

The synthesis and analysis of polymers and small molecules for use in organic electronics

Samuel Jarvis Cryer

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I Declaration of Originality

All work presented within this thesis was performed by myself (unless stated otherwise) within the department of Chemistry and Physics at Imperial College London between October 2013 and June 2017. This was done under the supervision of Professor Iain McCulloch.

S. J Cryer June 2017

II Copyright Declaration

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III Contributions and Acknowledgements

The fabrication of devices discussed in this thesis was undertaken by Andrew Wadsworth at Imperial College London (OPV) and Mark Nikolka at Cambridge University (OFET) and I am very thankful for their time and effort in these endeavours.

The journey through this PhD has been a tough one with a personal breakdown in the middle being a monumental mountain to overcome; which I could not have done without the considerable help from my family, friends and supervisor. In particular, I will never be able to thank enough my parents Binny and Mike Cryer, Sophie, Richard and Michael O'Rourke, and Jenny, Robert, Grace and George Ripley who carried me through my darkest days with their unending love and support. I know this journey has been tough for them too! I would also like to thank my supervisor Iain McCulloch who has supported me both academically and personally through this PhD and always been there for me when I've needed his help – his guidance and management has taught me so much and has made me a better scientist and academic. This PhD has therefore not just taught me a vast amount academically, but also personally about myself and although painful at times, as a result has given me the skills to be truly happy in my life. And for that I could not be more appreciative.

Organic chemistry is a highly practical field and much like cooking, everyone has their own style. In particular, I must thank Bob Schroeder, Maud Jenart and Hugo Bronstein for their continuous patience in teaching me the art of chemistry through all of the tips, tricks and advice they gave me – “if you're doing it like in the text book, you're probably doing it wrong”. I would also like to thank Karl Thorley for his extended help in using the HPC and performing complex molecular modelling calculations and for always answering all of my questions. I have been so lucky to be surrounded by such great colleagues, many of whom have become extremely close friends. In particular, I have to thank Abby, Adam, Alex,

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Finally, I would like to thank the Centre for Plastic Electronics for awarding me the funding that has allowed me to pursue the last 4 years of research and all of the wonderful staff and students who I've met along the way.

IV Abstract

Organic Semiconducting materials (OSCs) are integral to the next generation of devices such as flexible screens and solar panels, thanks to their flexible, solution processable and synthetically cheap nature. Although the field of OSCs has moved forward rapidly in the last decade, further research must be conducted to improve performance and efficiencies so as to be competitive with current silicon technologies whilst opening up new markets.

One method of improving the current technology is through the chemical modification of these materials to tune their parameters whether this is optical, energetic or morphological. In this thesis, we report the complex synthesis of new thiazole based polymers for use in organic field effect transistors (OFETs) and organic photovoltaics (OPV) with exceptional planarity through a ‘conformational lock’ between the thiazole and thiophene units. Although these polymers performed poorly in OPV and OFET, their interesting properties give new insight into thiazole based polymers, whilst also showing a novel ring closure reaction previously unpublished.

This thesis also reports on the synthesis of new diketopyrrolopyrrole polymers with electron rich flanking units used to form strong push-pull hybridisation across the backbone to create low band gap, near-IR absorbing materials. The high molecular weight **pDTP-DPP-TT** behaved in a rod like manner due to a ‘hydrogen-bond’ bond-like’ interaction between the **DPP** core and the **DTP** flanking unit. This results in exceptionally high extinction coefficients – a prerequisite for high currents in OPV devices.

Finally, the thesis reports on the extension of the **XBR** family with the addition of two new non-fullerene acceptor materials **CBR** and **CBI**. The use of non-fullerene acceptors in OPV should not only heavily bring down the materials cost of devices, but also open up new absorption pathways to allow greater device efficiencies. This work looked into how

chemical modifications of the central core and flanking units can be used to tune the electronic energy levels, as well as the optoelectronic properties of the materials both individually and in devices.

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VI List of Publications

As a consequence of the projects I have been involved with during my PhD, both discussed herein and otherwise, the following publications have been produced:

Dithiopheneindeno[1,2-b]fluorene (TIF) Semiconducting Polymers with Very High-Mobility in Field-Effect Transistors. Chen, H.; Hurhangee, M.; Nikolka, M.; Zhang, W.; Kirkus, M.; Neophytou, M.; **Cryer, S. J.**; Harkin, D.; Hayoz, P.; Abdi-Jalebi, M.; McNeill, C. R.; Sirringhaus, H. and McCulloch, I.; *Advanced Materials*, Submitted June **2017**.

Synthesis of a Luminescent Arsole[2,3-d:5,4-d']bis(thiazole) Building Block and Comparison to Its Phosphole Analogue. Green, J. P.; **Cryer, S. J.**; Marafie, J.; White, A. J. P.; and Heeney, M.; *Organometallics*, Article ASAP June 5, **2017** – DOI: 10.1021/acs.organomet.7b00241

Non-Fullerene Electron Acceptors for Use in Organic Solar Cells. Nielsen, C. B.; Holliday, S.; Chen, H.-Y.; **Cryer, S. J.**; and McCulloch, I.; *Acc. Chem. Res.*, **2015**, 48 (11), 2803-2812. – DOI: 10.1021/acs.accounts.5b00199

Bis-lactam-based donor polymers for organic solar cells: Evolution by design (Conference Paper). Rumer, J. W.; Schroeder, B. C.; Nielsen, C. B.; Ashraf, R. S.; Beatrup, D.; Bronstein H.; **Cryer, S. J.**; Donaghey, J. E.; Holliday, S.; Hurhangee, M.; James, D.I.; Lim, S.; Meager, I.; Zhang, W.; and McCulloch, I.; *Thin Solid Films*, **2014**, 560, 82-85.

Manuscripts are currently being prepared for other work in this thesis for subsequent publication.

VII Abbreviations

AGC	Apollo Guidance Computer
BHJ	Bulk heterojunction
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
BT	Benzothiadiazole
Bu ₄ NPF ₆	Tetrabutylammonium hexafluorophosphate
CB	Chlorobenzene
CHCl ₃	Chloroform
CPDT	Cyclopenta[2,1-b:3,4-b']dithiophene
CS	Charge separation
CT	Charge transfer
CV	Cyclic voltammetry
Đ	Polydispersity index
D/A	Donor/acceptor
DCB	Dichlorobenzene
DCM	Dichloromethane
DFT	Density functional theory
DMSO	Dimethyl sulfoxide
DP	Degree of polymerisation
DPP	Diketopyrrolopyrrole
DSC	Differential scanning calorimetry
DTP	Dithienopyrrole
EA	Electron affinity
ECL	Effective conjugation length
EQE	External quantum efficiency
eV	Electron Volt
FF	Fill factor
GCMS	Gas chromatography mass spectrometry
GPC	Gel permeation chromatography
h	Hours
HF	Hartree Fock
HOMO	Highest occupied molecular orbital
IDT	Indacenodithiophene
IDTBR	Indacenodithiophene-benzothiadiazole-rhodanine
IP	Ionisation potential
I _{SD}	Source-drain current
ITO	Indium tin oxide

J _{SC}	Short circuit current
LDA	Lithium diisopropylamine
LUMO	Lowest unoccupied molecular orbital
MALDI-TOF	Matrix-assisted laser desorption/ionisation-time-of-flight
M _n	Number average molecular weight
M _w	Weight average molecular weight
<i>n</i> -BuLi	<i>n</i> -Butyl lithium
NBS	<i>N</i> -Bromosuccinimide
NFA	Non-fullerene acceptor
NMR	Nuclear magnetic resonance
OFET	Organic field effect transistor
OIDFBR	Octylindenofluorene-benzothiazdiazole-rhodanine
OLED	Organic light emitting diode
OPV	Organic photovoltaic
OSC	Organic semiconductor
P3HT	Poly (3-hexylthiophene)
PBTTT	Poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene)
PC[60]BM	Phenyl-C61-butyric acid methyl ester
PC[70]BM	Phenyl-C71-butyric acid methyl ester
PCE	Power conversion efficiency
Pd(OAc) ₂	Palladium acetate
Pd(PPh ₃) ₄	Tetrakis(triphenylphosphine)palladium(0)
Pd ₂ dba ₃	Tris(dibenzylideneacetone)dipalladium(0)
PEDOT:PSS	Poly(3,4-ethylenedioxy)thiophene/poly(styrene sulfonate)
PFO	Polyfluorene
PheDOT	3,4-phenylenedioxythiophene
PMMA	Poly(methyl methacrylate)
PPh ₃	Triphenylphosphine
PQT	Poly(5,5-bis-3-alkyl-2-thienyl-2,2-bithiophene)
RFID	Radio frequency identification
RT	Room temperature
T	Thiophene
TBAF	Tetrabutylammonium fluoride
TBT	Benzodithiophene
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMSCl	Trimethylsilyl chloride

TT	Thieno[3,2- <i>b</i>]thiophene
TzBTz	Benzodithiazole
UV-vis	Ultraviolet-visible
V_D	Drain voltage
V_G	Gate voltage
V_{OC}	Open circuit voltage
V_T	Threshold voltage
XRD	X-ray diffraction
δ	Chemical shift
ϵ	Extinction co-efficient
ϵ_0	Permittivity of free space
ϵ_r	Material dielectric constant
λ_{max}	Wavelength at the absorption maximum
μ	Mobility

“Flying is learning how to throw yourself at the ground and miss.”

Douglas Adams

Chapter 1

Introduction

1.1 Background

1.1.1 From wooden sticks to silicon chips – humanity’s progress

The epochs of human history can be defined by humanity’s use of materials. From the Stone Age, to the Bronze Age, to our modern day – the understanding and mastering of new materials has always heralded grand advances in technology and often new stages in human development. It is hard to argue that the current age has undoubtedly been that of the silicon transistor – since its invention in 1948 in Bell laboratories,¹ little under 80 years ago, our world has radically changed to one which is ruled by technology. A fascinating example of just how far we have come is to compare the computing power that was used in the Apollo Guidance Computer (AGC) to take man to the moon (Apollo 11 – 1969) to that of the iPhone 6, something millions of people carry around in their pockets every day. The iPhone has 130,000 more transistors, runs 80,800,000 times more instructions per second, and clocks 32,600 times faster than the AGC, which measured $60 \times 31 \times 15$ cm and weighed a whopping 32 kg. Theoretically, one iPhone 6 could guide 120 million Apollo rockets at the same time!

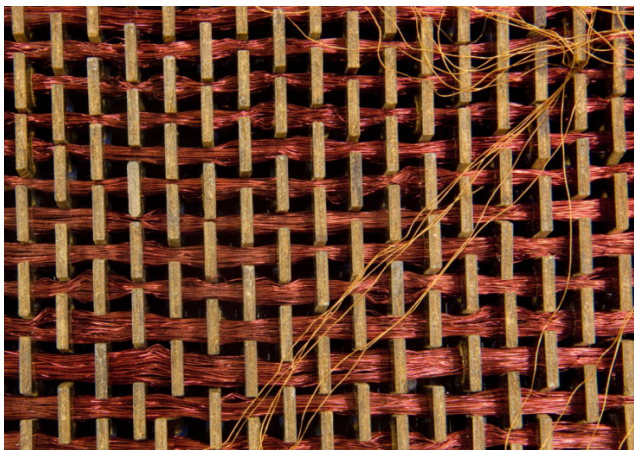


Figure 1.1 – The memory of the AGC required the 1s and 0s to be hand-woven through small magnets using copper wire (left). The iPhone 6 (right)

This unrelenting march of electronic progress has largely followed Gordon Moore’s prediction that the ‘number of transistors on a chip will double every two years’² – with

manufacturers squeezing more and more computing power into smaller and smaller spaces. With Moore himself stating in an interview in 2015 that we were hitting the ‘atomic limitations ... in the next couple of [chip] generations’³ – the end of Moore’s law, miniaturisation, and the breakneck pace of technological innovation is beginning to slow down. Therefore, new technologies need to be researched, developed, and implemented to take humanity into its next material age.

1.1.2 A plastic fantastic future

Along with silicon, another class of material that has reached ubiquity in the 20th Century is plastics. Although plastics such as vulcanised rubber and celluloid have been used since the early 19th Century, it was not until the early 1930s that the availability of cheap chemical precursors from the burgeoning oil industry allowed mass production to occur.

Bakelite (made cheaply from the condensation of phenol and formaldehyde) was one of the first synthetic plastics to be widely commercially available. It was heralded for its electrical non-conductivity and heat resistant properties, and was used in items as diverse as fashion items, consumer electronics, and toys (to name a few). Over the next decades, common plastics such as polystyrene, polyvinyl chloride, and nylon were invented, and with them a whole host of technological and cultural developments transpired. The swinging 60s would have been a lot less swinging without vinyl records and silicone implants! It was in the latter part of the century that the scientific molecular design of polymers gave rise to high-performance plastics for specific applications. HDPE plastics for high-pressure usage and hard-wearing polycarbonates, car headlamps, and interiors were but some of the materials with specific applications in mind when the chemists designed them. Nowadays plastics are used in almost every industry – from high-end composites for Boeing planes to biocompatible plastic shells for drug delivery in the body – a world without plastics would be a very different one indeed. If you ask any person on the street what a plastic is, they will

likely tell you it is often a flexible material that does not conduct electricity, making the discovery of Heeger et al.'s in 1977 all the more interesting and the start of the plastic electronic revolution.

1.1.3 Plastic electronics

The discovery Heeger et al. made in 1977 was that a thin film of doped polyacetylene could conduct electrical charge through the polymer.⁴ Since then, a veritable profusion of new conductive plastic materials have been developed, with the last decade seeing these highly specialised materials being designed for use in devices such as organic solar cells (OPVs), organic light emitting diodes (OLEDs), and organic field effect transistors (OFETs).

There are a multitude of advantages to making electronic devices out of plastic rather than traditional silicon methodologies, such as the ability of plastics to be flexible and processable from solution (e.g. ink formulations), allowing them to be used for roll-to-roll processing of electronic devices. The next generation of technological devices is often imagined to be flexible/roll-up screens and paper-thin electronics. This cannot be easily achieved with silicon transistors or current OLEDs due to the rigid, inflexible nature of the materials being used as both the light emitters and the transistor back-pane driving each pixel on the screen. Plastic electronics can challenge this limitation by fulfilling both the transistor OFET and OLED roles in a fully plastic screen. We are already seeing curved screens in Samsung devices using polymer displays, and PlasticLogic have prototyped an RGB, flexible e-ink display using this technology.⁵

Another area of application for plastic electronics is that of organic photovoltaics (OPV) – using organic materials to convert photons from the sun into electrical charge which can be used or stored. Anthropogenic climate change is a fact, and one that humanity has to deal

with fast through the reduction of burning fossil fuels and the subsequent diversification into multiple sources of renewable energy generation. Solar will undoubtedly play a great role.

