 31.19, 31.65, 115.71, 115.89, 124.06(m), 125.34(m), 128.74, 128.89(d, J=2.8), 143.23.

MS m/z 260.4 (M^+) .

10.2.11 (2,3-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)boronic acid — 85



Compound 82 (19.52 g, 0.075 mol) in THF (250 mL) and under nitrogen was cooled to -78 °C. *n*-BuLi (2.5 M, 33.20 mL, 0.083 mol) was added dropwise ensuring that the temperature was below -60 °C. After complete addition of *n*-BuLi the reaction was stirred for 1 h at -78 °C. Trimethyl borate (11.74 g, 0.113 mol) was added dropwise while ensuring that the temperature was below -60 °C. The reaction was stirred for 1 h at -78 °C before being allowed to warm to room temperature overnight. 10 % HCl acid was added and the solution stirred for 1 h. The product was extracted into ether and washed with water and brine. The organic extract was dried over MgSO₄, filtered and the solvent was removed. The crude product was stirred in hexane for 1 h (water added to hydrolyse anhydride). Solid white powder filtered off yielding boronic acid, 85:³⁰

Yield 21.96 g, 89 %

 $\delta_{H} \text{ (DMSO-d_6)} \quad 0.87(3\text{H, t}, J=6.8, \text{CH}_3), \ 1.23-1.40(4\text{H, m}, 2\times\text{CH}_2), \ 1.55-1.69(2\text{H, m}, \text{CH}_2), \ 2.62(2\text{H, t}, J=7.6, \text{CH}_2-\text{Ar}), \ 7.25-7.44(4\text{H, m}, \text{ArH}), \ 7.49(2\text{H, d}, J=8.0, \text{ArH}), \ 8.44(2\text{H, bs}, \text{B(OH}_2)). \ 1.55-1.69(2\text{H, m}, \text{CH}_2), \ 1.55-1.69(2\text{H, m}, \text{CH}$

 δ_F (DMSO-d₆) -146.13(1F, dd, J=22.4, 4.9), -130.73(1F, d, J=22.0).

 δ_C (DMSO-d₆) 14.48, 22.53, 31.10, 31.48, 35.38, 125.28, 129.20, 129.25, 130.11(m), 131.96(m), 143.38, 147.55(dm, J=247.2), 153.68(dm, J=245.3).
10.2.12 1-bromo-4-butoxybenzene — 81



4-Bromophenol, **77** (43.25 g, 0.25 mol), 1-bromobutane (37.68, 0.275 mol) and potassium carbonate (51.88 g, 0.375 mol) in butanone (200 ml) were heated under reflux for 24 h. Potassium carbonate was removed by filtration and the solvent was removed under vacuum. The product was distilled (80–95 °C, 0.4 hPa) giving an oil, **81**.¹³⁵

Yield 55.09 g, 96 %

bp 80–95 °C, 0.4 hPa (Lit. 79–80 °C, 0.4 hPa).¹³⁵

$$\begin{split} &\delta_{H} \quad 0.99\;(3\mathrm{H,\,t},\,J{=}7.4,\,\mathrm{CH}_{3}),\,1.50\;(2\mathrm{H,\,sext},\,J{=}7.4,\,\mathrm{CH}_{2}),\,1.77\;(2\mathrm{H,\,quin},\,J{=}7.1,\,\mathrm{CH}_{2}),\,3.92\;(2\mathrm{H,\,t},\,J{=}6.5,\,\mathrm{CH}_{2}{-}\mathrm{O}),\,6.78\;(2\mathrm{H,\,d},\,J{=}9.0,\,\mathrm{ArH}),\,7.37\;(2\mathrm{H,\,d},\,J{=}9.1,\,\mathrm{ArH}). \end{split}$$

 δ_C 13.98, 19.35, 31.35, 68.03, 112.66, 116.40, 132.29, 158.38.

MS m/z 228.1 (M^+) , 230.1 (M^+) .

¹³⁵S. E. Denmark, R. C. Smith, and S. A. Tymonko. *Tetrahedron*, 2007, **63**, 5730–5738.

10.2.13 4'-butoxy-2,3-difluorobiphenyl — 84



Bromide 81 (17.61 g, 0.069 mmol), was added to Na_2CO_3 (22.26 g, 0.21 mmol) in water (70 mL) and DME (180 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.40 g, 0.35 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid 76 (16.34 g, 0.10 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into ether and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane) yielding a colourless oil 84.

Yield 17.88 g, 76 %

$$\begin{split} & \delta_{H} \quad 0.99(3\mathrm{H,\,t},\,J{=}7.39,\,\mathrm{CH_3}),\, 1.51(2\mathrm{H,\,sext},\,J{=}7.4,\,\mathrm{CH_2},\,1.80(2\mathrm{H,\,quin},\,J{=}7.4,\,\mathrm{CH_2}),\, 4.01(2\mathrm{H,\,t},\,J{=}6.5,\,\mathrm{O-CH_2},\, 6.98(2\mathrm{H,\,d},\,J{=}8.7,\,\mathrm{ArH}),\, 7.07{-}7.19(3\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.47(2\mathrm{H,\,dd},\,J{=}8.6,\,1.7,\,\mathrm{ArH}). \end{split}$$

 δ_F -144.01(1F, dm, J=20.1), -138.11(1F, dt, J=20.8, 6.4).

 $\delta_{C} \quad 13.95, \ 19.35, \ 31.39, \ 67.85, \ 113.67, \ 115.39, \ 115.57, \ 124.02(\mathrm{m}), \ 125.13(\mathrm{m}), \ 130.17(\mathrm{d}, \ J{=}3.1), \ 137.76, \ 159.27.$

MS m/z 262.2 (M^+) .

10.2.14 (4'-butoxy-2,3-difluoro-[1,1'-biphenyl]-4-yl)boronic acid — 87



Compound 84 (16.88 g, 0.064 mol) in THF (250 mL) and under nitrogen was cooled to -78 °C. *n*-BuLi (2.5 M, 29.20 mL, 0.073 mol) was added dropwise ensuring that the temperature was below -60 °C. After complete addition of *n*-BuLi the reaction was stirred for 1 h at -78 °C. Trimethyl borate (10.29 g, 0.099 mol) was added dropwise while ensuring that the temperature was below -60 °C. The reaction was stirred for 1 h at -78 °C before being allowed to warm to room temperature overnight. 10 % HCl acid was added and the solution stirred for 1 h. The product was extracted into ether and washed with water and brine. The organic extract was dried over MgSO₄, filtered and the solvent was removed. The crude product was stirred in hexane for 1 h (water added to hydrolyse anhydride). Solid white powder filtered off yielding boronic acid, 87.

Yield 15.87 g, 81 %

$$\begin{split} \delta_{H} \ (\mathsf{DMSO-d_6}) & 0.94(3\mathrm{H, t}, \, J{=}7.4, \, \mathrm{CH_3}), \, 1.45(2\mathrm{H, sext}, \, J{=}7.4, \, \mathrm{CH_2}, \, 1.72(2\mathrm{H, quin}, \, J{=}6.6, \, \mathrm{CH_2}, \\ 4.02(2\mathrm{H, t}, \, J{=}6.5, \, \mathrm{O-CH_2}), \, 7.05(2\mathrm{H, d}, \, J{=}8.7, \, \mathrm{ArH}), \, 7.27(1\mathrm{H, t}, \, J{=}7.2, \, \mathrm{Ar-H}), \, 7.39(1\mathrm{H, t}, \, J{=}7.3, \, \mathrm{ArH}), \, 7.51(2\mathrm{H, d}, \, J{=}8.2, \, \mathrm{ArH}), \, 8.42(2\mathrm{H, bs}, \, \mathrm{B(OH)_2}). \end{split}$$

 δ_F (DMSO-d₆) -146.34(1F, dd, J=22.4, 5.0), -130.76(1F, dd, J=22.9, 3.4).

 δ_C (DMSO-d₆) 14.27, 19.31, 31.27, 67.81, 115.26, 125.04, 126.62, 130.22(m), 130.54, 130.57, 131.62(d, J=9.9), 147.31(dd, J=247.1, 15.7), 153.84(dd, J=245.7, 12.3), 159.42.