The majority of photovoltaic panels currently being manufactured are made from silicon. Even with the great abundance of silicon on our planet, the processing conditions required to manufacture a grade suitable for modern electronics (>99.9% atomic purity) means the manufacturing cost in terms of both money and energy is extremely large. To add to this, the cost of building a new factory capable of processing silicon materials can run upwards of \$1 billion.

Organic photovoltaics or ‘plastic solar cells’ offer an alternative to crystalline silicon by reducing the cost of production in terms of both money and energy. They can achieve this by being manufactured via a printed roll-to-roll process on high volumes and large scales. OPV efficiencies have been steadily increasing over the last decade thanks to multi-disciplinary research across many countries, and stable devices are now consistently hitting efficiencies of over 10%.^{6,7} Polymer-based OPVs are also the only solar material to outperform silicon in low lighting and indoor spaces, opening up areas of energy harvesting that were previously inaccessible. This is due to the improved ability of conductive polymers to absorb near the infra-red region (compared with silicon, which absorbs primarily in the UV), making OPV more useful in predominately cloudy countries such as the UK.

Plastic electronics therefore offers an abundance of technological advances that are surely not so far around the corner. The prospect of flexible, energy efficient screens powered by the roll-up solar panel in our bag is being made an ever-closer reality by research laboratories around the world, and a research community I have been a proud part of during my PhD. The rest of this introduction will discuss what these plastic materials are made of, how they operate optically and electrically, and how these materials are defined and characterised.

1.2 Polymer chemistry⁸

Plastics are more technically known as polymers, and are comprised of a single unit (a monomer), repeated multiple times to form a macromolecular structure. The term polymer comes from the ancient greek ‘polús’ (πολύς) meaning ‘many’ and ‘méros’ (μέρος) meaning ‘parts’ and is a succinct description of the material. A simple example is that is an alkane series comprised of increasing numbers of $-\text{CH}_2-$ blocks.

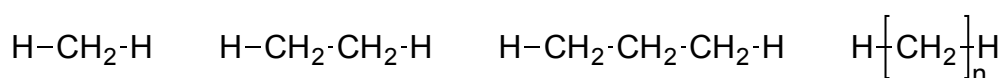


Figure 1.2 – From left to right: methane, ethane, propane, and polyethylene

Methane, ethane, and propane are all gases at room temperature and pressure, but as you increase the number of repeat units, the properties start to change drastically. Once ‘n’ (Figure 1.2) is higher than ~ 1000 molecules, the material becomes a tough plastic solid as the long chains start to entangle, with increasing Van der Waals forces between strands. The material properties a polymer displays, such as its mechanical strength, plasticity, thermal stability, or elasticity are highly dependent on both what the monomer unit is comprised of and the length of the chain itself. Due to the synthetic processes involved, the chain lengths are often polydisperse, with a bell curve distribution.

1.2.1 Polymer definitions^{9,10}

The width of the polymer length distribution depends on the synthetic process involved, as described in Section 1.2.2, therefore a number of terms can be used to approximate, compare and analyse these materials. The Gaussian distribution of the molecular weights of a polymer is quantified by the values M_n (number average molecular weight) and M_w (weight average molecular weight), where N_i is the number of polymer chains.

$$M_n = \frac{\sum N_i M_i^2}{\sum N_i} \quad (1.1)$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (1.2)$$

$$\mathbb{D} = \frac{M_w}{M_n} \geq 1 \quad (1.3)$$

The polydispersity index ($\mathbb{D}$) quantifies the molecular mass distribution between the chains around a central point by taking the ratio of M_w to M_n (Equation 1.3).

As the distribution across the bell curve becomes smaller, M_w and M_n draw closer together, causing $\mathbb{D}$ to approach unity. A value of 1 would infer every single polymer chain is exactly the same length (and therefore mass).¹¹ Another methodology for understanding the extent to which polymerisation has occurred is the degree of polymerisation (DP). This is a representation of the average number of monomer units within a given chain, and is given by:

$$\mathbf{DP} = \frac{[A]_0}{[A]_t} = \frac{M}{m_r} \quad (1.4)$$

Where $[A]_0$ is the initial concentration of monomers at $t = 0$ and $[A]_t$ is the concentration of monomers at time $t > 0$. M can be M_w or M_n (giving DP_w or DP_n , respectively), while m_r is the molecular mass of the monomer unit.

1.2.2 Polymer synthesis – chain and step growth

The two main polymerisation mechanisms are step growth and chain growth – both of which have advantages and disadvantages in terms of the resultant material properties and general ease of synthesis. Although some key polymers in the plastic electronics world are synthesised via a chain growth type mechanism (such as P3HT), the majority use palladium-catalysed step growth polymerisation of two monomer species. Unlike chain growth mechanisms, there are no intrinsic initiation or termination steps, and past the point $t = 0$, very little monomer is present in the reaction mixture.

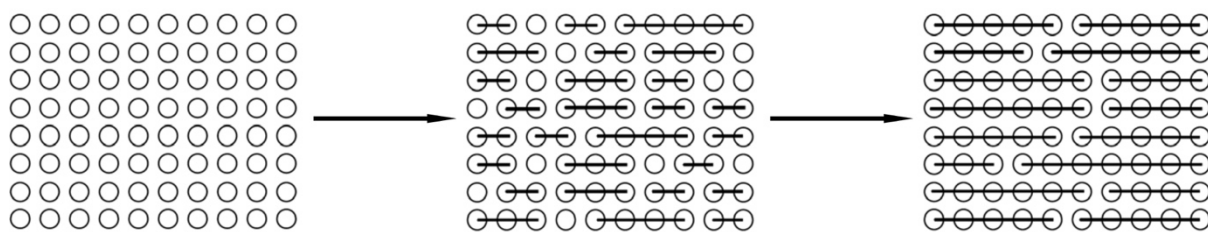
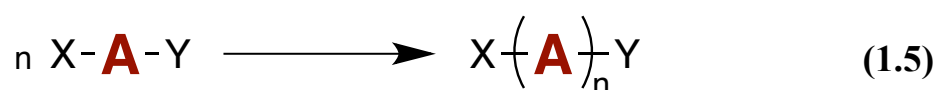


Figure 1.3 – Process of step-wise polymerisation from a) monomers, b) monomers to pentamers, c) trimers to septamers

To achieve high molecular weights using a step-growth mechanism, the percentage conversion and therefore the degree of polymerisation must be high (>99.9%). This is simple when using a single bi-functional monomer where the ratio of X and Y are inherently equal:



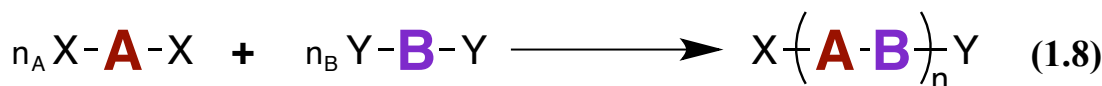
It was W. H. Carothers who first proposed a link between the number average degree of polymerisation (DP_n) and a quantity ‘p’ – the degree of conversion. This can be represented as the number of unreacted molecules at time $t > 0$ (N_t) and the initial number of molecules at $t=0$ (N_0).

$$p = \frac{N_0 - N_t}{N_0} \quad (1.6)$$

Rearranging for N_t and subbing into equation 1.4 where $[A]_0 = N_0$, we can find an expression for the number average degree of polymerisation giving Carothers’ equation:

$$DP_n = \frac{1}{1-p} \quad (1.7)$$

For a single monomer system such as the one shown in equation 1.5, it seems obvious that the degree of polymerisation is directly proportional to the negative inverse of the degree of conversion. However, the majority of step-growth polymerisations used in plastic electronics and this thesis use a co-monomer system of A and B:



In the situation above, the stoichiometric ratio of monomers A and B can be given by

$r = n_A/n_B$, which when subbing into Carothers' equation for p_A and p_B gives the degree of polymerisation for step-growth polymers with two co-monomers.

$$DP_n = \frac{1+r}{1+r-2rp} \quad (1.9)$$

The results of this equation are as follows – if the molar ratio (r) of the two monomers A and B is not kept as close to unity as possible, then high molecular weights cannot be achieved.

As r approaches unity, equation 1.9 cancels down to equation 1.7.

The graph below (Figure 1.4) shows an example of the effect that a small mismatch in the stoichiometry of two monomers can have. As the degree of conversion approaches unity, the degree of polymerisation (i.e., the molecular weight of the polymer) increases. As the ratio of monomer A to monomer B increases from 0.99 to 0.999, we see a huge increase in the potential DP achieved in the reaction. This has great consequences in the laboratory, as a slightly impure monomer can throw off the stoichiometry, having a huge effect on the molecular weights achieved. The importance of this is discussed in the next section.

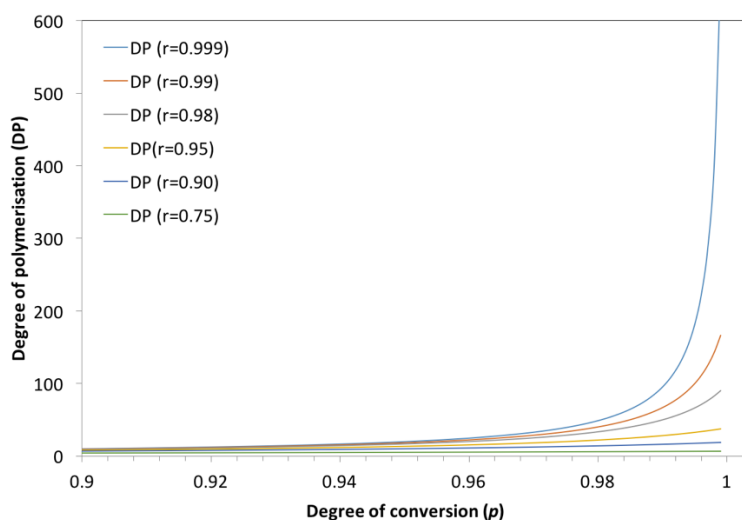


Figure 1.4 – A graph showing the decrease in DP as p approaches unity for varying r

1.2.3 Predictable polymer properties

Polymers possess a number of properties that make them useful in plastic electronic applications, such as high mechanical strength, elasticity, plasticity, thermal stability, and conductivity. Particularly useful is their potentially viscous nature, which allows them to be formulated into inks and used in hybrid ink-jet or gravure printing.^{12,13} The importance of having higher molecular weights and being in the polymer regime (as opposed to oligomer or small molecule) is illustrated in Figure 1.5.

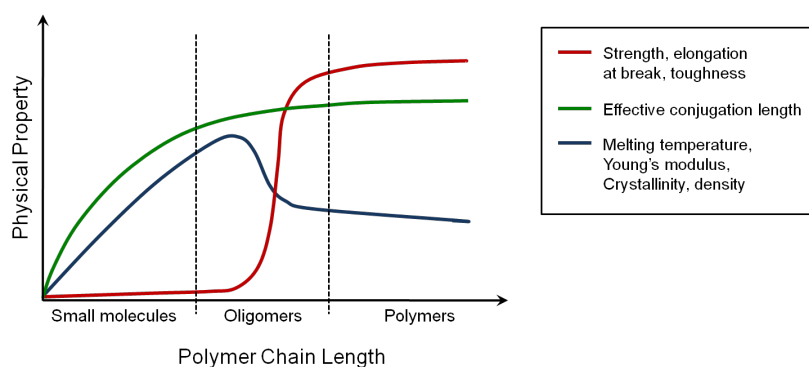


Figure 1.5 – Degree of polymerisation vs. physical properties

The graph above is a general representation of how the physical properties of a conjugated material change as length is increased from individual monomers to a long chained polymer. As the polymer chain length increases, oligomers are formed, where the properties are no longer the same as the monomer, but are also highly unpredictable and can change simply by the addition of another monomer unit. Once the degree of polymerisation increases above a certain length (different for each polymer), these physical properties change very little with the addition of another monomer unit and are therefore more consistent and predictable. Being within this ‘polymer regime’ is important from both a processing point of view and performance. If one only just reaches into the polymer regime in terms of chain length, and the polydispersity is large, then you could effectively be doping your polymer with a number of smaller oligomers, drastically affecting the packing between polymer chains (an extremely important property in plastic electronics). There is also gathering evidence that larger

molecular weights have been proven to increase efficiency in a number of OPV and OFET devices, suggesting that being within this polymer regime is also important for device performance.^{14,15}

A-B co-polymerisation is therefore inherently challenging, as an almost perfect stoichiometry of reagents is required to achieve longer chain lengths. Although difficult, the benefit of a two-monomer system is that it opens up a plethora of synthetic systems that would be prohibitively harder to achieve in a single monomer system. The types of polymers and their benefits are discussed further in Section 1.6.

1.3 Conducting polymer fundamentals

A semiconductor is a material in which charge carriers will form when sufficient potential is applied to overcome the intrinsic barrier or ‘band gap’ of the material. Once a potential that approaches the band gap is applied, a large population of charge carriers is created. This band gap is what defines a semiconductor, and is typically between 0.7-3 eV in energy (above $k_B T = 0.025$ eV at room temperature). In a semi-metal silicon semiconductor, the band gap is controlled through doping with impurities such as electron-withdrawing boron or electron-donating phosphorous to give *p*-type or *n*-type materials, respectively. Conjugated organic materials develop semiconductivity by a different mechanism through their overlapping atomic orbitals as explained further in Section 1.3.1.

1.3.1 The p_z band¹⁶

As organic materials, the majority of the atoms in polymers are covalently bonded carbon atoms – therefore, the bonding in carbon is of high importance. A carbon atom comprises of s -, p_x -, p_y -, and p_z -orbitals surrounding a nucleus. In a structure like diamond, the atomic orbitals hybridise to form four sp^3 hybridised electronic orbitals that assume a tetrahedral geometry about the nucleus with the ability to form 4 covalent bonds. The orbitals of bonded

atoms overlap and combine to form a lower energy σ -bonding orbital and a higher energy σ^* - (or anti-) bonding orbital. The two electrons sit in the σ -bonding orbital and form what is known as a covalent bond.

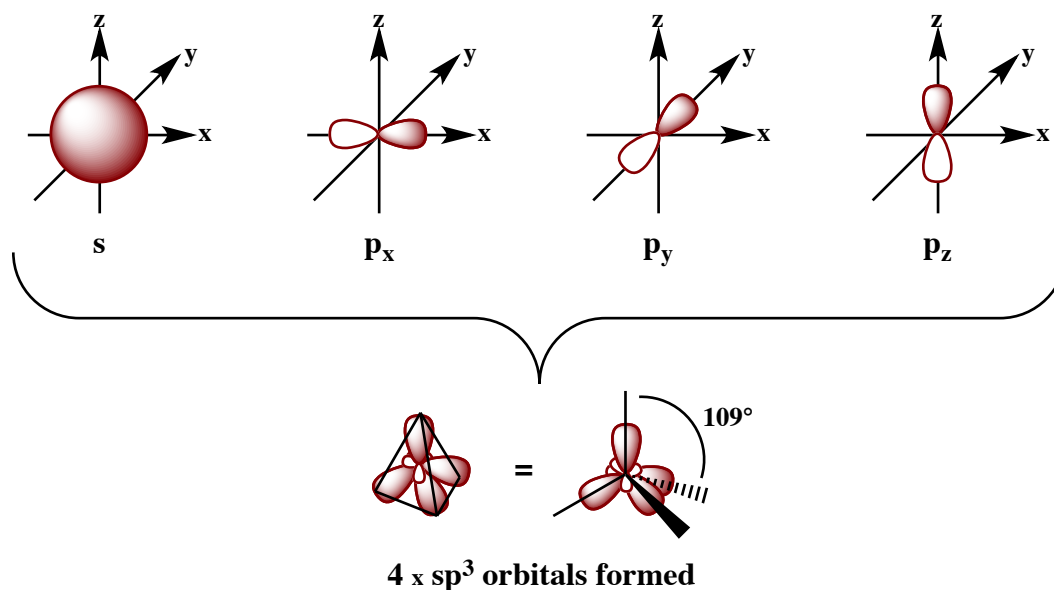


Figure 1.6 – Orbital hybridisation gives four sp^3 orbitals, which can overlap with other orbitals to form sigma bonds

If we take ethylene gas, each carbon molecule is only ‘attached’ to three atoms – this is because only three of the orbitals in each carbon have hybridised to form three sp^2 orbitals, leaving an unhybridised but occupied p_z orbital that is in the z -plane. The two p_z orbitals in ethylene (one on each carbon) then proceed to exhibit an electronic wavefunction overlap and can form higher and lower energy orbitals known as the π -bonding (containing two electrons) and π^* -anti-bonding orbitals (devoid of electrons), respectively. Whereas the σ -bond is a direct overlap of orbitals, the π -bond overlap is not, and is therefore weaker in comparison. The electrons within the π -bond are referred to as being ‘delocalised’ between the orbitals (Figure 1.7).

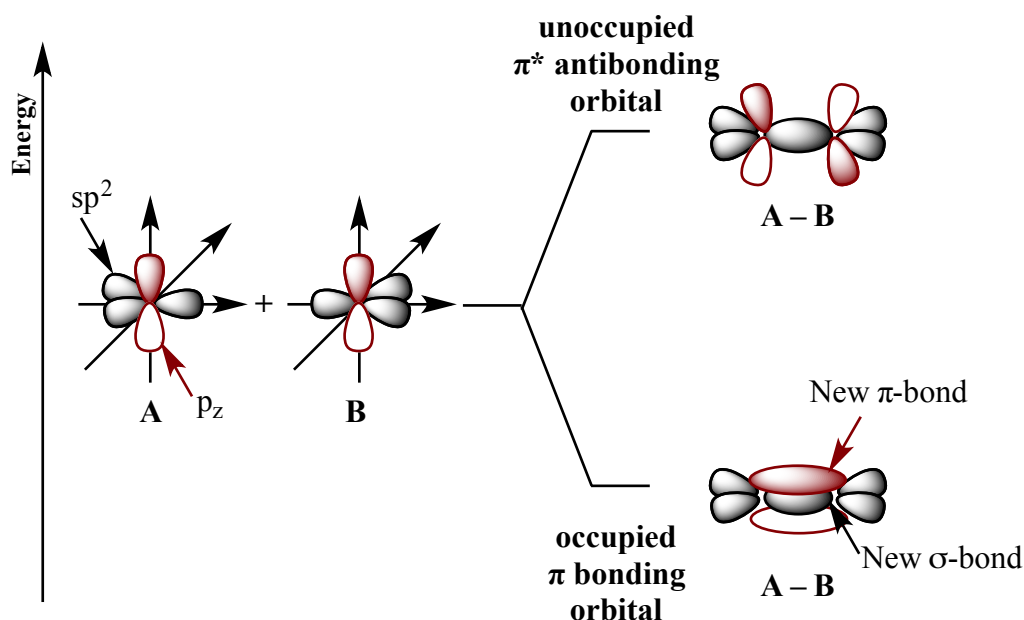


Figure 1.7 – Linear combination of two sp^2 orbitals to form a new σ -bond and two p_z orbitals to form a new π -bond

If two ethylene molecules are attached by another sigma bond to form 1,3-butadiene, there are now four p_z orbitals across the molecule, resulting in increased orbital hybridisation compared with ethylene, and additional filled π -bonding and empty π^* -anti-bonding orbitals. This change in energy of the frontier orbitals means the highest occupied molecular orbital (HOMO) increases in energy and the lowest unoccupied molecule orbital (LUMO) decreases in energy. This is a statistical function of the combination of bonding and anti-bonding interactions.

On addition of further ethylene molecules and therefore p_z orbitals, the linear combination of these orbitals results in the energy gap between the HOMO and LUMO decreasing as the HOMO is destabilised and the LUMO is stabilised – continuing until the band gap is small enough to give the material semi-conducting properties (Figure 1.8). In summary, through the linear combination of atomic orbitals an insulating molecule with a band gap of 7.6 eV (ethylene) has been reduced to below 3.0 eV (polyacetylene = 1.5 eV), resulting in a semiconducting polymer.

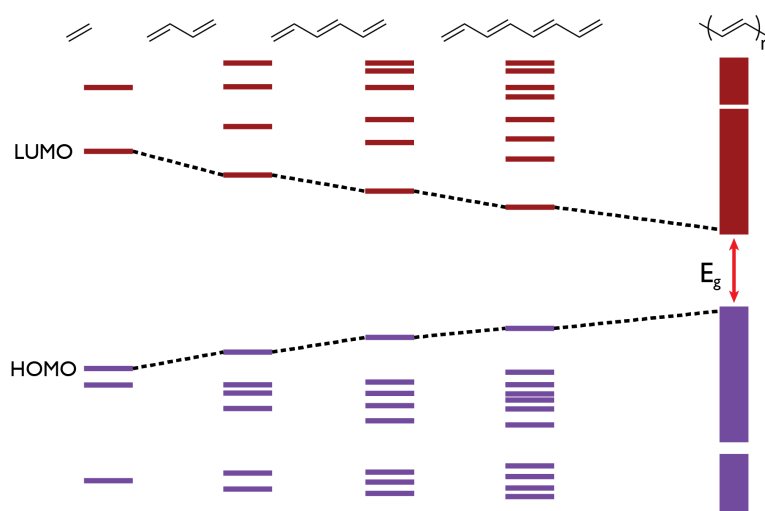


Figure 1.8 – Orbital hybridisation/overlap resulting in decreasing band gap from ethylene to polyacetylene, giving rise to semiconducting behaviour

This system of continuous connected p_z orbitals with delocalised electrons is often referred to as a ‘conjugated system’. As stated previously, as the conjugation length increases (i.e., more p_z orbitals are added) the band gap between the HOMO and LUMO gets smaller, but this decrease only continues until a certain chain length, after which increasing the chain length gives no further decrease to the band gap. Defined as the ‘effective conjugation length’ (ECL),¹⁷ it is usually approximated to be 10-15 monomers in length (although this is highly monomer dependent).¹⁸

As seen in Figure 1.8, the geometry and overlap of these p_z molecular orbitals is crucial to achieving semiconducting properties within a conjugated polymer. If a break in the conjugation occurs due to a twist along the backbone or a defect has occurred in the synthesis, then the ECL and therefore the band gap can be greatly affected, altering material performance.

1.3.2 Defining charge

During charge injection in OFETs and OLEDs and charge generation and extraction in OPV, the movement of charge through the bulk of a polymer is defined by the frontier orbital

energy levels within it. Therefore, defining how these frontier orbitals are derived and how a charge interacts with them is of importance as it allows the prediction of a polymer's optical and electrical properties, which can be tuned to enhance device performance. Fundamentally, the HOMO level can be approximated from the 'ionisation potential' (IP), i.e., the energy required to remove an electron from a neutral molecule to the vacuum level to form a positive ion. On the other hand, the LUMO level can be approximated from the 'electron affinity' (EA), i.e., the energy required to add an electron to a neutral molecule from vacuum level to form a negative ion. Therefore, the fundamental energy (E_{fund}) gap between the HOMO and LUMO can be approximated by:¹⁹

$$E_{\text{fund}} = IP - EA \quad (1.10)$$

A charged species formed on the addition or removal of an electron is known as a polaron,²⁰ which is defined by the change in the configuration of the molecular lattice that occurs around the charge in order to redistribute it and minimise the overall energy of the molecules. This new energy level appears within the E_{fund} gap. It is then this combined entity of charge and lattice distortion (a polaron) that can move through the polymer material.

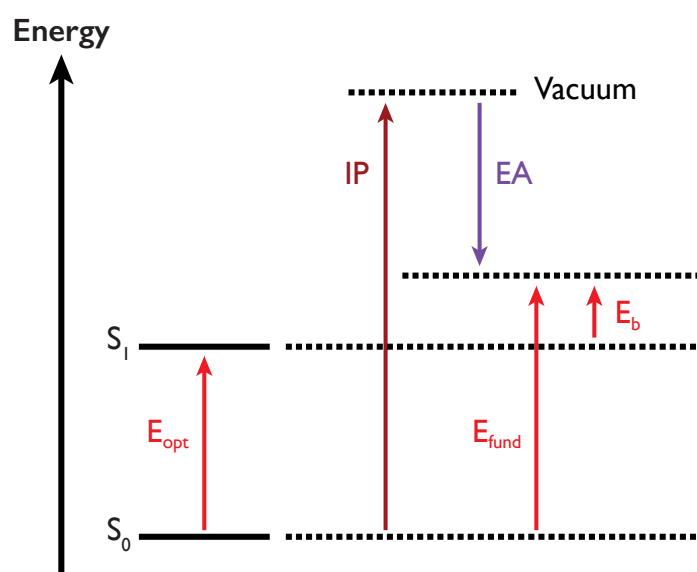


Figure 1.9 – Definitions of fundamental and optical energy levels¹⁹

The optical band gap (E_{opt}) is defined by the energy of the lowest electron transition accessible (S_0 to S_1) via the absorption of a single photon of light to form an exciton (an electron/hole polaron pair). Generally, E_{fund} is greater than E_{opt} because the electron/hole pair is electrostatically bound to one another by the binding energy (E_b).

$$E_{\text{fund}} = E_{\text{opt}} + E_b \quad (1.11)$$

Like in a polaron, the formation of an exciton induces lattice distortions to stabilise the energy, and therefore an exciton can be referred to as a ‘polaron pair’. This stabilisation along with the binding energy means the energy levels of the exciton both sit well within the fundamental energy gap.

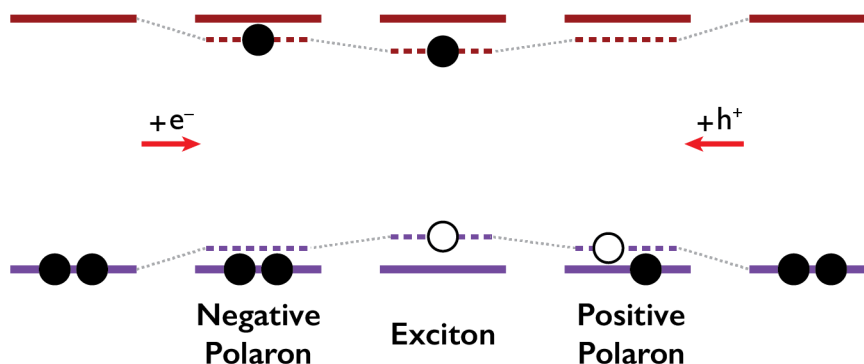


Figure 1.10 – Difference in energy between electron and hole polarons, and an exciton

The transport gap ($E_{\text{transport}}$) or band gap represents the minimum energy required to create a positive charge carrier somewhere in the material (IP energy) minus the energy gained by adding a negative charge carrier (EA energy), and is theoretically the same as E_{fund} . In practice, the strong polarisation effect of a charge being adjacent to π -conjugated molecules stabilises the cationic and anionic states, often resulting in the transport gap being smaller in energy than the fundamental gap (E_{fund}). For this thesis though, we will make the assumption that $E_{\text{transport}} = E_{\text{fund}}$.

1.3.3 Charge transport¹⁶

The movement of electrons and holes within polymers is fundamentally important to all organic electronic devices, and is characterised by the term ‘mobility’. Mobility is defined as the velocity of the charge carrier (v) within a specified field (F), and is characteristically used to benchmark the performance of organic electronic materials.²¹

$$\mu = \frac{v}{F} \quad (1.12)$$

This movement of charges in an organic semiconductor can occur via two different mechanisms: high mobility intrachain transport and low mobility hopping (inter- and intrachain).

High mobility intrachain transport is band-like in nature, as would be expected for a conjugated polymer with a delocalised orbital across its backbone. Consider a charge on a conjugated polymer within a device – this charge has a wavefunction that is affected by the field applied across the device, and therefore this charge travels along the conjugated chain of the polymer in the direction of the field. However, it is debateable as to how effective this type of intrachain transport is in polymeric materials. For example, if the polymer backbone is aligned perpendicular to the field, this transport will not occur. If there is a break in conjugation due to twisting/defects in the polymer back-bone, this transport will not occur. As the temperature increases, lattice vibrations (phonons) will scatter polarons, thereby reducing this type of transport. This is often where a synthetic chemist or device physicist can design materials and processes that increase the likelihood of this type of intrachain transport occurring (see section 1.6).