10.2.15 2,3-difluoro-4'-heptylbiphenyl — 83



Bromide 80 (17.61 g, 0.069 mmol), was added to Na_2CO_3 (22.26 g, 0.21 mmol) in water (70 mL) and DME (180 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.40 g, 0.35 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid 76 (16.34 g, 0.10 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into ether and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane) yielding a colourless oil 83.

Yield 19.33 g, 97 %

 $\delta_{H} \quad 0.89(3\mathrm{H,\,t},\,J{=}6.5,\,\mathrm{CH}_3),\,1.21{-}1.45(8\mathrm{H,\,m},\,4{\times}\mathrm{CH}_2),\,1.65(2\mathrm{H,\,quin},\,J{=}7.46,\,\mathrm{CH}_2,\,2.65(2\mathrm{H,\,t},\,J{=}7.8,\,\mathrm{CH}_2{-}\mathrm{Ar}).$

 δ_F -143.75(1F, d, J=19.7), -138.05(1F, dt, J=20.4, 7.2).

$$\begin{split} & \pmb{\delta_C} \quad 14.21,\, 22.78,\, 29.29,\, 31.52,\, 31.92,\, 35.81,\, 115.71,\, 115.88,\, 124.04(\mathrm{m}),\, 125.34(\mathrm{m}),\, 128.73,\, 128.89(\mathrm{d},\, J=2.66),\, 143.24. \end{split}$$

MS m/z 288.4 (M^+) .

10.2.16 (2,3-difluoro-4'-heptyl-[1,1'-biphenyl]-4-yl)boronic acid — 86



Compound 83 (19.32 g, 0.067 mol) in THF (250 mL) and under nitrogen was cooled to -78 °C. *n*-BuLi (2.5 M, 26.80 mL, 0.074 mol) was added dropwise ensuring that the temperature was below -60 °C. After complete addition of *n*-BuLi the reaction was stirred for 1 h at -78 °C. Trimethyl borate (10.44 g, 0.10 mol) was added dropwise while ensuring that the temperature was below -60 °C. The reaction was stirred for 1 h at -78 °C before being allowed to warm to room temperature overnight. 10 % HCl acid was added and the solution stirred for 1 h. The product was extracted into ether and washed with water and brine. The organic extract was dried over MgSO₄, filtered and the solvent was removed. The crude product was stirred in hexane for 1 h (water added to hydrolyse anhydride). Solid white powder filtered off yielding boronic acid, 86.

Yield 20.38 g, 92 %

 $\begin{aligned} \delta_{H} \text{ (DMSO-d_6)} & 0.86(3\mathrm{H, t} J = 6.8, \mathrm{CH}_3), \ 1.19 - 1.38(8\mathrm{H, m} 4 \times \mathrm{CH}_2), \ 1.60(2\mathrm{H, quin}, J = 5.7, \mathrm{CH}_2), \\ 2.62(2\mathrm{H, t}, J = 7.6, \mathrm{Ar-CH}_2), \ 7.26 - 7.30(1\mathrm{H, m}, \mathrm{ArH}), \ 7.32(2\mathrm{H, d} J = 8.3, \mathrm{ArH}), \ 7.38 - 7.43(1\mathrm{H, m}, \mathrm{ArH}), \ 7.49(2\mathrm{H, d} J = 6.8, \mathrm{ArH}), \ 8.44(2\mathrm{H, bs}, \mathrm{B(OH)}_2). \end{aligned}$

 δ_F (DMSO-d₆) -146.14(1F, d, J=21.5), -130.75(1F, d, J=21.8).

 δ_C (DMSO-d₆) 14.53, 22.68, 29.12, 29.25, 31.46, 31.83, 35.42, 125.28, 129.17, 129.20, 129.26, 130.25(m), 131.79, 131.92(m), 143.39, 147.46(dd, J=247.5, 16.0), 154.74(dd, J=245.7, 12.4).



10.2.17 4"-(8-(4-bromophenyl)octyl)-3,4-difluoro-1,1',4',1"-terphenyl — 88

Bromide 67 (30.98 g, 73 mmol), was added to Na_2CO_3 (7.4 g, 73 mmol) in water (200 mL) and DME (330 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.28 g, 0.24 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid 73 (5.69 g, 24 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM) yielding a white solid 88.

Yield 6.60 g, 51 %

mp 114 °C.

$$\begin{split} & \delta_{H} \quad 1.29-1.42(8\mathrm{H,\,m,\,2\times CH_2}),\, 1.54-1.62(2\mathrm{H,\,m,\,CH_2}),\, 1.62-1.69(2\mathrm{H,\,m,\,CH_2}),\, 2.57(2\mathrm{H,\,t,\,}J{=}7.7,\\ \mathrm{Ar-CH_2}),\, 7.08(2\mathrm{H,\,d,\,}J{=}8.3,\,\mathrm{ArH}),\, 7.26(1\mathrm{H,\,m,\,ArH}),\, 7.29(2\mathrm{H,\,d,\,}J{=}8.3,\,\mathrm{ArH}),\, 7.38(1\mathrm{H,\,m,\,ArH}),\\ 7.40(2\mathrm{H,\,d,\,}J{=}8.3),\, 7.48(1\mathrm{H,\,ddd,\,}J{=}11.8,\, 7.6,\, 2.2,\,\mathrm{ArH}),\, 7.57(2\mathrm{H,\,d,\,}J{=}8.2,\,\mathrm{ArH}),\, 7.62(2\mathrm{H,\,d,\,}J{=}8.4,\,\mathrm{ArH}),\, 7.69(2\mathrm{H,\,d,\,}J{=}8.3,\,\mathrm{ArH}). \end{split}$$

 δ_F -141.16(1F, dd, J=21.3, 10.2), -138.44(1F, dt, J=20.7, 10.2).

$$\begin{split} &\delta_{\pmb{C}} \quad 29.24, \ 29.41, \ 29.52, \ 29.54, \ 29.57, \ 31.40, \ 31.70, \ 35.44, \ 36.09, \ 115.97(\mathrm{d}, \ J=17.8), \ 117.68(\mathrm{d}, \ J=17.3), \ 122.98(\mathrm{dd}, \ J=5.7, \ 3.3), \ 127.14, \ 127.40, \ 127.65, \ 127.76, \ 128.98, \ 130.27, \ 131.35, \ 137(\mathrm{m}), \ 138.09, \ 140.48, \ 140.80, \ 141.91, \ 150.06(\mathrm{dd}, \ J=248.7, \ 12.8), \ 150.67(\mathrm{dd}, \ J=247.8, \ 12.5). \end{split}$$

MS m/z 532.0, 534.0 (M^+) .



10.2.18 4["]-(9-(4-bromophenyl)nonyl)-3,4-difluoro-1,1['],4['],1["]-terphenyl — 89

Bromide 68 (24.61 g, 56 mmol), was added to Na_2CO_3 (5.95 g, 56 mmol) in water (200 mL) and DME (330 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.21 g, 0.19 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid 73 (4.38 g, 19 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM) yielding a white solid 89.