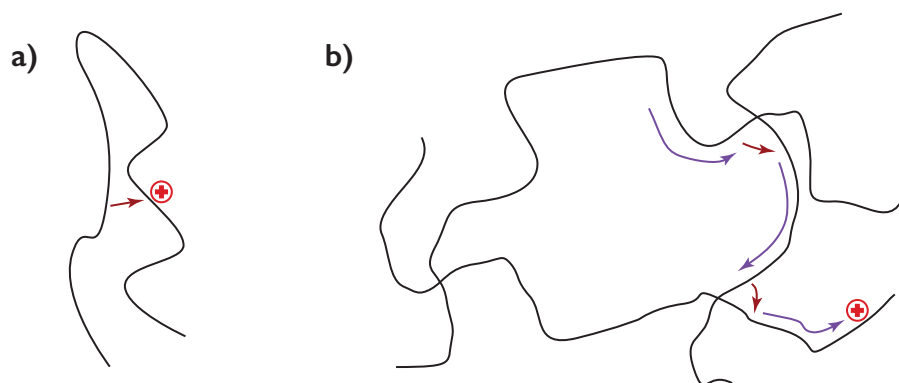


Figure 1.11 – a) Intrachain hopping on single chain; b) Hopping mechanisms across multiple chains. Red = Hopping transport, Purple = Intrachain ‘band-like’ transport

The second charge transport mechanism is hopping, or ‘thermally activated tunnelling’ – the quantum mechanical tunnelling process by which charge carriers can ‘jump’ or ‘hop’ from one position to another. Although this is usually an interchain effect, intrachain hopping can also occur when a chain crosses over itself, or between areas of broken conjugation (Figure 1.11). Hopping mobilities are lower than previously discussed band-like transport mobilities, partially due to the activation energy required for each hop to take place.

The more organised a system is, the more delocalisation the wavefunction can undergo, resulting in more band-like transport and higher mobilities. As a system becomes more disordered, charges become more localised, resulting in a reduction in band-like transport and a regime where the mobility is dictated by the hopping mechanism. As the system becomes even more disordered, hopping transport reduces further. Therefore, systems with many grain boundaries, impurities, breaks in conjugation, and high-energy traps (greater than $k_B T$) will tend to have poorer performance.

Whether for OPV or OFET, it is clear the morphology of the polymer, how it stacks, and the long and short range order within it are strongly linked to charge transfer and ultimately its performance. The majority of polymers used for OPV and OFET are therefore highly structured ‘semi-crystalline’ materials with conjugated planar backbones to facilitate and

promote π - π -stacking between the chains. This long-range order helps to not only promote band-transport by increasing conjugation length, but also to bring the chains closer together (π - π -stacking), improving hopping performance as well.²²

To further understand the importance of charges and their transport through organic electronic devices, it is pertinent to explore them further in terms of OPV and OFET devices.

1.4 OPV devices

OPV concerns a number of different classes of device archetypes, including dye-sensitised solar cells (DSSCs), small molecular and polymer heterojunction solar cells, and more recently, perovskites.^{23,24} All of these archetypes comprise of an active organic material which is solution processable and performs the primary job of photon absorption and electron excitation. The OPV part of this thesis comprises of work solely in relation to polymer bulk heterojunction (BHJ) solar cells.

1.4.1 General operating principles

A polymer OPV is comprised of at least two organic materials, a ‘donor’ and ‘acceptor’, sandwiched between an anode and cathode. As discussed in Section 1.3.2, when the donor absorbs a photon of light greater than E_{opt} , an electron is promoted from the HOMO to the LUMO to form an electron/hole pair (exciton), which is coulombically bound by an energy of E_b . In inorganic semiconductors, the dielectric of the background lattice is high enough that E_b is screened and becomes effectively negligible ($E_b \ll k_B T$), resulting in free charges on excitation. In organic semiconductors, the E_b is no longer negligible due to the low dielectric of the material, and therefore a heterojunction architecture is required in order to split the charges and transport them to the electrodes. A heterojunction device consists of an electron-rich ‘donor’ material and an electron-poor ‘acceptor’ material. Excitation in the donor results in a bound exciton which can undergo charge transport (intrachain ‘band-like’ or hopping

transport) for approximately 10 nm before geminate recombination will occur.²⁵ Therefore, an acceptor material is required with a lower LUMO level so that electron transfer occurs to a ‘charge-transfer’ (CT) state across the donor/acceptor interface (Figure 1.12 – Step 3). From here, further electron transfer into a ‘charge-separated’ (CS) state results in a free electron in the acceptor LUMO and a free hole in the donor HOMO (Figure 1.12 – Step 4). Once a CS state has been achieved, the hole and electron polarons are driven to the anode and cathode respectively due to the electric field across the device, where they can be stored or made to do work.

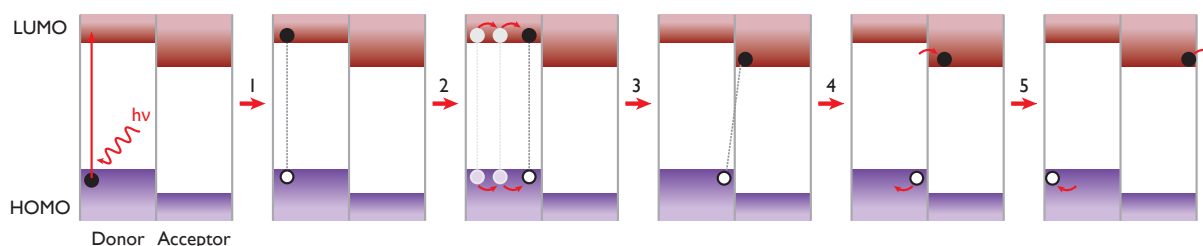


Figure 1.12 – Absorption of a photon leads to: 1) exciton generation, 2) exciton movement, 3) charge transfer, 4) charge separation, and 5) conduction

Although an offset between the donor and acceptor LUMOs is required, it is a common misconception that there needs to be a LUMO/LUMO offset (ΔE_{CS}) greater than the E_b for charge separation to occur,^{19,26} often quoted as >0.3 eV. Although historically this has been the observed phenomenon and it has been quoted as necessary to achieve high photocurrents, there is growing evidence that this is not the case, with Baran et al. recently showing a donor/acceptor blend achieving power conversion efficiencies of 7.8% with a ΔE_{CS} of 0.05 eV²⁷ and 9.95% with a ΔE_{CS} of 0.2 eV. Although it is clear that some degree of ΔE_{CS} is required for exciton transfer to the CT state to be favourable, the exact magnitude of this offset is still debatable.²⁶

Historically, the most pervasive acceptor materials used have been the fullerene derivatives PC[60]BM and PC[70]BM (Phenyl-C61/71-butyric acid methyl ester), although newer ‘non-

fullerene' small molecules are becoming more common and achieving comparable efficiencies. Matching the energy levels of the donor polymer to the acceptor material is crucial, as maximising the number of charge-separated states is vital for high efficiency devices.

1.4.2 Device architecture

The first polymer-fullerene devices featured a bilayer device architecture with a layer of donor polymer followed by a layer of fullerene acceptor sandwiched between electrodes. The thickness of each active layer was approximately 100-200 nm to allow absorption of sufficient light, and as excitons tend to undergo geminal recombination after only 10 nm; the majority of charge carriers in such bi-layer devices were recombining before they could enter a charge separated state.

Blending of the two active layers into a bulk heterojunction (BHJ) device creates a bicontinuous intermixed network of donor/acceptor (D/A) material with domain sizes on similar length scales to the exciton diffusion length. The act of blending also increases the surface area of the D/A interface, thereby increasing the probability of exciton separation before exciton relaxation, whilst also increasing the probability of bimolecular recombination of CS states.

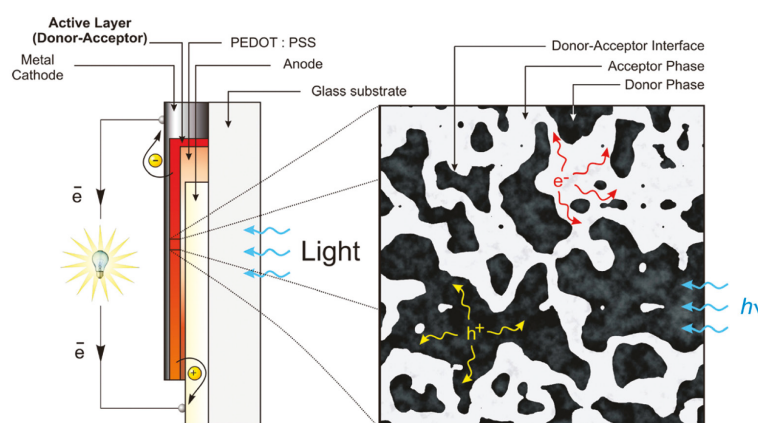


Figure 1.13 – Device architecture of a bulk-heterojunction device.

*Reproduced with permission*²⁸

Optimisation during the fabrication of a BHJ device is an important step, as small changes in fabrication parameters can extensively change the morphology, and hence the performance.

The use of additives,²⁹ the donor:acceptor ratio, solvent systems used, film thicknesses, annealing temperature,³⁰ and solution concentrations are just some of the tools a device chemist has at their disposal to optimise their devices and boost performance.

1.4.3 Device physics – judging performance

In order to have to be able to judge one set of materials or architectures against another, a set of standard measurements have been agreed upon for device measurement and assessment. A single OPV device must therefore be measured at a temperature of 298 K, under 1 kW/m^2 of irradiance using the air mass 1.5 (AM1.5) light spectrum. The AM1.5 spectrum corresponds to the solar radiation observed on passing through 1.5 times the air mass equivalent to that of the optical path length at the tropics at sea level (Figure 1.14).

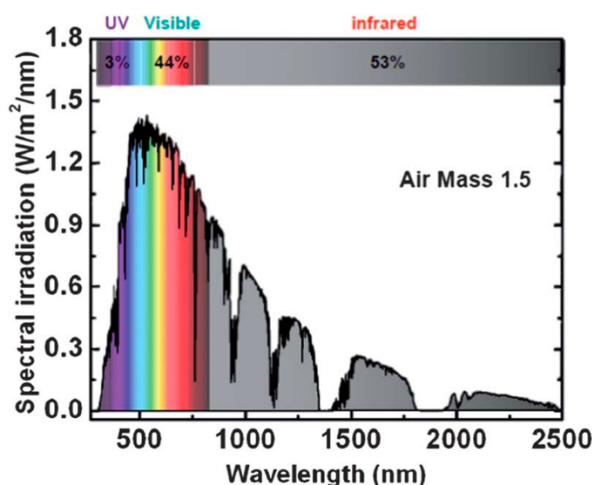


Figure 1.14 – Distribution of the AM1.5 spectrum³¹

A number of terms must be defined and understood for direct device comparison to be meaningful: these are the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF), as seen in Figure 1.15.

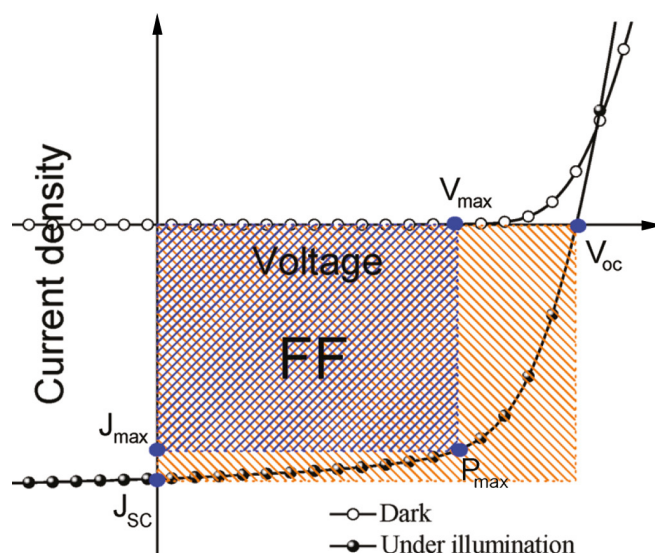


Figure 1.15 – Current density vs. voltage graph for a common solar cell²⁸

If the terminals of an OPV cell are connected into a short circuit, the Fermi levels of the electrodes equalise (therefore no voltage difference is observed), causing current to flow through the device. This current (in relation to the size of the device) is given by the charge density, and the current at short-circuit is the maximum current that can be extracted from our device, hence J_{SC} . Under AM1.5 illumination, the incident photons at short circuit are creating enough current to counter the potential difference created by the two electrodes. J_{SC} is affected by factors such as domain size, connectivity and molecular packing, absorption spectra, extinction coefficient, and the exciton diffusion length.²⁸ The optical absorption of a BHJ device has a large influence on J_{SC} – in a polymer-fullerene blend, the absorption is primarily done by the polymer (due to the poor light absorption properties of fullerenes) and is therefore directly related to the band gap of the polymer. The more the band gap overlaps with the AM1.5, the more incident photons the donor polymer can absorb, increasing the J_{SC} .

If the terminals of our device are not connected, we have an open-circuit where there is no fermi-level equalisation, and therefore a maximum potential exists across the device. In the absence of any current, this is the maximum voltage possible, known as the V_{OC} . The V_{OC}

can be approximated by the distance between the HOMO of the donor and the LUMO of the acceptor (Figure 1.16).

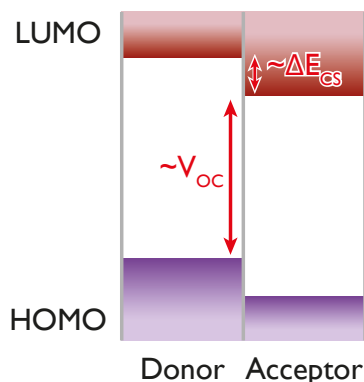


Figure 1.16 – Diagram showing approximation of the V_{OC}

Exciton separation relies on the donor LUMO being greater than the acceptor LUMO (Section 1.4.1), and therefore the donor LUMO must be above this level for CT/CS to occur. Because of this, there is a trade-off in a polymer/fullerene device of increasing the V_{OC} (lowering the polymer HOMO) and decreasing the overlap with the AM1.5 (increasing the polymer band gap and reducing J_{SC}), or vice-versa. Therefore, it can be seen that careful synthetic design of the polymer HOMO and LUMO levels is required to maximise the power output of any OPV device.

The fill factor (FF) is a measure of the efficiency at which current is extracted from the device, and is calculated by looking at the current density (J_{max}) and voltage (V_{max}) at the maximum power point (P_{max}), as shown in Figure 1.15 (blue hashed square vs. orange hashed square). It can be calculated using Equation 1.13.

$$FF = \frac{J_{max} \cdot V_{max}}{J_{SC} \cdot V_{OC}} \quad (1.13)$$

Ideally, the FF would be 100%, but as the voltage increases from 0 V, there tends to be a decrease in current density as charge extraction becomes less efficient, decreasing J_{SC} . The

power conversion efficiency (PCE) of a device is given by Equation 1.14, where P_{inc} is the incident light power on the device.

$$PCE = \frac{P_{max}}{P_{inc}} = \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_{inc}} \quad (1.14)$$

In order to achieve the maximum power output (P_{max}), the device must be run in forward bias mode, which means the device must consume some power in order to operate at maximum efficiency.

Another important parameter of an OPV that is easier to measure experimentally is the external quantum efficiency (EQE) – Equation 1.15. This is the relationship between the number of incident photons at a particular wavelength and the number of electrons generated under short circuit conditions. For any photon with an energy less than the E_{opt} of a donor polymer, the EQE would be 0%. Conversely, an EQE of 100% for a particular wavelength would imply that each photon of light had resulted in a charge carrier being collected.

$$EQE (\%) = \frac{1240 \cdot J_{sc}}{\lambda \cdot P_{inc}} \quad (1.15)$$

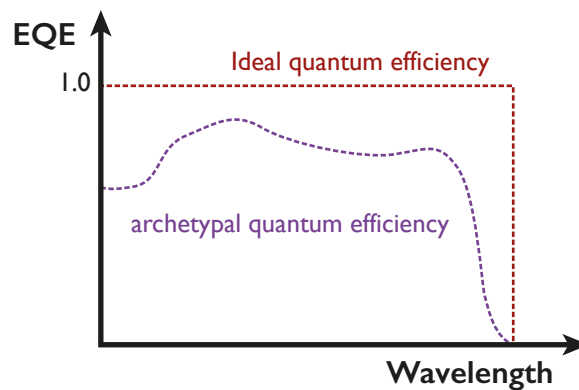


Figure 1.17 – Comparison between the ideal quantum efficiency curve and an archetypal example

1.4.4 Non-fullerene acceptors

The majority of research into donor/acceptor polymer OPV devices has focused on using PCBM derivatives as the acceptor materials. Their perceived advantages are many: they have

delocalised LUMOs across their large surface area, helping to accept and transport electrons; high electron mobilities; the ability to undergo multiple reversible electrochemical reductions; high dielectric constants;³² and finally their morphological tendency to form pure and mixed domains in BHJ devices on good length scales for charge separation.^{33,34}

The tendency to use PCBM has resulted in almost all of the synthetic materials research in OPV over the last 15 years being focused entirely on new donor materials to effectively tune to and match with PCBM. Seeing as the V_{OC} is directly related to the LUMO of our acceptor, the ubiquity of PCBM presents a limitation in our OPV system, with consequences on the V_{OC} , J_{SC} , and ultimately device performance.

PCBM is not without disadvantages: It has weak absorption within the AM1.5 spectrum, shows some degree of morphological instability due to diffusion in the solid state over time, limited spectral tunability, and an astronomically high synthetic cost.^{35,36} It is unsurprising therefore that after tens of years and hundreds of novel donor polymers, a new generation of ‘non-fullerene’ acceptors (NFAs) are finally coming to fruition, allowing full optimisation of BHJ systems. It could be argued that the delayed emergence of NFA materials is because they must encompass all of the favourable properties of fullerene derivatives – which is no easy feat – whilst also improving on areas such as ease of synthesis, processability, and improved optical absorptivity. Holliday et al. were some of the first to fulfil the majority of these criteria with the indacenodithiophene core acceptors, flanking them with benzothiadiazole and rhodanine moieties (IDTBR), which are usually known for their high extinction coefficients and dye properties.³⁷ The devices used synthetically cheap materials (P3HT donor and IDTBR acceptor – Figure 1.18) and reached efficiencies of 6.4% whilst also being air stable.

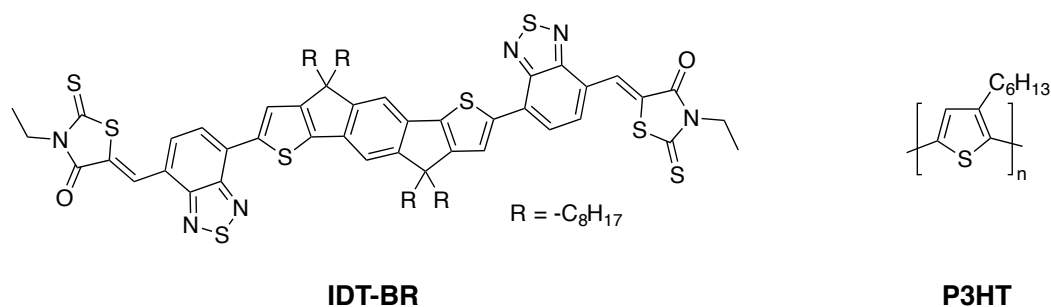


Figure 1.18 – Non-fullerene acceptor IDTBR (left) and donor polymer P3HT (right)

These new acceptor molecules open up new pathways to photocurrent generation via *n*-type excitation in the acceptor material followed by hole transfer onto the donor. This is referred to as the Channel-II pathway (Figure 1.19). This is compared to polymer fullerene devices, where the vast majority of *p*-type excitation and photocurrent generation occurs in the donor material.

The addition of the Channel-II mechanism requires stringent matching of not only the LUMO energy levels for efficient electron charge-transfer and separation (Channel-I), but also HOMO energy level matching for efficient hole charge transfer and separation (Channel-II). This represents a considerable challenge for the synthetic chemist, but one that comes with the potential to create materials with complementary absorptions across the whole AM1.5 spectrum.

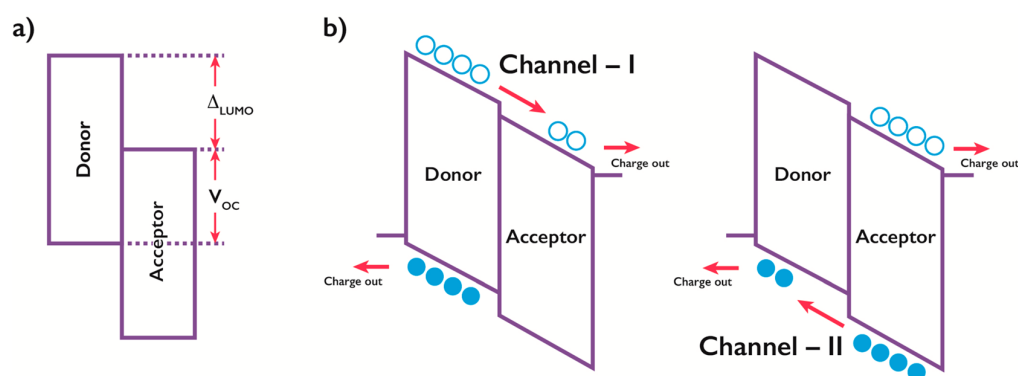


Figure 1.19 – a) energy level diagrams for a donor-acceptor device; b) Channel-I (left) and Channel-II (right) photocurrent generation pathways for *p*-type and *n*-type materials, respectively³⁸

With the cost of crystalline-silicon decreasing rapidly over the last decade and the field of OPV having not progressed as far as expected in the same time, the development of fullerene alternatives has somewhat reinvigorated the field. The practicable and inexpensive synthesis of these materials brings new hope to the prospect of future commercialisation.

1.5 OFET devices

Much like organic photovoltaics, organic field effect transistors comprise of an active organic semiconducting polymer layer that conducts charge under defined circumstances. As mentioned in Section 1.1, the silicon transistor has shaped our world, but the OFET offers an alternative solution through low temperature and low cost fabrication (spin coating/roll-to-roll) with the potential to excel in disposable products where silicon simply cannot, such as RFID tags and flexible displays. Although current performance is far from that of silicon in terms of switching speeds in complimentary circuits, progress is being made, and commercial products that could not exist using silicon technology are already on the market, such as the Plastic-Logic screen⁵ and the Polyera flexible display watch.

A transistor can be simply thought of as a switch in which the response to an input voltage will allow a current to flow through the device or not. It therefore represents a binary set of information that can be built into the logic circuits that drive electronics.

1.5.1 Operating principles

All OFETs are field-effect transistors (FETs), meaning that a field is created across the active layer to allow charge transport to occur in the semiconducting material. OFETs have three electrodes: the source, drain, and gate; a semiconducting layer; and a dielectric layer – see Figure 1.20.

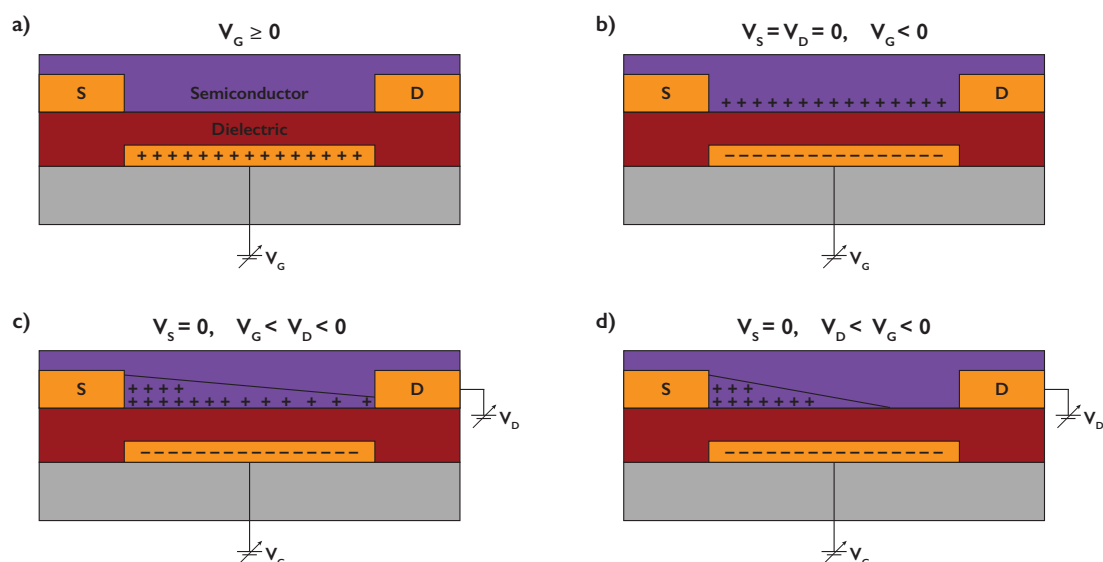


Figure 1.20 – OFET with a p-type semiconductor. a) positive V_G – cut-off regime; b) negative V_G applied, accumulation layer forms; c) linear regime – V_D applied – scales with I_{DS} ; d) saturation regime – when $V_D > V_G$, channel ‘pinches-off’ – I_{DS} now independent of V_D

On application of a voltage to the gate electrode (V_G), an electric field is produced across the dielectric, shifting the HOMO/LUMO levels in the organic semiconductor compared to the workfunction of the electrode and causing a build-up of charge at the dielectric/semiconductor interface. A *p*-type semiconductor is shown in Figure 1.20 – where holes are the main charge carriers and electrons will not be conducted.

The three main regimes that occur in an OFET (Figure 1.20) are the cut-off (**a**), linear (**c**) and saturation regimes (**d**). A positive V_G results in the transistor effectively being off, meaning that no current (I_{DS}) flows between the source and drain (**a**). When a negative voltage is applied to the gate, an accumulation layer builds (**b**), but without any voltage applied to the drain (V_D), no current will flow through the device. When V_D is applied and set low ($< V_G$), it scales linearly with I_{DS} (linear regime) until ‘pinch-off’ occurs when $V_D = V_G$ (**c**). This is because there is no longer an electric field across the dielectric when $V_D = V_G$, and therefore

even if V_D increases, I_{DS} stays the same – this is the saturation regime (**d**). The reverse is true for an n -type material, which would conduct electrons instead of holes.

Depending on the energy levels of the semiconducting layer and electrodes used, there can be ‘charge leakage’ when the current is off and no V_G is present. Depending on whether these are electrons or holes, it can mean a positive or negative voltage must be applied before a conductive channel can be formed at the dielectric/semiconductor interface. The voltage at which this channel forms is called the ‘threshold voltage’ (V_T).

1.5.2 Device parameters

During the linear regime, the current (I_{DS}) can be approximated via the following equation, where W and L are the width and length of the channel, respectively, μ is the carrier mobility, and C_i is the capacitance per unit of area of the dielectric layer:

$$I_{DS,lin} = \frac{W}{L} \mu C_i (V_G - V_T) V_D \quad \text{for } |V_G - V_T| \gg |V_D| \quad (1.16)$$

When $V_D = V_G - V_T$, the transistor transitions to the saturation regime and pinch-off occurs, meaning I_{DS} is no longer proportional to V_D . Therefore, I_{DS} is given by:

$$I_{DS,sat} = \frac{W}{L} \mu C_i (V_G - V_T)^2 \quad (1.17)$$

A good transistor has a low V_T , a large I_{DS} for small V_G and V_D , and also a small off current between the source and drain when the transistor is ‘off’. Similar to OPV, we can benchmark the performance of a transistor by extracting data from the device under a specific set of conditions. The most often quoted value is the mobility (μ) – the speed at which charge travels through the semiconductor under an applied electric field. Another important value is the I_{on}/I_{off} ratio, which gives the ratio between the I_{DS} at maximum V_G and when $V_G = 0$. Reliable devices can only be achieved if the signal-to-noise ratio is high, which is best served with a large I_{on}/I_{off} ratio.

This performance data can be extracted from two graphs, the transfer characteristics and the output characteristics (Figure 1.21).

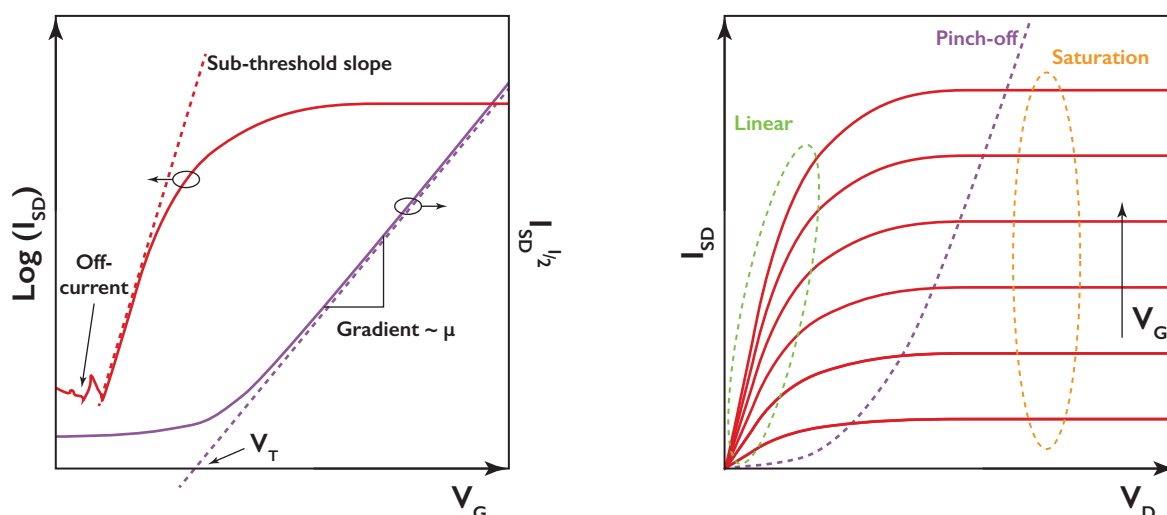


Figure 1.21 – Typical transfer characteristics (left) and output characteristics (right) for a semiconducting polymer OFET

The mobility (μ) is calculated from the gradient of the square root of I_{SD} , and therefore the placement of the calculation tangent is open to interpretation. McCulloch et al. published an interesting piece in Science in 2016 looking at the over-inflation of mobility values due to overestimation. One example showed how a ‘kink’ in the transfer curve could change the estimation from $6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $0.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ – a significant difference.³⁹

Various device architectures can be fabricated for OFETs, with the most common being that of the bottom gate, bottom contact (Figure 1.22 – a) – often due to ease of fabrication. This is comprised of a gate electrode on which a dielectric insulator (often SiO_2) sits, followed by patterned source and drain electrodes. These devices can be pre-purchased with varying dielectric materials/contacts and then a thin semi-conducting layer can be spin coated on top.