Yield 5.59 g, 55 %

mp 81 °C.

$$\begin{split} &\delta_{H} \quad 1.25 - 1.40(10\mathrm{H,\,m,\,CH_2}),\, 1.53 - 1.61(2\mathrm{H,\,m,\,CH_2}),\, 1.61 - 1.69(2\mathrm{H,\,m,\,CH_2}),\, 2.55(2\mathrm{H,\,t},\, J = 7.7,\\ \mathrm{Ar-CH_2}),\, 7.04(2\mathrm{H,\,d}\,\, J = 8.3,\, \mathrm{ArH}),\, 7.16 - 7.25(1\mathrm{H,\,m,\,ArH}),\, 7.27(2\mathrm{H,\,d},\, J = 9.0,\, \mathrm{ArH}),\, 7.32 - 7.37(1\mathrm{H,\,m,\,ArH}),\, 7.38(2\mathrm{H,\,d},\,\, J = 8.3),\,\, 7.43(1\mathrm{H,\,ddd},\,\, J = 11.6,\,\, 7.6,\,\, 2.2,\,\, \mathrm{ArH}),\,\, 7.55(2\mathrm{H,\,d},\,\, J = 8.2,\,\, \mathrm{ArH}),\, 7.58(2\mathrm{H,\,d},\,\, J = 8.4,\, \mathrm{ArH}),\, 7.66(2\mathrm{H,\,d},\,\, J = 8.3,\, \mathrm{ArH}). \end{split}$$

 δ_F -137.36(1F, dd, J=21.0, 10.9), -137.36(1F, dt, J=21.2, 6.2).

$$\begin{split} & \delta_{\boldsymbol{C}} \quad 14.23, \; 22.77, \; 29.24, \; 29.84, \; 31.40, \; 31.70, \; 35.44, \; 36.09, \; 115.97(\mathrm{d}, \; J{=}17.8), \; 117.68(\mathrm{d}, \; J{=}17.3), \\ & 123.00, \; 127.14, \; 127.40, \; 127.65, \; 127.76, \; 128.32, \; 128.50, \; 128.98, \; 130.27, \; 138.01(\mathrm{d}, \; J{=}15.6), \; 140.80, \\ & 141.91, \; 150.06(\mathrm{dd}, \; J{=}248.7, \; 12.8), \; 150.67(\mathrm{dd}, \; J{=}247.8, \; 12.5). \end{split}$$

MS m/z 546.4, 548.4 (M^+) .

10.2.19 4-(8-(3",4"-difluoro-[1,1',4',1"-terphenyl]-4-yl)octyl)-2',3'-difluoro-4"pentyl-1,1'4'1"-terphenyl — 90



Bromide 88 (0.40 g, 0.75 mmol), was added to Na₂CO₃ (0.24 g, 2.25 mmol) in water (10 mL) and DME (40 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.044 g, 0.038 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 85 (0.34 g, 1.13 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 90.

Yield 0.34 g, 68 %

mp 95.6 °C.

$$\begin{split} &\delta_{H} \left(\mathsf{DCM-d_2} \right) \quad 0.92(3\mathrm{H,\,t},\,J{=}7.0,\,\mathrm{CH_3}),\, 1.13{-}1.44(12\mathrm{H,\,m},\,\mathrm{CH_2}),\, 1.60{-}1.72(6\mathrm{H,\,m},\,\mathrm{CH_2}),\, 2.62{-}2.71(6\mathrm{H,\,m},\,\mathrm{Ar-H_2}),\, 7.22{-}7.29(5\mathrm{H,\,m},\,\mathrm{Ar-H}),\, 7.30(4\mathrm{H,\,d},\,J{=}7.6,\,\mathrm{Ar-H}),\, 7.36{-}7.41(1\mathrm{H,\,m},\,\mathrm{Ar-H}),\, 7.43{-}7.49(1\mathrm{H,\,m},\,\mathrm{Ar-H_2}),\, 7.50(4\mathrm{H,\,d},\,J{=}8.0,\,\mathrm{Ar-H}),\, 7.56(2\mathrm{H,\,d},\,J{=}8.2,\,\mathrm{Ar-H}),\, 7.61(2\mathrm{H,\,d},\,J{=}8.5,\,\mathrm{Ar-H}),\, 7.68(2\mathrm{H,\,d},\,J{=}8.5,\,\mathrm{Ar-H}). \end{split}$$

 δ_F (DCM-d₂) -142.25(2F, s), -139.23(1F, m), -136.50(1F, dt, J=20.1, 9.8).

$$\begin{split} &\delta_{C} \; (\mathsf{DCM-d_2}) \quad 15.81, \, 24.55, \, 31.31, \, 31.42, \, 33.16, \, 33.44, \, 33.50, \, 33.55, \, 37.52, \, 37.60, \, 37.62, \, 117.68 (\mathrm{d}, J = 17.8), \, 119.52 (\mathrm{d}, J = 17.2), \, 124.9 (\mathrm{m}), \, 126,67 (\mathrm{m}), \, 128.70, \, 129.21, \, 129.31, \, 130.65, \, 130.69, \, 130.95, \, 131.48 (\mathrm{m}), \; 133.86, \; 139.48, \; 139.54, \; 139.93 (\mathrm{m}), \; 142.54, \; 144.65, \; 145.34 (\mathrm{d}, J = 3.4), \; 150.44 (2\mathrm{C}, \; \mathrm{dd}, J = 249.6, \, 15.5), \; 151.86 (\mathrm{dd}, J = 247.6, \, 12.9), \; 152.51 (\mathrm{dd}, J = 246.9, \, 12.8). \end{split}$$

MS m/z 713.024 (M^+) .

EA Calc: C 82.55 %, H 6.79 %. Found: C 82.70 %, H 6.85 %.

HPLC 98.2 %.

10.2.20 4-(8-(3",4"-difluoro-[1,1',4',1"-terphenyl]-4-yl)octyl)-2',3'-difluoro-4"heptyl-1,1'4'1"-terphenyl — 91



Bromide 88 (0.40 g, 0.75 mmol), was added to Na₂CO₃ (0.24 g, 2.25 mmol) in water (10 mL) and DME (50 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.043 g, 0.038 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 86 (0.38 g, 1.13 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 91.

Yield 0.25 g, 45 %

mp 92.1 °C.

$$\begin{split} \delta_{H} \ (\mathsf{DCM-d_2}) & 0.88(3\mathrm{H, t}, \ J=\!6.8, \ \mathrm{CH_3}), \ 1.22-1.41(16\mathrm{H, m}, \ \mathrm{CH_2}), \ 1.65(6\mathrm{H, quin}, \ J=\!8.7, \ \mathrm{CH_2}), \\ 2.61-2.69(6\mathrm{H, m}, \ \mathrm{Ar-CH_2}), \ 7.21-7.31(9\mathrm{H, m}, \ \mathrm{ArH}), \ 7.35-7.50(1\mathrm{H, m}, \ \mathrm{ArH}), \ 7.42-7.48(1\mathrm{H, m}, \ \mathrm{ArH}), \\ 7.49(4\mathrm{H, d}, \ J=\!7.8, \ \mathrm{ArH}), \ 7.55(2\mathrm{H, d}, \ J=\!8.2, \ \mathrm{ArH}), \ 7.60(2\mathrm{H, d}, \ J=\!8.5, \ \mathrm{ArH}), \ 7.67(2\mathrm{H, d}, \ J=\!8.5, \ \mathrm{ArH}), \\ \mathrm{ArH}). \end{split}$$

 δ_F (DCM-d₂) -144.17(2F, s), -144.13(1F, m), -138.44(1F, dt, J=20.1, 9.8).

 δ_C (DCM-d₂) 13.95, 22.76, 29.26, 29.37, 29.39, 29.49, 31.53, 31.58, 31.91, 35.59, 35.70, 115.75(d, J=17.8), 117.59(d, J=17.1), 123.00(m), 124.74(m), 126.77, 127.28, 127.38, 128.71, 128.76, 129.02, 129.55(m), 131.91(m), 137.53, 137.61, 140.59, 142.73, 143.40, 143.45, 148.49(2C, dm, J-250.9) [2x C-F signals not visible].

MS m/z 741.111 (M^+) .

EA Calc: C 82.67 %, H 7.07 %. Found: C 81.95 %, H 7.23 %..

HPLC 99.0 %.

10.2.21 4-butoxy-4"-(8-(3",4"-difluoro-[1,1',4',1"-terphenyl]-4-yl)octyl)-2',3'difluoro-1,1'4'1"-terphenyl — 92



Bromide 88 (0.40 g, 0.75 mmol), was added to Na₂CO₃ (0.24 g, 2.25 mmol) in water (10 mL) and DME (40 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.043 g, 0.038 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 87 (0.35 g, 1.13 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 92.