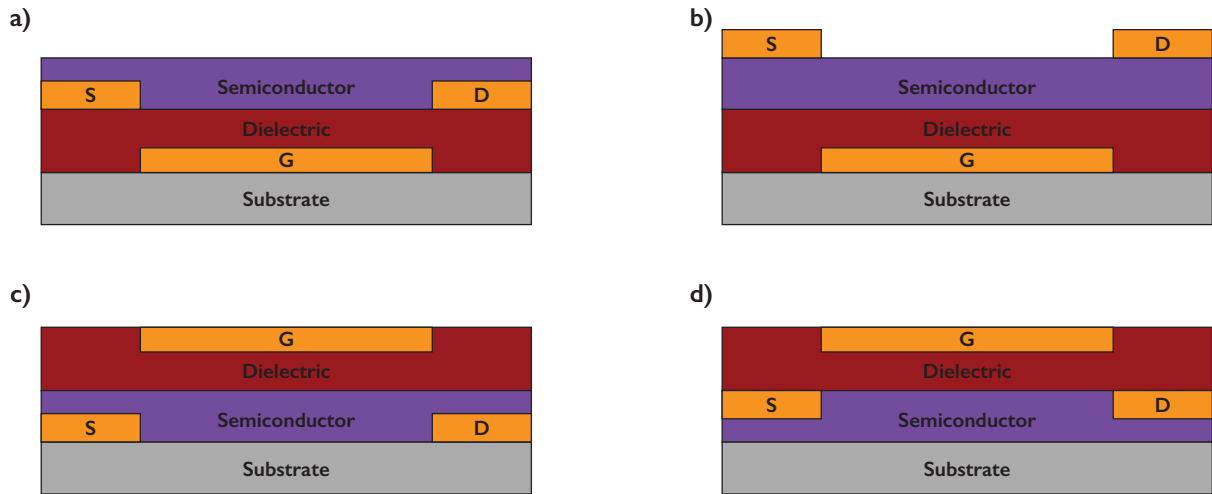


Figure 1.22 – Common device architectures for OFETs: a) bottom gate, bottom contact; b) bottom gate, top contact; c) top gate, bottom contact; d) top gate, top contact

The dielectric layer plays a key role in OFET performance, and must be specifically chosen for each individual material, device architecture, and fabrication technique. To achieve high I_{on}/I_{off} ratios, a high I_{DS} is required, and therefore a high dielectric capacitance (C_i – equation 1.18) is favourable. The capacitance is related to the intrinsic dielectric constant (or relative permittivity) of the material (ϵ_r) and its thickness (d), where ϵ_0 is the permittivity of free space.¹⁶

$$C_i = \frac{\epsilon_0 \epsilon_r}{d} \quad (1.18)$$

A high dielectric constant and thin dielectric layer are therefore beneficial for any OFET, although the thickness must be high enough to form homogenous, defect free films. Use of SiO_2 as a dielectric layer is popular due to its high permittivity ($\epsilon_r = 3.9$), although its non-flexible nature and pendant hydroxyl surface groups (requiring treatment) mean that other materials have been sought. The most common flexible organic materials used are PMMA ($\epsilon_r = 3.6$)⁴⁰ and CYTOP ($\epsilon_r = 2.1$),⁴¹ again for their ease of processing and relatively high ϵ_r values (for organics).

1.6 Synthetic design

1.6.1 Desirable properties

The previous sections have discussed what polymers are, how they relate to plastic electronics, and the inner workings of photovoltaic and transistor devices. It is evident from the inherent device physics and morphological properties that polymers for plastic electronics have a large number of often conflicting requirements. The job of the synthetic chemist is to tailor a polymers molecular design to try to find a balance between these requirements in a synthetically achievable compound.

The backbone of the polymer, with its delocalisation of p_z orbitals, primarily dictates the electronic properties of a conjugated polymer. The more rigid the backbone, the less twisting between units, the greater the overlap of orbitals, and the more enhanced the charge transport properties. This desired rigidity results in insoluble materials, and therefore additional solubilising alkyl chains need to be added to make the polymer processable. Through the engineering of the backbone and side-chains, the synthetic chemist can control the molecular weight, intermolecular interactions, planarity, aromatic resonance energy, and bond length alternation. The combination of these highly interlinked properties within our polymer dictates the final crystallinity, packing, morphology, HOMO/LUMO levels, and ultimately the performance in devices.

As useful as it would be to pick out an individual property to modify, their interdependency makes exact control difficult: for example, the addition of a branched solubilising alkyl chain will increase solubility, but also affect the intermolecular interactions, the planarity, the energetics, and solid state packing of the polymer.

It is desirable for conjugated polymers used in both OPV and OFET to have high molecular weights, good solubility, appropriate electronics, and excellent charge transport. In OPV, the

energies of the HOMO/LUMO levels are exceptionally important in that they must match the energies of the acceptor material with the correct offset in the BHJ blend, overlap with as much of the AM1.5 spectrum as possible (small bandgap), whilst also maximising the V_{oc} output from the device. The polymers must also pack efficiently to facilitate charge transport whilst simultaneously allowing interpenetration of acceptor material clusters to ensure domain sizes on the scale of exciton diffusion. In OFET devices, although there is some availability to change electrode materials and hence the workfunctions of the metals used, charge injection into either the HOMO or LUMO is dependent on the energetics of the semiconducting layer. Unlike OPV, usually the material is only used as *p*-type (hole injection into HOMO) or *n*-type (electron injection into LUMO) – in these instances, the band gap is of less importance, as long as the HOMO or LUMO is at the correct level related to the electrode workfunction.

Ambipolar semiconductors are a class of OFET materials where the band gap is of greater importance, as they must allow charge injection into both the HOMO and LUMO. These materials exhibit both *n*- and *p*-type behaviour depending on whether the gate voltage bias is positive or negative. Ambipolar materials could potentially be incredibly useful in new integrated circuitry architectures thanks to their ability to avoid the need for both *n*- and *p*-type transistors next to each other on the same chip.

Of great importance in OFET is the molecular packing of the semiconducting layer. Strong molecular alignment along the channel of the transistor can boost band-transport, and interchain π - π -interactions stiffen the polymer backbones whilst also facilitating hopping transport. As these interactions get stronger and the molecular weight gets bigger, the solubility of the polymer in solution becomes an issue. Therefore, the addition of solubilising alkyl chains onto the polymer is required to aid the processability, but their length and type can themselves affect the polymer packing. Although semi-crystallinity can be advantageous,

the drawback of designing polymers that are too crystalline is their tendency to form crystalline grains, which have grain boundaries between them. If these boundary defects become too concentrated, they can impede charge transport.

1.6.2 Molecular design

Section 1.3.1 discussed how the linear combination of p_z orbitals led to increasing conjugation along the polymer backbone and a decrease in the polymer band gap (Figure 1.8). Since the introduction of the concept in 1865,⁴² aromaticity has been defined in a multitude of ways, with Hückel's $4n + 2$ rule (denoting the number of π -electrons required for an atom to be aromatic) being an important step forward.^{43–45} An extension to this for polycyclic ring systems was Clar's π -sextet rules,^{46,47} denoting the extra stability in a $6n$ π -electron benzenoid species, where aromatic π -sextets are defined as six π -electrons localised in a single benzene-like ring separated from adjacent rings by formal C-C single bonds. Clar's rules then state that the Kekulé resonance structure with the largest number of disjoint aromatic π -sextets i.e., benzene like moieties, is the most important for the characterisation of properties of polycyclic aromatic hydrocarbons (PAHs).^{48,49} The greater the number of 'aromatic moieties' in a molecule, the more stable and therefore lower in energy it is.

In terms of the energetics in conjugated polymers, the greater number of π -sextets in the polymer chain, the more stable the polymer is (increased aromatisation), compared with fewer π -sextets in the chain giving the less stable 'quinoid' form (decreased aromatisation).

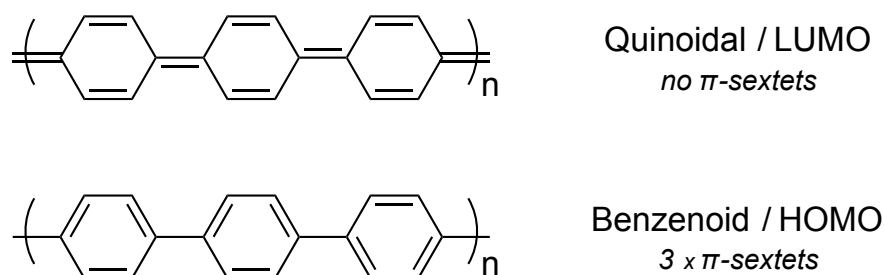


Figure 1.23 – Stabilised aromatic structure (bottom). Higher energy quinoidal structure (top)

Figure 1.23 shows poly(*p*-phenylene) (PPP) in its lower energy aromatic form (π -electron density is focused within the benzene ring – HOMO), and the higher energy quinoidal form (disruption to aromaticity, leading to higher energy – LUMO).¹⁶ Notice how the quinoidal form no longer has any rotational freedom between the benzene rings, forcing the backbone into a highly planar and regular structure.

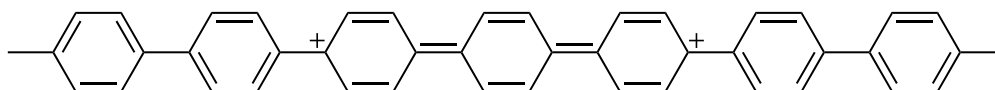


Figure 1.24 – Bipolaron on a PPP chain showing existence of aromatic and quinoidal structures on the same polymer chain

On addition of a polaron onto the polymer backbone, the quinoidal nature of the polymer tends to dominate due to the bond distortion and rearrangement caused by the addition of a charge. The aromatic and quinoidal structures can even coexist on the same chain (Figure 1.24). The large addition of energy needed to induce the quinoidal form can be reduced through synthetic design – for example in Figure 1.25, we see how the addition of a benzene ring system can reduce the band gap.

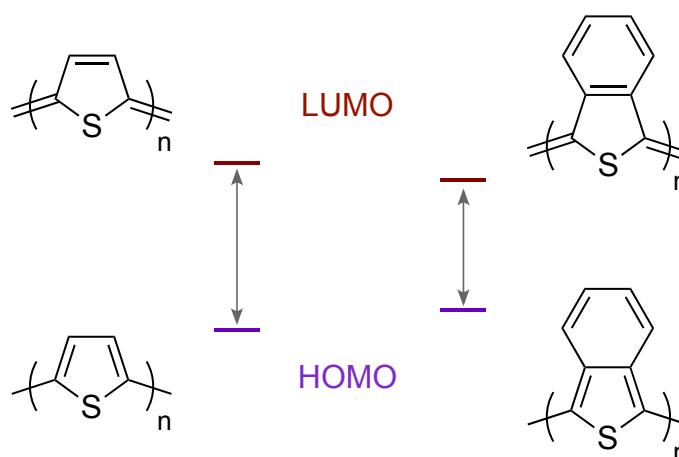


Figure 1.25 – Reducing the band gap by using quinoidal structures

If we compare the HOMO of the thiophene (left) vs. the benzothiophene (right), it can be seen that the addition of the benzene unit to the benzothiophene will result in an increased HOMO energy due to increased quinoidal character. When considering the LUMOs, that of

the thiophene is completely quinoidal in character, while the benzothiaphene now includes a π -sextet, increasing aromaticity and stabilising the LUMO in comparison to the thiophene.

Using a single aromatic monomer with increasing conjugation has been highly successful in the past, with regio-regular poly-3-hexylthiophene (rrP3HT) being the workhorse of plastic electronics for many years. It overcomes the solubility issues of poly(*p*-phenylene) and polythiophene with the addition of a hexyl chain at the three position. The regio-regular nature of the alkyl chain position (always head-to-tail) reduces back-bone twisting,⁵⁰ resulting in the polymer forming semi-crystalline domains with efficient π - π -stacking and good charge transport ($0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in OFETs).^{51,52} With a band gap of 2.0 eV, it has performed excellently in BHJ-OPV devices with NFAs, as seen in Section 1.4.4.

Figure 1.26 shows how increased steric hindrance between two 6-membered rings due to the protruding hydrogen atoms causes increased twisting along the backbone compared with two 5-membered thiophene equivalents. Head-to-head interactions between side-chains can also cause significant twisting between monomer units, breaking conjugation, affecting π - π -stacking between polymer chains, and ultimately hindering performance. On moving from 95% rrP3HT to 90% rrP3HT in comparable OPV devices, PCE drops from 2.4% to 0.7%.

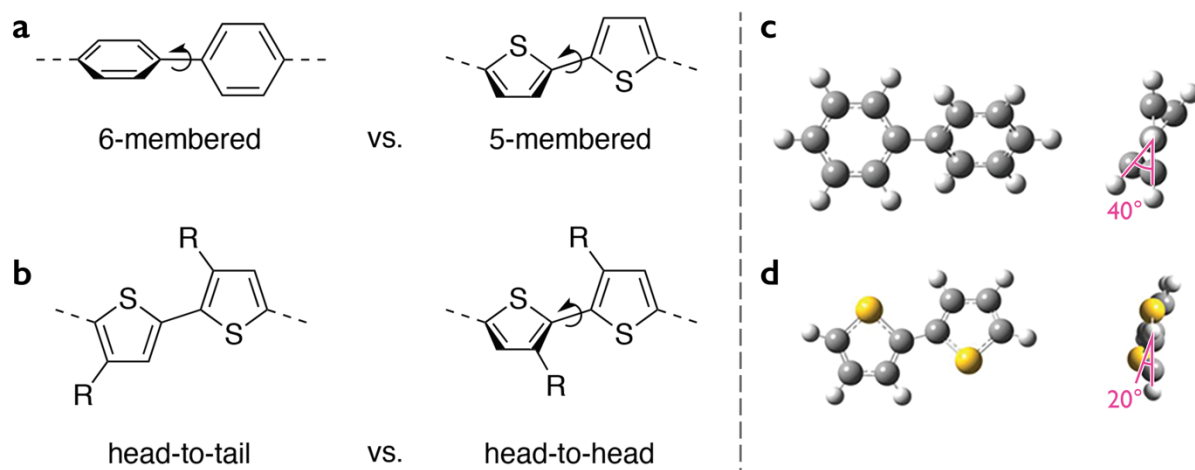


Figure 1.26 – Twisting effects between: a) 6-membered vs. 5-membered rings; b) regio-regular vs. irregular alkyl chains; c) benzene-benzene – 40° twist; d) thiophene-thiophene – 20° twist

A band gap of greater than 1.9 eV will only absorb the solar photon flux from ~30% of the AM1.5 solar spectrum, whereas a band gap of 1.1 eV will cover ~77% of the AM1.5 spectrum. Smaller band gaps are not just desirable for OPV, but ambipolar transistors can also benefit from them as they allow injection from both electrodes.

Therefore, a variety of techniques are required to reduce the bandgap to below 2.0 eV to improve solar absorption. One of these is the so called ‘donor/acceptor’ (D/A) approach (not to be confused with the differing donor and acceptor materials in BHJ devices), where two monomers – one electron rich and one electron poor – are co-polymerised in an $[-A-B-]$ manner. This style of repetitive co-polymerisation means orbital hybridisation of the frontier orbitals along the polymer backbone occurs, resulting in a reduced band gap (Figure 1.27).

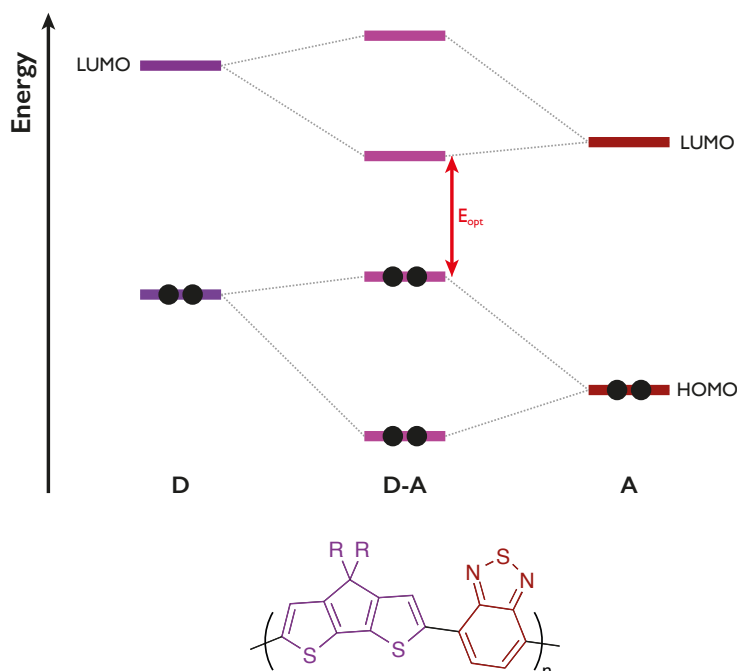


Figure 1.27 – Orbital hybridisation between CPDT (left) and BT (right)

The D/A approach is beneficial, in that a degree of localisation allows somewhat independent tunability of the HOMO/LUMO levels through individual monomer selection and modification.

Another way to affect the polymer properties is the use of bridging atoms. Figure 1.28 shows three monomers: the first has a head-to-head alkyl linkage, resulting in severe twisting of the two thiophene units and a lack of conjugation. The middle unit (cyclopentadithiophene) uses a bridging carbon atom to fix the planarity of the thiophenes⁵³ whilst keeping the same alkyl chain density, with the solubilizing groups protruding from the bridging carbon in an sp^3 manner. The bridging atoms planarising effect can increase π - π -stacking, but the sp^3 alkyl chains protruding from the plane can also hinder it.

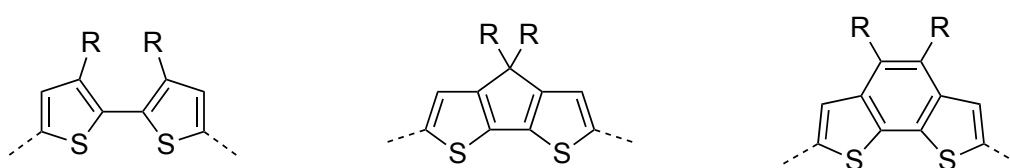


Figure 1.28 – Head-to-head bi-thiophene (left), cyclopentadithiophene (centre), benzodithiophene (right)

The benzodithiophene (right) uses two bridging carbons to give an aromatic benzene ring in the middle flanked by two thiophenes. Here, the planarity of the thiophene units is fixed as for cyclopentadithiophene, except the alkyl chains are now also in the plane of the ring system – reducing the π - π -distance between adjacent polymer chains even further.

1.6.3 Palladium cross-coupling

With the majority of polymers in the literature using a two monomer system, arguably one of the most crucial steps in the polymer synthesis is the formation of the carbon-carbon bonds between the alternating $[-A-B-]$ co-monomer units. As stated in Section 1.2.2, the majority of polymerisations proceed via stepwise palladium-catalysed cross-couplings. These exceptionally powerful carbon-carbon bond forming reactions generally use organometallics on one monomer and an organohalide on the other. The most common reactions used are Stille⁵⁴ and Suzuki,⁵⁵ which use tin and boron as the organometallic moieties, respectively, and are named after their discoverers.

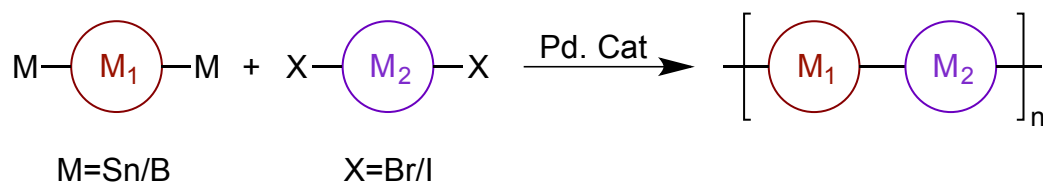


Figure 1.29 – Typical palladium cross-coupling used in generic step-wise polymerisation reactions

The general process is as follows (Figure 1.30): An organohalide (R^1-X) will insert itself into a Pd(0) compound via an oxidative addition mechanism. The organometallic will then insert itself into the Pd(II) complex via a transmetalation step (R^2-M). Reductive elimination of the two aryl groups then forms a new carbon-carbon bond whilst regenerating the Pd(0) species ready to repeat the cycle. This elimination step can only occur if R^1 and R^2 are in a cis-position with respect to one another. Although toxic, Stille chemistry is generally reliable, high yielding, and follows the prescribed path above. Suzuki chemistry is comparatively non-

toxic, although optimisation of the conditions is often required to gain efficient coupling.

This is made more difficult by the required addition of a base in Suzuki chemistry, which is required in the transmetalation step.

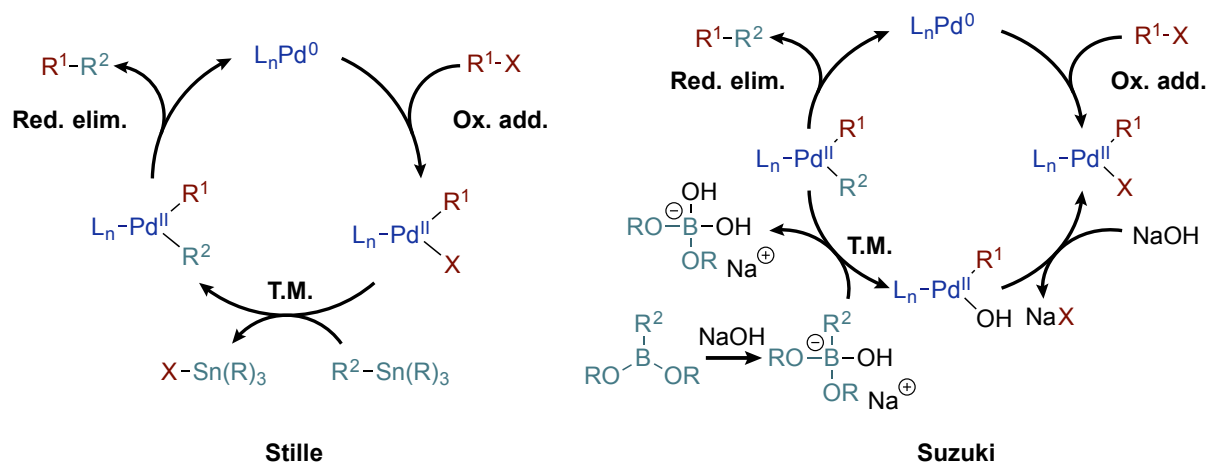


Figure 1.30 – Generic Stille and Suzuki palladium cross coupling cycles.

Note: NaOH base interchangeable

Suzuki and Stille polymerisations are popular due to their generality, scalability, and well-understood dynamics. When using materials that have been synthesised in small quantities (<300 mg) and are expensive in both time and money, these well-studied and predictable reactions provide a greater probability of synthesising a high molecular weight polymer. As well as having a maximised conjugation length and more predictable electronic properties, high molecular weight polymers are also much more desirable in terms of their processability (viscosity/solubility) and ability to be formulated into inks for fabrication. However, excessively high molecular weights can themselves lead to solubility issues, inhibiting fabrication and morphological properties, and hence a balance must be sought.

On performing an $[-A-B-]$ style co-polymerisation, there are two factors which are reaction independent: the first is the previously mentioned required 1:1 stoichiometry of the two co-monomers, which is required to achieve high molecular weights in a step-wise polymerisation. The second is solubility – the active end of a polymer chain can only react if

the chain is still in solution. If the monomer system has lower solubility than predicted, it can either crash out at a low molecular weight even at high temperatures, or if it is only partially in solution it can continue to polymerise to the extent it becomes completely insoluble (high molecular weight).

As with many aspects of synthesising new materials for use in plastic electronics, it is the job of the synthetic chemist to evaluate all of the many factors these materials require and develop a rational hypothesis as to what will result in the highest performing materials.

1.7 Scope and aim of the thesis

This thesis focusses on the synthesis and analysis of a series of novel polymers for OPV and OFET applications, as well as a series of novel non-fullerene acceptors for OPV. The work performed for this thesis will be split up and presented in four chapters as follows:

Chapter 2 – The design and synthesis of TzBTz- and TBT-based monomers

Chapter 2 initially focuses on the design and synthesis of a novel thiazole-based monomer that proved to be insoluble on polymerisation with a thiophene-based co-monomer. The addition of longer alkyl chains onto the thiazole monomer combined with both longer and branched chains on the co-monomer resulted in two high molecular weight polymers.

Chapter 3 – The characterisation and analysis of polymers pTzBTzC12-TBTC12 and pTzBTzC12-TBTCbranch

Chapter 3 discusses the characterisation performed to evaluate the optical and electronic properties of the two polymers synthesised in Chapter 2. This is followed by discussion of the testing of the polymers in OPV and OFET devices.

Chapter 4 – DTP-DPP-based polymers for OPV and OFET

Chapter 4 discusses the challenging synthesis of a novel low band gap diketopyrrolopyrrole (DPP) monomer that utilised dithienopyrrole (DTP) flanking units to enable strong push-pull

hybridisation across the monomer unit, making it a near-infrared absorber. The monomer was then polymerised into two new polymers that were characterised optically and electrically.

Chapter 5 – Carbazole-based non-fullerene acceptors for use in OPV

Chapter 5 discusses the synthesis of a series of carbazole-based non-fullerene acceptors based on the highly successful 'FBR' unit. These new materials were characterised before being tested in OPV devices.

Chapter 2

The design and synthesis of TzBTz- and TBT-based monomers

2.1 Introduction and previous work

The first section of this thesis builds on the work performed by the author for their MRes Thesis⁵⁶ on the synthetic pathway to a new monomer **DTzBTBTz** (Figure 2.34). This work was initially based on the work performed by Biniek et al. in 2012⁵⁷ who synthesised the monomer **DTBTBT** for use in OPV and OFET devices (Figure 2.31).

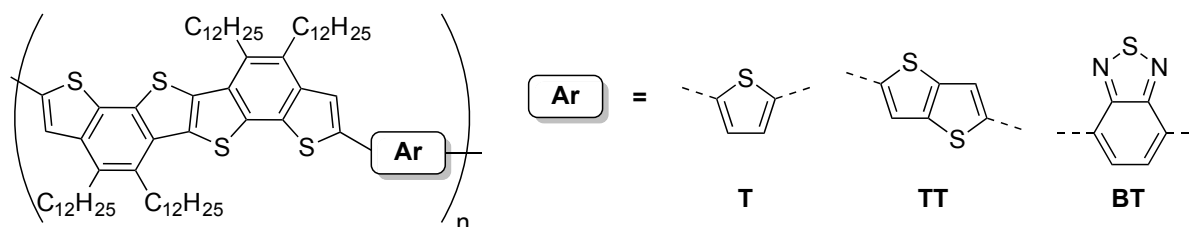


Figure 2.31 – DTBTBT polymers

DTBTBT is comprised of a highly planar electron rich core with alkyl chains co-planar to the central unit providing good solubility whilst also aiding π - π -stacking compared with the sp^3 out of plane alkyl chains seen in molecules such as **CPDT** (Figure 2.32).