Yield 0.25 g, 46 %

mp 105.6 °C.

$$\begin{split} & \delta_{H} \; (\mathsf{DCM-d_2}) \quad 0.99(3\mathrm{H,\,t},\,J{=}7.4),\, 1.32{-}1.43(8\mathrm{H,\,m},\,\mathrm{CH}_2),\, 1.46{-}1.55(2\mathrm{H,\,m},\,\mathrm{CH}_2),\, 1.60{-}1.71(4\mathrm{H,\,m},\,\mathrm{CH}_2),\, 1.79(2\mathrm{H,\,quin},\,J{=}7.4,\,\mathrm{CH}_2),\, 2.61{-}2.71(4\mathrm{H,\,m},\,\mathrm{Ar}{-}\mathrm{CH}_2),\, 4.02(2\mathrm{H,\,t},\,J{=}6.5,\,\mathrm{CH}_2),\, 7.00(2\mathrm{H,\,d},\,J{=}8.7,\,\mathrm{Ar}\mathrm{H}),\, 7.20{-}7.34(7\mathrm{H,\,m},\,\mathrm{Ar}\mathrm{H}),\, 7.36{-}7.41(1\mathrm{H,\,m},\,\mathrm{Ar}\mathrm{H}),\, 7.44{-}7.55(5\mathrm{H,\,m},\,\mathrm{Ar}\mathrm{H}),\, 7.56(2\mathrm{H,\,d},\,J{=}8.0,\,\mathrm{Ar}\mathrm{H}),\, 7.61(2\mathrm{H,\,d},\,J{=}8.3,\,\mathrm{Ar}\mathrm{H}),\, 7.68(2\mathrm{H,\,d},\,J{=}8.2\mathrm{m}\,\mathrm{Ar}\mathrm{H}). \end{split}$$

 δ_F (DCM-d₂) -144.33(2F, m), -141.15(1F, m), -138.44(1F, dt, J=20.4, 10.3).

$$\begin{split} &\delta_{C} \; (\mathsf{DCM-d_2}) \quad 13.70, \, 19.30, \, 29.37, \, 29.49, \, 31.36, \, 31.53, \, 31.58, \, 35.59, \, 35.69, \, 67.89, \, 114.63, \, 115.75(\mathrm{d}, J=17.9), \, 117.59(\mathrm{d}, J=17.4), \, 123.06(\mathrm{m}), \, 124.61(\mathrm{dm}, J=16.9), \, 126.70, \, 126.77, \, 127.28, \, 127.38, \, 128.69, \, 128.71, \; 128.76, \; 129.02, \; 129.22(\mathrm{m}), \; 130.00, \; 130.03, \; 131.96, \; 137.53, \; 137.60, \; 137.99, \; 140.54, \; 142.73, \, 143.55, \, 148.60(\mathrm{d}, J=249.1), \; 149.86(\mathrm{d}, J=247.4), \; 150.50(\mathrm{d}, J=247.1), \; 159.37. \end{split}$$

MS m/z 715.056 (M^+) .

EA Calc: C 80.65 %, H 6.49 %. Found: C 78.90 %, H 6.54 %.

HPLC 96.9 %.

10.2.22 4-(8-(3",4"-difluoro-[1,1',4',1"-terphenyl]-4-yl)nonyl)-2',3'-difluoro-4"-pentyl-1,1'4'1"-terphenyl — 93



Bromide 89 (0.38 g, 0.70 mmol), was added to Na₂CO₃ (0.22 g, 2.10 mmol) in water (10 mL) and DME (40 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.016 g, 0.014 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 86 (0.32 g, 1.05 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 93.

Yield 0.30 g, 58 %

mp 77.0 °C.

$$\begin{split} & \delta_{H} \left(\mathsf{DCM-d_2} \right) \quad 0.92(3\mathrm{H,\,t},\,J{=}6.9,\,\mathrm{CH_3}),\, 1.27{-}1.43(14\mathrm{H,\,m},\,\mathrm{CH_2}),\, 1.61{-}1.71(6\mathrm{H,\,m},\mathrm{CH_2}),\, 2.66(6\mathrm{H,\,t},\,J{=}7.8,\,\mathrm{Ar-CH_2}),\, 7.19{-}7.30(9\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.31{-}7.36(1\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.42(1\mathrm{H,\,ddd},\,J{=}11.6,\, 7.6,\, 2.3,\, \mathrm{ArH}),\, 7.50(4\mathrm{H,\,d},\,J{=}8.0,\,\mathrm{ArH}),\, 7.54(2\mathrm{H,\,d},\,J{=}8.2,\,\mathrm{ArH}),\, 7.58(2\mathrm{H,\,d},\,J{=}8.4,\,\mathrm{ArH}),\, 7.66(2\mathrm{H,\,d},\,J{=}8.3,\,\mathrm{ArH}). \end{split}$$

 δ_F (DCM-d₂) -143.22(2F, s), -140.20(1F, m), -137.46(1F, dt, J=20.3, 9.8).

 δ_C (DCM-d₂) 13.89, 22.63, 29.35, 29.50, 29.53, 31.25, 31.53, 31.63, 35.59, 35.68, 115.75(dm, J=17.6), 117.59(d, J=17.4), 123.02(m), 124.74, 126.76, 127.28, 127.38, 128.72, 128.76, 129.02, 129.53(m), 137.52, 137.60, 137.97(m), 140.59, 142.74, 143.42, 143.43, 148.49(dd, J=249.7, 15.6), 149.92(dd, J=247.6), 150.56(dd, J=246.9, 12.8).

MS m/z 727.100 (M^+) .

EA Calc: C 82.55 %, H 6.79 %. Found: C 81.90 %, H 7.13 %.

HPLC 97.8 %

10.2.23 4-(8-(3",4"-difluoro-[1,1',4',1"-terphenyl]-4-yl)nonyl)-2',3'-difluoro-4"-heptyl-1,1'4'1"-terphenyl — 94



Bromide 89 (0.20 g, 0.37 mmol), was added to Na_2CO_3 (0.12 g, 1.11 mmol) in water (10 mL) and DME (40 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.0043 g, 0.0037 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 86 (0.18 g, 0.55 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 94.

Yield 0.14 g, 50 %

mp 69.7 °C.

$$\begin{split} &\delta_{H} \left(\mathsf{DCM-d_2} \right) \quad 0.91(3\mathrm{H,\,t},\,J{=}6.8,\,\mathrm{CH_3}),\, 1.26{-}1.44(18\mathrm{H,\,m},\,\mathrm{CH_2}),\, 1.61{-}1.73(6\mathrm{H,\,m},\,\mathrm{CH_2}),\, 2.62{-}2.73(6\mathrm{H,\,m},\,\mathrm{Ar-CH_2}),\, 7.13{-}7.34(9\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.36{-}7.42(1\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.44{-}7.49(1\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.51(4\mathrm{H,\,d},\, J{=}7.9,\,\mathrm{ArH}),\, 7.57(2\mathrm{H,\,d},\, J{=}8.1),\, 7.61(2\mathrm{H,\,d},\, J{=}8.3,\,\mathrm{ArH}),\, 7.69(2\mathrm{H,\,d},\, J{=}8.3,\,\mathrm{ArH}). \end{split}$$

 δ_F (DCM-d₂) -144.18(2F, s), -141.15(1F, m), -138.44(1F, dt, J=20.2, 9.9).

$$\begin{split} &\delta_{C} \left(\mathsf{DCM-d_2} \right) \quad 13.95, 22.76, 29.36, 29.40, 29.53, 31.53, 31.58, 31.93, 35.59, 35.71, 115.75 (d, J=17.8), \\ &117.59 (d \ J=17.3), 123.03 (m), 124.74 (m), 126.76, 127.27, 127.38, 128.71, 128.76, 129.02, 129.65 (m), \\ &131.92, 137.53, 137.60, 138.03, 140.60, 142.74, 143.41, 143.44, 148.49 (2C, dd, J=249.7, 15.7), 149.92 (dd, J=247.6, 12.5), 150.56 (dd, J=246.9, 13.0). \end{split}$$

MS m/z 755.173 (M^+) .

EA Calc: C 82.73 %, H 7.21 %. Found: C 82.81 %, H 7.39 %.

HPLC 98.7 %.

10.2.24 4-butoxy-4"-(8-(3",4"-difluoro-[1,1',4',1"-terphenyl]-4-yl)nonyl)-2',3'difluoro-1,1'4'1"-terphenyl — 95



Bromide 89 (0.16 g, 0.29 mmol), was added to Na₂CO₃ (0.09 g, 0.29 mmol) in water (10 mL) and DME (40 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) $(3.35 \times 10^{-3} \text{ g}, 2.9 \times 10^{-3} \text{ mmol})$ was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 87 (0.13 g, 0.44 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 95.

Yield 0.11 g, 52 %

mp 79.3 °C.

$$\begin{split} & \delta_{H} \left(\mathsf{DCM-d_2} \right) \quad 1.00(3\mathrm{H,\,t},\,J{=}7.4,\,\mathrm{CH_3}),\, 1.29{-}1.44(10\mathrm{H,\,m},\,\mathrm{CH_2}),\, 1.46{-}1.57(2\mathrm{H,\,m},\,\mathrm{CH_2}),\, 1.60{-}1.71(4\mathrm{H,\,m},\,\mathrm{CH_2}),\, 1.79(2\mathrm{H,\,quin},\,J{=}7.5),\, 2.62{-}2.71(4\mathrm{H,\,m},\,\mathrm{Ar-CH_2}),\, 4.02(2\mathrm{H,\,t},\,J{=}6.5,\,\mathrm{O-CH_2}),\, 7.00(2\mathrm{H,\,d},\,J{=}8.9,\,\mathrm{ArH}),\, 7.21{-}7.34(7\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.36{-}7.41(1\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.43{-}7.54(5\mathrm{H,\,m},\,\mathrm{ArH}),\, 7.56(2\mathrm{H,\,d},\,J{=}8.2,\,\mathrm{ArH}),\, 7.61(2\mathrm{H,\,d},\,J{=}8.5,\,\mathrm{ArH}),\, 7.68(2\mathrm{H,\,d},\,J{=}8.5,\,\mathrm{ArH}). \end{split}$$

 δ_F (DCM-d₂) -144.40(1F, dm, J=19.4), -144.24(1F, dm, J=19.9), -141.15(1F, m), -138.46(1F, dt, J=20.2, 8.7).

$$\begin{split} &\delta_{C} \ (\mathsf{DCM-d_2}) \quad 13.69, \ 19.30, \ 29.33, \ 29.48, \ 29.51, \ 31.36, \ 31.15, \ 31.57, \ 35.58, \ 35.67, \ 67.89, \ 114.64, \\ &115.75(\mathrm{d}, \ J=\!17.8), \ 117.58(\mathrm{d}, \ J=\!17.2), \ 123.03(\mathrm{m}), \ 124.06(\mathrm{dm}, \ J=\!16.8), \ 126.76, \ 127.27, \ 127.38, \\ &128.68, \ 128.71, \ 128.75, \ 129.99, \ 130.02, \ 131.96, \ 137.53, \ 137.61, \ 140.60, \ 142.74, \ 143.36, \ 148.39(\mathrm{dd}, \ J=\!249.7, \ 11.2), \ 148.55(\mathrm{dd}, \ J=\!249.9, \ 10.7), \ 149.92(\mathrm{dd}, \ J=\!247.6, \ 12.8), \ 150.57(\mathrm{dd}, \ J=\!247.0, \ 12.7). \end{split}$$

MS m/z 729.085 (M^+) .

EA Calc: C 80.74 %, H 6.64 %. Found: C 80.54 %, H 6.84 %.

HPLC 99.4 %.

10.2.25 4"-(8-(2',3'-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)octyl)-3,4-difluoro-1,1'4'1"-terphenyl — 97



Bromide 88 (2 g, 3.75 mmol), was added to Na_2CO_3 (1.2 g, 11.3 mmol) in water (50 mL) and DME (100 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.043 g, 0.038 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 86 (1.28 g, 5.63 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 9:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 97.¹

Yield 1.65 g, 67 %

mp 49.4 °C.

 δ_H (DCM-d₂) 0.91 (3H, t, J=6.7, CH₃), 1.29–1.43(12H, m, CH₂), 1.57–1.70(6H, m, CH₂), 2.61–2.71 (6H, m, Ar-CH₂), 6.99–7.03 (1H, m, ArH), 7.09–7.14(1H, m, ArH), 7.25–7.30(5H, m, ArH), 7.38–7.40(1H, m, ArH), 7.44(2H, d, J=7.9, ArH), 7.48–7.51(1H, m, ArH), 7.57(2H, d, J=8.2, ArH), 7.62(2H, d, J=8.5, ArH), 7.69(2H, d, J=8.3, ArH).

 δ_F (DCM-d₂) -145.23(1F, dd, J=20.6, 5.5), -144.62(1F, dd, J=20.5, 5.2), -141.13(ddd, J=18.0, 11.4, 7.5), -138.42(dt, J=20.5, 10.1).

$$\begin{split} &\delta_{C} \ (\mathsf{DCM-d_2}) \quad 13.84, \ 22.52, \ 28.69, \ 29.22, \ 29.39, \ 29.44, \ 29.50, \ 31.50, \ 31.53, \ 31.58, \ 35.59, \ 35.67, \\ &115.78(\mathrm{d}, \ J=17.8), \ 117.58(\mathrm{d}, \ J=18.4), \ 123.02(\mathrm{m}), \ 124.31(\mathrm{m}), \ 124.88(\mathrm{m}), \ 126.77, \ 127.28, \ 128.30(\mathrm{m}), \\ &124.88(\mathrm{m}), \ 126.77, \ 127.28, \ 127.38, \ 128.30(\mathrm{m}), \ 128.67, \ 128.70, \ 129.02, \ 130.32, \ 130.70, \ 130.84, \ 131.21, \\ &132.25, \ 137.54, \ 137.61, \ 138.00(\mathrm{m}), \ 140.61, \ 142.20, \ 142.72, \ 143.05, \ 147.98(\mathrm{dd}, \ J=247.0), \ 149.50(\mathrm{dd}, \ J=243.8, \ 12.4), \ 149.94(\mathrm{dd}, \ J=247.7, \ 12.7), \ 150.58(\mathrm{dd}, \ J=247.0, \ 12.9). \end{split}$$

MS m/z 637.034 (M^+) .

EA Calc: C 81.10 %, H 6.96 %. Found: C 78.87 %, H 6.55 %.

HPLC 89.03 % (9.4 % impurity)

¹Prepared in part by C. Holmes.

10.2.26 4"-(8-(2',3'-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)nonyl)-3,4-difluoro-1,1'4'1"-terphenyl — 98



Bromide 89 (1.5 g, 2.75 mmol), was added to Na_2CO_3 (0.87 g, 8.25 mmol) in water (50 mL) and DME (100 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.032 g, 0.028 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 86 (0.94 g, 4.10 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 9:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 98.²

Yield 1.14 g, 64 %

mp 66.2 °C.

$$\begin{split} \delta_{H} & (\mathsf{DCM-d_2}) & 0.92(1\mathrm{H, t, J=7.2, CH_3}), \ 1.25-1.46(14\mathrm{H, m, CH_2}), \ 1.65(6\mathrm{H, quin, J=6.8, CH_2}), \\ 2.61-2.75(6\mathrm{H, m, Ar-CH_2}), \ 6.96-7.05(1\mathrm{H, m, ArH}), \ 7.12(1\mathrm{H, td, J=8.2, 1.8, ArH}), \ 7.22-7.32(5\mathrm{H, m, ArH}), \ 7.36-7.41(1\mathrm{H, m, ArH}), \ 7.42-7.51(3\mathrm{H, m, ArH}), \ 7.57(2\mathrm{H, d, J=8.3, ArH}), \ 7.62(2\mathrm{H, d, J=8.5, ArH}), \ 7.69(2\mathrm{H, d, J=8.7, ArH}). \end{split}$$

 δ_F (DCM-d₂) -145.20(1F, dd, J=20.3, 6.5), -144.59(1F, dd, J=20.3, 6.2), -141.55(1F, m), -138.38(1F, dt, J=20.1, 8.6).

$$\begin{split} &\delta_{C} \ (\text{DCM-d}_{2}) \quad 13.85, \ 22.52, \ 28.68, \ 29.37, \ 29.39, \ 29.53, \ 29.53, \ 29.56, \ 29.81, \ 31.50, \ 31.54, \ 31.58, \\ &35.61, \ 35.67, \ 115.75(\text{d}, \text{J}=17.8), \ 117.59(\text{d}, \text{J}=17.3), \ 123.01(\text{dd}, \text{J}=6.2, \ 3.4), \ 124.25-124.37(\text{m}), \ 124.87(\text{t}, \text{J}=4.4), \ 126.77, \ 127.27, \ 127.38, \ 128.67, \ 128.70, \ 129.03, \ 130.77(\text{d}, \ \text{J}=13.6), \ 132.24, \ 137.54, \ 137.60, \\ &137.92-138.08(\text{m}), \ 140.61, \ 142.73, \ 143.07, \ 147.99(\text{dd}, \ \text{J}=247.2, \ 13.5), \ 149.51(\text{dd}, \ 243.7, \ 12.3), \ 149.94(\text{dd}, \ \text{J}=247.6, \ 12.9), \ 150.59(\text{dd}, \ 246.9, \ 13.0). \end{split}$$

MS m/z 651.068 (M^+) .

EA Calc: C 81.20 %, H 7.12 %. Found: C 80.96 %, H 7.27 %.

HPLC 99.0 %.

²Prepared in part by C. Holmes.

10.2.27 4'(8-(4-bromophenyl)octyl)-3,4-difluoro-1,1'-biphenyl — 99



Bromide 67 (18.00 g, 42.43 mmol), was added to Na_2CO_3 (4.45 g, 42.43 mmol) in water (50 mL) and DME (100 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.16 g, 0.14 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid 70 (2.23 g, 14.14 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), yielding a white solid 99.

Yield 4.65 g, 72 %

mp 100–101 °C.

$$\begin{split} \delta_{H} & (\mathsf{DCM-d_2}) \quad 1.24-1.40(8\mathrm{H, m, CH_2}), \ 1.51-1.67(4\mathrm{H, m, CH_2}), \ 2.56(2\mathrm{H, t}, \ J=7.7, \ \mathrm{Ar-CH_2}) \\ 2.63(2\mathrm{H, t}, \ J=7.7, \ \mathrm{Ar-CH_2}), \ 7.07(2\mathrm{H, d}, \ J=8.4 \ \mathrm{ArH}), \ 7.19-7.28(3\mathrm{H, m, ArH}), \ 7.30-7.35(1\mathrm{H, m, ArH}), \ 7.35-7.44(3\mathrm{H, m, ArH}), \ 7.46(2\mathrm{H, d}, \ J=8.4, \ \mathrm{ArH}). \end{split}$$

 δ_F -141.73(1F, dt, J=20.4, 11.0), -138.67(1F, dt, J=20.4, 10.4).

 $\begin{aligned} &\delta_{C} \left(\mathsf{DCM-d_2} \right) \quad 29.19, 29.32, 29.43, 31.36, 31.50, 35.30, 35.53, 115.66(\mathrm{d}, J=17.7), 117.45(\mathrm{d}, J=17.3), \\ &119.09, \ 122.90(\mathrm{m}), \ 126.73, \ 129.06, \ 130.31, \ 131.20, \ 136.34, \ 138.42(\mathrm{m}), \ 142.18, \ 143.00, \ 149.72(\mathrm{dd}, J=246.9, \ 12.6), \ 150.50(\mathrm{dd}, J=246.7, \ 12.8). \end{aligned}$

MS m/z 456.2, 458.3 (M^+) .



10.2.28 4'(8-(4-bromophenyl)nonyl)-3,4-difluoro-1,1'-biphenyl — 100

Bromide 68 (13.15 g, 30.00 mmol), was added to Na_2CO_3 (3.18 g, 30.00 mmol) in water (50 mL) and DME (100 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.12 g, 0.10 mmol) was added and flushed through with DME (10 mL). The inert atmosphere was re-established and heating begun. Boronic acid 70 (1.58 g, 10.00 mmol) was added in portions and flushed through with DME (10 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 4:1 hexane/DCM), yielding a white solid 100.

Yield 3.65 g, 77 %

mp 34–35 °C.

$$\begin{split} & \pmb{\delta_{H}} \quad 1.23-1.40(10\mathrm{H,\ m,\ CH_2}),\ 1.53-1.68(4\mathrm{H,\ m,\ CH_2}),\ 2.55(2\mathrm{H,\ t,\ }J{=}7.7,\ \mathrm{Ar-CH_2}),\ 2.64(2\mathrm{H,\ t,\ }J{=}7.8,\ \mathrm{Ar-CH_2}),\ 7.05(2\mathrm{H,\ d,\ }J{=}8.4,\ \mathrm{ArH}),\ 7.17-7.31(4\mathrm{H,\ m,\ ArH}),\ 7.33-7.41(3\mathrm{H,\ m,\ ArH}),\ 7.44(2\mathrm{H,\ d,\ }J{=}8.2,\ \mathrm{ArH}). \end{split}$$

 δ_F -140.71(1F, m), -137.65(1F, dt, J=20.5, 10.5).

$$\begin{split} & \pmb{\delta_C} \quad 29.26, \ 29.40, \ 29.54, \ 29.57, \ 31.42, \ 31.55, \ 35.44, \ 35.67, \ 115.86(\mathrm{d}, \ J=17.7), \ 117.52(\mathrm{d}, \ J=17.3), \\ & 119.35, \ 122.85(\mathrm{m}), \ 126.88, \ 129.10, \ 130.27, \ 131.35, \ 136.37, \ 138.38(\mathrm{m}), \ 141.91, \ 142.84, \ 149.81(\mathrm{dd}, \ J=247.9, \ 12.8), \ 150.58(\mathrm{dd}, \ J=247.75, \ 12.7). \end{split}$$

MS m/z 470.2, 472.2 (M^+) .

10.2.29 4-(9-(3',4'-difluoro-[1,1'-biphenyl]-4-yl)octyl)-2',3'-difluoro-4''-pentyl-1,1'4'1''-terphenyl — 101



Bromide 99 (1.00 g, 2.18 mmol), was added to Na_2CO_3 (0.69 g, 6.54 mmol) in water (20 mL) and DME (80 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.025 g, 0.022 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 85 (0.99 g, 3.27 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 9:1 hexane/DCM), then recrystallised from hexane/EtOH yielding a white solid 101.

Yield 1.02 g, 73 %

mp 77.4 °C.

$$\begin{split} \delta_{H} \left(\mathsf{DCM-d_2} \right) & 0.92(3\mathrm{H, t}, J{=}7.0, \mathrm{CH_3}), 1.32{-}1.44(12\mathrm{H, m}, \mathrm{CH_2}), 1.60{-}1.71(6\mathrm{H, m}, \mathrm{CH_2}), 2.60{-}2.71(6\mathrm{H, m}, \mathrm{Ar}{-}\mathrm{CH_2}), 7.19{-}7.35(10\mathrm{H, m}, \mathrm{Ar}\mathrm{H}), 7.41(1\mathrm{H}, \mathrm{ddd}, J{=}11.9, 7.7, 2.2, \mathrm{Ar}\mathrm{H}), 7.46(2\mathrm{H}, \mathrm{d}, J{=}8.3, \mathrm{Ar}\mathrm{H}), 7.51(4\mathrm{H}, \mathrm{d}, J{=}7.8, \mathrm{Ar}\mathrm{H}). \end{split}$$

 δ_F (DCM-d₂) -144.15(2F, s), -141.71(1F, m), -138.64(1F, dt, J=20.5, 10.2).

 $\begin{aligned} &\delta_{C} \ (\mathsf{DCM-d_2}) \quad 13.89, 22.63, 29.37, 29.39, 29.49, 31.25, 31.54, 31.62, 35.55, 35.68, 35.69, 115.66(d, J=17.7), 117.46(d, J=17.3), 122.90(m), 124.74, 126.74, 128.72, 127.77, 129.07, 129.53(m), 131.92, 136.33, 138.49(m), 143.02, 143.39, 143.43, 148.50(dd, J=249.6, 15.6), 149.72(dd, J=247.0, 12.8), 150.50(dd, J=246.7, 12.9). \end{aligned}$

MS m/z 637.065 (M^+) .

EA Calc: C 81.10 %, H 6.96 %. Found: C 81.06 %, H 7.17 %.

HPLC 97.0 %

10.2.30 4-(9-(3',4'-difluoro-[1,1'-biphenyl]-4-yl)nonyl)-2',3'-difluoro-4''-pentyl-1,1'4'1''-terphenyl — 102



Bromide 100 (1.00 g, 2.12 mmol), was added to Na_2CO_3 (0.67 g, 6.36 mmol) in water (20 mL) and DME (80 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.024 g, 0.021 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 85 (0.98 g, 3.18 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 9:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 102.

Yield 1.07 g, 78 %

mp 45.4 °C.

$$\begin{split} \delta_{H} \ (\mathsf{DCM-d_2}) & 0.92(3\mathrm{H, t}, \ J=7.0, \mathrm{CH}_3), \ 1.26-1.42(14\mathrm{H, m}, \mathrm{CH}_2), \ 1.57-1.72(6\mathrm{H, m}, \mathrm{CH}_2), \ 2.60-2.72(6\mathrm{H, m}, \mathrm{Ar-CH}_2), \ 7.19-7.34(10\mathrm{H, m}, \mathrm{ArH}), \ 7.40(1\mathrm{H, ddd}, \ J=11.9, \ 7.7, \ 2.2, \ \mathrm{ArH}), \ 7.45(2\mathrm{H, d}, \ J=8.3, \ \mathrm{ArH}), \ 7.51(4\mathrm{H, d}, \ J=7.9, \ \mathrm{ArH}). \end{split}$$

 δ_F (DCM-d₂) -144.20(2F, s), -141.75(1F, m), -138.67(1F, dt, J=20.5, 9.3).

$$\begin{split} &\delta_{C} \ (\mathsf{DCM-d_2}) \quad 13.89, \, 22.63, \, 29.36, \, 29.52, \, 29.55, \, 31.24, \, 31.53, \, 31.55, \, 31.62, \, 35.55, \, 35.67, \, 115.66 (\mathrm{d}, J=17.8), \, 117.45 (\mathrm{d}, J=17.2), \, 122.90 (\mathrm{m}), \, 124.75 (\mathrm{m}), \, 126.73, \, 128.72, \, 128.76, \, 129.07, \, 129.55 (\mathrm{m}), \, 136.32, \, 138.45, \, 143.04, \, 143.40, \, 143.43, \, 148.50 (\mathrm{dd}, \ J=249.6, \, 15.7), \, 149.71 (\mathrm{dd}, \ J=247.1, \, 12.4), \, 150.49 (\mathrm{dd}, \ J=246.6, \, 12.8). \end{split}$$

MS m/z 651.070 (M^+) .

EA Calc: C 81.20 %, H 7.12 %. Found: C 80.57 %, H 7.15 %.

HPLC 99.3 %

10.2.31 4'(8-(3',4'-difluoro-[1,1'-biphenyl]-4-yl)octyl)-2,3-difluoro-4-pentyl-1,1'biphenyl — 103



Bromide 99 (1.00 g, 2.18 mmol), was added to Na_2CO_3 (0.69 g, 6.54 mmol) in water (20 mL) and DME (80 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.025 g, 0.022 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 96 (0.75 g, 3.27 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 9:1 hexane/DCM), then recrystallised from EtOH/EtOAc yielding a white solid 103.

Yield 0.53 g, 43 %

mp 54.5 °C.

$$\begin{split} \delta_{H} \left(\mathsf{DCM-d_2} \right) & 0.91(3\mathrm{H, t}, J{=}7.0, \mathrm{CH_3}), 1.30{-}1.43(12\mathrm{H, m}, \mathrm{CH_2}), 1.57{-}1.69(6\mathrm{H, m}, \mathrm{CH_2}), 2.60{-}2.72(6\mathrm{H, m}, \mathrm{Ar{-CH_2}}), 7.01(1\mathrm{H, t}, J{=}7.4, \mathrm{Ar{H}}), 7.11(1\mathrm{H, td}, J{=}7.8, 1.7, \mathrm{Ar{H}}), 7.19{-}7.25(1\mathrm{H, m}, \mathrm{Ar{H}}), 7.27(4\mathrm{H, dd}, J{=}8.2, 2.3, \mathrm{Ar{H}}), 7.30{-}7.34(1\mathrm{H, m}, \mathrm{Ar{H}}), 7.37{-}7.42(1\mathrm{H, m}, \mathrm{Ar{H}}), 7.42{-}7.47(4\mathrm{H, m}, \mathrm{Ar{H}}). \end{split}$$

 δ_F (DCM-d₂) -144.25(1F, dd, J=20.0, 6.0), -143.75(1F, dd, J=20.0, 5.5), -140.75(1F, m), -137.70(1F, dt, J=20.3, 10.1).

$$\begin{split} &\delta_{C} \left(\mathsf{DCM-d_2} \right) \quad 13.84, 22.53, 28.69, 29.35, 29.38, 29.48, 29.82, 31.49, 35.54, 35.66, 115.66 (d, J=17.7), \\ &117.45 (d, J=17.1), 122.90 (m), 124.31 (m), 124.88 (m), 126.73, 128.26, 128.37, 128.66, 128.69, 129.07, \\ &132.26, 136.33, 138.45 (m), 143.03, 143.05, 147.96 (dd, J=246.8, 13.3), 149.49 (dd, J=243.6, 12.4), \\ &149.71 (dd, J=247.0, 12.7), 150.49 (dd, J=246.9, 13.0). \end{split}$$

MS m/z 560.985 (M^+) .

EA Calc: C 79.26 %, H 7.19 %. Found: C 79.17 %, H 7.36 %.

HPLC 98.3 %

10.2.32 4'(8-(3',4'-difluoro-[1,1'-biphenyl]-4-yl)nonyl)-2,3-difluoro-4-pentyl-1,1'biphenyl — 104



Bromide 100 (1.00 g, 2.12 mmol), was added to Na_2CO_3 (0.67 g, 6.32 mmol) in water (20 mL) and DME (80 mL). An inert atmosphere was established by repeated flushing with nitrogen and then evacuation (3x). Tetrakistriphenylphosphine palladium(0) (0.024 g, 0.021 mmol) was added and flushed through with DME (5 mL). The inert atmosphere was re-established and heating begun. Boronic acid 96 (0.73 g, 3.18 mmol) was added in portions and flushed through with DME (5 mL). The reaction was heated under reflux overnight. After cooling, the product was extracted into DCM and washed with water and brine. The organic extracts were dried over MgSO₄, filtered and the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane, 9:1 hexane/DCM) yielding a white solid 104.

Yield 0.25 g, 45 %

mp 31.0 °C.

$$\begin{split} \delta_{H} \left(\mathsf{DCM-d_2} \right) & 0.91(3\mathrm{H,\,t},\,J{=}7.1,\,\mathrm{CH_3}),\,1.27{-}1.42(14\mathrm{H,\,m},\,\mathrm{CH_2}),\,1.58{-}1.69(6\mathrm{H,\,m},\,\mathrm{CH_2}),\,2.59{-}2.72(6\mathrm{H,\,m},\,\mathrm{Ar{-}CH_2}),\,7.01(1\mathrm{H,\,tm},\,J{=}7.5,\,\mathrm{ArH}),\,7.11(1\mathrm{H,\,td},\,J{=}7.3,\,1.8,\,\mathrm{ArH}),\,7.19{-}7.28(5\mathrm{H,\,m},\,\mathrm{ArH}),\,7.29{-}7.34(1\mathrm{H,\,m},\,\mathrm{ArH}),\,7.37{-}7.47(5\mathrm{H,\,m},\,\mathrm{ArH}). \end{split}$$

 δ_F (DCM-d₂) -145.77(1F, dd, J=19.8, 6.2) -144.64(1F, dd, J=19.8, 6.2), -141.75(1F, m), -138.68(1F, dt, J=20.4, 9.6).

$$\begin{split} &\delta_{C} \ (\mathsf{DCM-d_2}) \quad 13.84, \ 22.52, \ 28.68, \ 29.35, \ 29.37, \ 29.52, \ 29.55, \ 29.81, \ 31.49, \ 31.54, \ 35.54, \ 35.66, \\ &115.66(\mathrm{d}, \ J=\!17.7), \ 117.45(\mathrm{d}, \ J=\!17.1), \ 122.89(\mathrm{m}), \ 124.30(\mathrm{m}), \ 124.88(\mathrm{m}), \ 126.73, \ 128.26, \ 128.36, \\ &128.66, \ 128.69, \ 129.07, \ 130.70, \ 130.84, \ 132.25, \ 136.32, \ 143.06, \ 147.96(\mathrm{dd}, \ J=\!247.1, \ 13.3), \ 149.48(\mathrm{dd}, \ J=\!243.9, \ 12.5), \ 149.71(\mathrm{dd}, \ J=\!246.9, \ 12.8), \ 150.49(\mathrm{dd}, \ J=\!246.7, \ 12.6). \end{split}$$

MS m/z 574.989 (M^+) .

EA Calc: C 79.41 %, H 7.37 %. Found: C 79.34 %, H 7.54 %.

HPLC 99.4 %

10.2.33 tetrakistriphenylphosphine palladium(0) — 107

Prepared based on the procedure reported by $\text{Coulson.}^{136} \text{Pd}(\text{PPh}_3)_4$ used for all Suzuki couplings.

Under nitrogen a stirred mixture of palladium (II) chloride (5.00 g, 2.8 mmol) and triphenylphosphene (37.00 g, 0.14 mol) in DMSO (340 mL) was heated to 150° until the formation of a red solution. Heating was stopped and hydrazine monohydrate was added with strong stirring, followed by rapid cooling of the mixture without stirring. The yellow precipitate was filtered under nitrogen, and washed with ethanol and ether. Yellow crystalline product 107 thoroughly dried and stored under nitrogen.

Yield 30.64 g, 95 %

¹³⁶D. R. Coulson, L. C. Satek, and S. O. Grim. "Tetrakis(triphenylphosphine)palladium(0)". In: *Inorganic Syntheses*. John Wiley & Sons, Inc., Hoboken, NJ, USA, Jan. 2007. 121–124.

10.3 Mesophase Behaviour Procedures

10.3.1 OPM

Microscopy was used to initially assign phase type and transition temperatures. Materials were placed onto untreated glass slides and topped with a coverslip. The materials were heated above the isotropic where the coverslip was then pressed to spread the liquid evenly. The materials were observed using an Olympus BX52 microscope, and heated with a Mettler FP-2 X or Linkam LTS350 hotstage. Images were captured via an Nikon Infinity X/Lite cameras, with Studio Capture software. OPM images in this work are all at x200 magnification and under cross polarised light unless otherwise specified.

10.3.2 DSC

Accurate transition temperatures and transitional enthalpies for the dimers were measured via a Mettler DSC822e differential scanning calorimeter, using an aluminium reference and indium standard. Approximately 1–5 mg of crystalline sample was placed in a 20 uL aluminium pan and then crimped closed. All materials were subjected to two heating & cooling runs in most cases at 10 °/min. Data was analysed in STARe software by Mettler (http://uk.mt.com).

10.3.3 XRD

The mesophase behaviour of some of the dimers was investigated by XRD. Generally this was used to investigate the nature of the smectic phases or to confirm the presence N_x phase. The sample was filled into glass capillary ($\emptyset = 20 \text{ mm}$) either as a fine powder or by capillary action and placed into the furnace perpendicular to both the beam-direction and the field. The magnetic field (1 T) is orthogonal to the beam direction. The beam was supplied by an CuK α source ($\lambda = 1.542 \text{ Å}$), with data collected by a MAR345 detector. The data was analysed with Datasqueeze (http://www.datasqueezesoftware.com) and the curves fitted with OriginPro (http://www.originlab.com/originpro) using Guassian or Lorentzian distribution functions to find the 2θ intensity maxima.

10.4 Electro-Optic Measurement Procedures

10.4.1 Cells

Two different types of glass cell were used in the electo-optic measurements. The first was a homogeneous anti-planar cell with a 5 µm cell gap, d. This cell was used for the birefringence measurements. The second type of cell was also homogeneous with a d = 3.6 µm but the rubbing direction on one surface was rotated 90° to the other. This twisted configuration was used in the transmission vs voltage/frequency measurements. Both cell were supplied by Instec Inc, US. Knowledge of the accurate cell gap was vital for the birefringence measurements and was found via the interference fringe method using UV-Vis spectroscopy.

A cell was placed into a holder within the UV instrument so that the glass surface is normal to the incident UV beam and absorbance was then measured across a spectrum of wavelengths. The interaction of the UV beam with the cell causes interference fringes to appear in the output. This effect is illustrated for an Instec 5 µm cell in Figure 10.1.



Figure 10.1. UV-Vis interference fringes from an Instec 5 µm homogeneous planar cell.

Using the data from the UV-Vis measurements an accurate cell gap was calculated with the following equation:

$$d = \frac{m\lambda_1\lambda_2}{\lambda_1 - \lambda_2}/2 \tag{10.1}$$

where λ_1 is the high wavelength and λ_2 is the low wavelength, *m* is the number of fringes between the two chosen wavelengths. The data from Figure 10.1 gives a cell gap of $d = 4.877 \,\mu\text{m}$.

10.4.2 Birefringence

Birefringence measurements carried out using the Berek compensator method, with a Nikon X compensator. A 3.6 µm planar cell was filled with sample via capillary action in the isotropic phase. With the set at sample at 45° to the polarisers for maximum transmission, the compensator dial was rotated clockwise until the dark fringe entered the center of the field of view where the dial reading was recorded. The compensator was rotated in the anticlockwise direction until the matching dark fringe was centred. This process was repeated three times and the averages used to calculate θ . Optical retardance (δ) was found using the calibration tables supplied by Nikon. Measurements were taken on cooling the sample from the isotropic phase. A green interference filter (Olympus IF 550) was used to generate monochromatic light, aiding identification of the dark fringe centres.

10.4.3 Voltage & Frequency Response

For the voltage and frequency response of the materials a homogeneous twisted cell was used. The cell was filled with the sample in the isotropic state by capillary action. Between crossed polarisers, with the sample in the nematic phase this type of cell normally bright. Both tested dimers are positive dielectrics (at 1 kHz) so reorient with the field on application of a voltage giving the dark state. A Wavetek function generator was used to generate an AC sine-wave field at the desired voltage and frequency. The max possible field strength able to be outputted was 10 V_{RMS} with a max frequency of 5 MHz. An photodiode was used to measure the transmission through the sample and data outputted to an oscilloscope. The oscilloscope also measured the voltage/frequency of the applied field. The filled cells were heated and held in the isotropic state for ~ 30 min before being cooled into the nematic phase and held at the selected temperature for ~ 30 min before taking measurements or applying voltages. The natural state of the nematic phase in the cell showed domains of opposite twist as shown in Figure 10.2 This occurred only prior to the application of a field across the cell, after only one twist state was exhibited.



Figure 10.2. Nematic phase with domains of opposite twist in a twisted planar cell.

Voltage response was measured by incrementally ramping a 1 kHz field from 0 V_{RMS} to 10 V_{RMS} transmission value were recorded at regular intervals. Approximate threshold voltages were determined observation of a colour change and decrease in brightness (seen through the ocular lens) combined with fall in the transmission recorded by the photodiode. The frequency response was measured in a similar way, except that the applied field used a fixed 10 V_{RMS} voltage and the frequency was ramped from 1 kHz to 5 MHz. At 1 kHz the field gives the dark state at a higher frequency the light state was achieved where the liquid crystal reorientates back to the twisted regime. As before, transmission values were recorded at regular intervals.

10.4.4 Switching Times

Switching times, were recorded using the oscilloscope. The turn-on process occurs on application of a voltage (t_0) causing the molecules reorientate from the planar twisted arrangement (light state) to align with the field in a more vertically aligned orientation (dark state). The switching time (t) was defined as the time taken for the transmission to go from 90% to %10, $(t = t_2 - t_1)$ as illustrated in Figure 10.3. The turn off times were measured in the same way, except the transmission rises from 10 % to 90 %. The same process was used to find the switch off times.



Figure 10.3. Illustration showing the calculation of switching time (t) from an oscilloscope.

The dual frequency switching times used the same measurement method. However, the turn-off process occurs on switching to the high frequency $(f_{\rm H})$ instead.

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