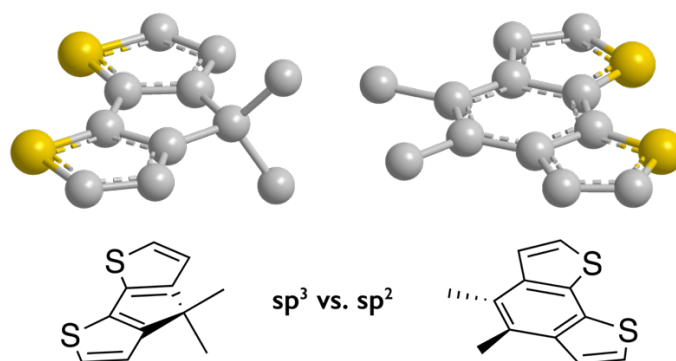


Figure 2.32 – CPDT: out of plane sp^3 chains (left) vs. TBT: in plane sp^2 chains (right)

Through co-polymerisation with electron rich components like thiophene (**T**) and thienothiophene (**TT**) (Figure 2.31), the materials performed well in OFET devices giving mobilities of 0.1 and 0.01 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. When **DTBTBT** was polymerised with the electron poor co-monomer benzothiadiazole (**BT**), orbital hybridisation across the two monomer backbones resulted in a push-pull effect, lowering the band gap and resulting in a PCE of 3.7% in a BHJ device blended with PC[71]BM. Although these results were

admirable for a novel monomer, the wide band gap of the **T** and **TT** co-polymers resulted in a barrier to injection in OFET devices due the offset between the low polymer HOMO and the electrode work-function. The low molecular weights and poor film morphology are also likely to have impeded charge transport, decreasing both OFET performance and the J_{SC} in OPV devices.⁵⁷

The initial aim for this body of work was therefore to synthesise a new core with the flanking thiophene units of the central core being replaced with thiazole units (Figure 2.33). The electronegative nitrogen atom aimed to decrease electron density in the central core, increasing push-pull orbital hybridisation with the electron rich monomers (**T** and **TT**) and improving charge injection.

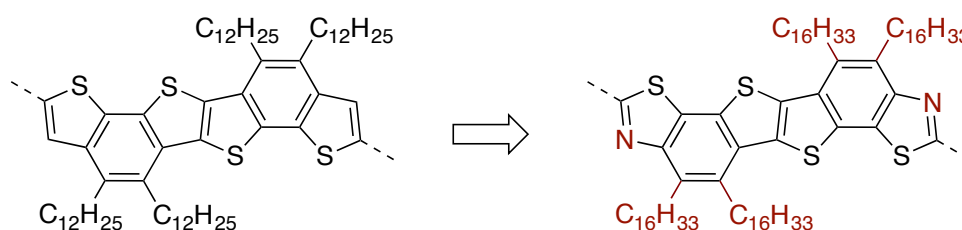


Figure 2.33 – DTBTBTC12 vs. DTzBTBTzC16. The proposed new monomer

Biniek et al. found that solubility issues encountered during the **DTBTBT** polymerisation reaction were most likely due to the short $-C_{12}H_{25}$ alkyl chains used on the highly planar monomer unit, resulting in low molecular weights. Therefore an increase in alkyl chain length to $-C_{16}H_{33}$ aimed to improve solubility further and increase molecular weights of the polymers; potentially improving charge transport in both OFET and OPV through M_w induced packing.⁵⁸

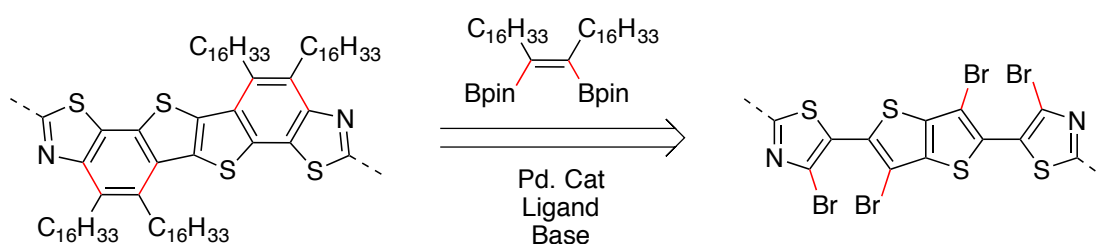


Figure 2.34 – Envisioned DTzBTBTz monomer synthesis

The initial synthesis proved to be incredibly difficult at the point of the double ring-closure step to form the final planar ring structure (Figure 2.34), with a multitude of inseparable products and a high level of decomposition being repeatedly observed under various reaction conditions. The most likely cause for this was that the introduction of the nitrogen atom into the backbone provided a point of attack for decomposition mechanisms to occur before ring closure could take effect. After multiple optimisation attempts of the Suzuki ring closure proved fruitless, it was decided investigation into a new idea to simplify the unit would be beneficial. This would allow improvement of the thiazole-based chemistry, with the plan being to eventually pull that new knowledge back to this more complex project.

Polyfused building blocks have always been of interest within organic electronics due to their reduced backbone disorder and proven ability in OFET devices.⁵⁹ High molecular weight cyclopentadithiophene (**CPDT** – Figure 2.35 – left) polymers have been shown to exhibit good *p*-type charge carrier mobilities of up to $3.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in OFET devices.⁶⁰ Their high mobility is attributed to the high molecular weight strands forming ordered crystallites, much like **P3HT**. This is contrary to what might be expected due to the sp^3 hybridisation of the bridging carbon, which causes the alkyl chains to be located out of the plane of the backbone. A suggested theory is that the high molecular weights promote interconnectivity between neighbouring crystallites, reducing grain boundaries and therefore increasing charge transport.⁶⁰

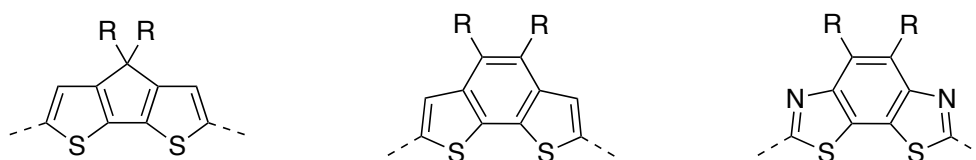


Figure 2.35 – CPDT (left), TBT (centre) and TzBTz (right)

Benzodithiophene (**TBT**) takes a similar structure to **CPDT** but with the alkyl chains sp^2 hybridised and in the plane of the molecule. It has not been as extensively studied as **CPDT**,

although polymers containing the unit have shown promising *p*-type mobilities of $0.134 \text{ cm}^2 \text{Vs}^{-1}$.^{61,62} The effect of the in-plane alkyl chains should allow the polymer backbones to stack closer, improving order and increasing mobility compared to **CPDT**. One possible reason for the current lower mobility values is simply that most **TBT** co-polymers use electron rich co-monomers, meaning no orbital hybridisation occurs. This could potentially result in mismatched orbital energetics resulting in hindered charge injection and extraction – a theory bolstered by the high threshold voltage OFET transfer curves seen for a number of **TBT** based polymers.⁶²

The **TzBTz** unit (Figure 2.35 – right) was proposed as a new synthetic target with the introduction of electron deficient thiazole units, which when co-polymerised with **TBT** (Figure 2.35 – centre), should undergo orbital hybridisation, raising the HOMO energy level and thus improving charge injection / extraction. Through this exploration of the asymmetry between the thiazole and thiophene based co-monomers, the **TzBTz-TBT** approach would make these new materials perfect candidates for ambipolar charge transport in OFETs and wider band gap light absorbing materials in OPV devices when combined with lower band gap non-fullerene acceptors (Figure 2.36).

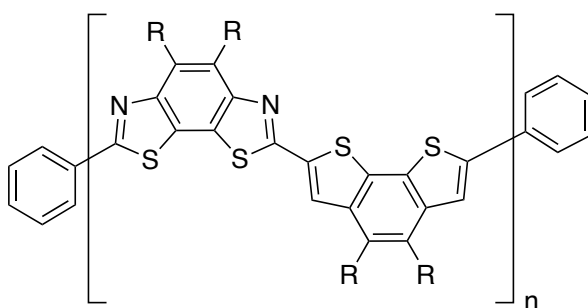


Figure 2.36 – Proposed *pTzBTz-TBT* polymer system

The co-planar sp^2 hybridized carbons should facilitate strong interchain π -stacking, much like in **DTBTBT** but with increased solubility due to both monomers having solubilising alkyl chains. An interesting investigation would be to switch the alkyl chains on the **TBT** unit

between linear and branched moieties to see if this alkyl chain branch affects the solid-state packing of the material with itself (impacting OFETs) and within mixed domains (impacting OFETS and BHJ-OPV). The proposal is that the branched chain will disrupt π - π -packing between polymer chains within the OFET devices, hindering charge transport and therefore performance, but will aid in blending with the acceptor moieties and therefore increase interconnectivity; improving ‘docking’ between the donor and acceptor thereby reducing domain segregation in BHJ devices.^{62,63}

The proposed flexible synthetic pathway to make the **TzBTz** monomer in which the addition of the alkyl chain occurs via a ring closure mechanism (much like the envisioned route for **DTzBTBTz**) should allow for the optimisation of this reaction on a simple single-ring system whilst making a new monomer/polymer series of scientific interest. The similarity between the **TzBTz** monomer and the **DTzBTBTz** monomer should be sufficient that it will allow the continued synthesis of the double ring-closure system to progress at a faster pace.

2.2 Synthesis of TzBTz monomer

Below is the initial synthetic scheme for the synthesis of the **TzBTz** monomer. The ring closure step to form compound **2.7** was incredibly low yielding even after optimisation and hence the new route was designed via compound **2.8** to achieve compound **2.10** in higher yields. Subsequent deprotection and bromination afforded the **TzBTz** monomer **2.12**.

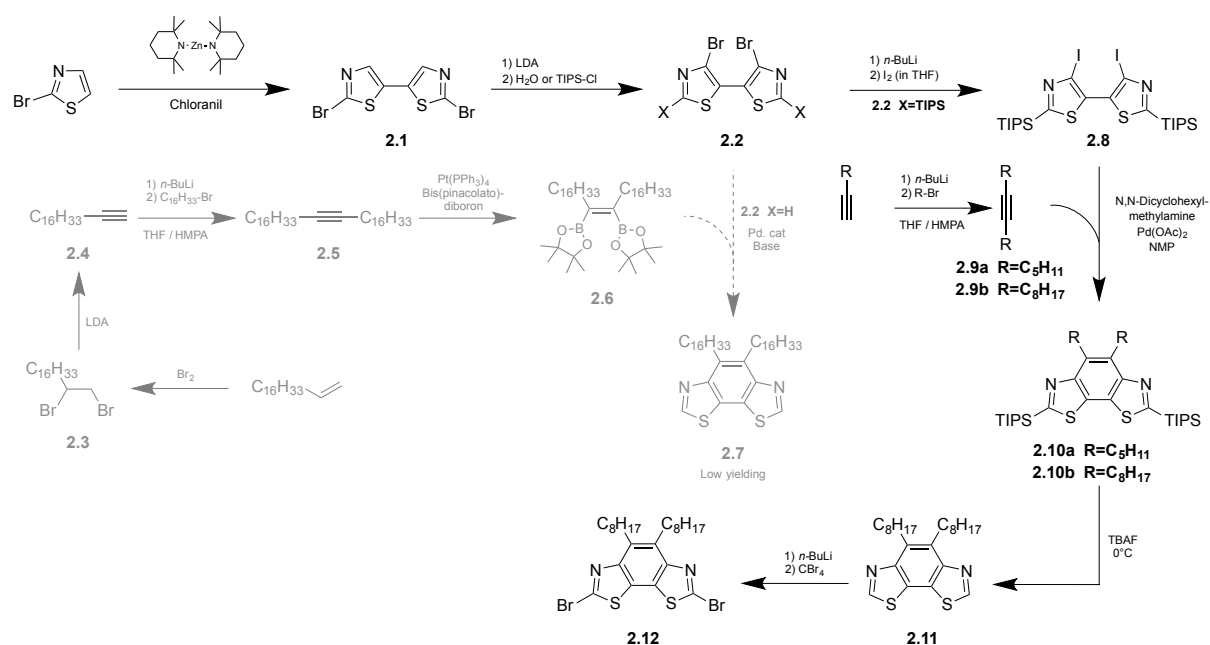


Figure 2.37 – Synthetic scheme for the TzBTz monomer

2.2.1 Synthesis of bi-thiazole pre-cursor

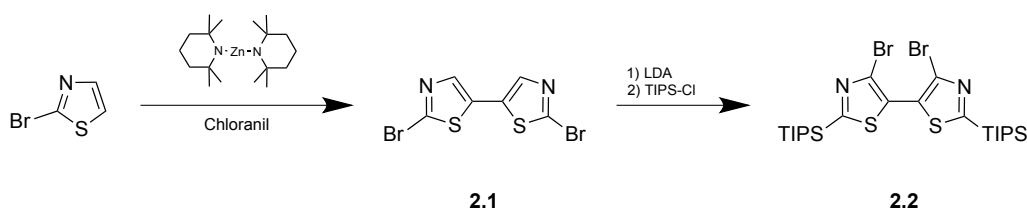


Figure 2.38 – Synthesis of bi-thiazole ring closure pre-cursor

The synthesis of **2.1** and **2.2** (Figure 2.38) was adapted from literature sources^{64,65} and successfully scaled to large quantities (up to 25 g) with high yields (>75%). The commercially available 2-bromothiazole was reacted with the Knochel base (tmp)₂Zn·2MgCl₂·2LiCl to form the bis(2-bromothiazol-5-yl)zinc intermediate at the 5-

position of the thiazole, before being treated with the two electron acceptor chloranil⁶⁶ to reduce the species and form the homo-coupled product **2.1**. A dark-red impurity ran close to the product on silica meaning standard purification by column chromatography was not possible. The impurity was deduced by GCMS to be the chloranil alcohol side product and by simply dissolving the crude mixture in toluene and washing repeatedly with NaOH solution, the sodium salt of the alcohol was formed, which was thusly washed out in the aqueous layer, removing the impurity. Recrystallisation of the crude product in acetone afforded **2.1** as long, light yellow crystals.

On addition of 2 equivalents of LDA the bi-thiazole species (**2.1**) will protonate at the 4-position before undergoing the ‘halogen-dance’ exchange wherein the negative charge migrates to form the thermodynamically more stable α -lithiated position^{67,68} pushing the bromines to the 4-position. The α -di-lithiated species can then be quenched with either water as a proton source to form **2.2** (**X=H**) or using TIPS-Cl to produce **2.2** (**X=TIPS**). Having initially had ring closure problems when using **2.2** (**X=H**) to form **2.7**, it was decided to eliminate the possibility of palladium-catalysed direct arylation at the α -proton of the bi-thiazole by using the TIPS protecting group – hence why it was chosen to block this reactive position from this point in the synthesis.^{69,70} Recrystallisation of the crude product in acetone afforded **2.2** (**X=TIPS**) as yellow crystals.

2.2.2 Synthesis of alkyl chain boronic ester (2.6)

The -C₁₆H₃₃ alkyl chain length was chosen to aid in continuity with the initial work undertaken to form the **DTzBTBTz** monomer in the previous MRes work (Figure 2.34). The synthesis on the alkyl chain was adapted from multiple literature sources^{57,71–73} and then optimised during the MRes year along with an MSci student (Sam Rowe). The commercially available 1-octadecene undergoes an electrophilic addition with elemental bromine via the brominium ion to give **2.3** (quant. yield). On addition of 3.5 equivalents of LDA, the 1,2,-

dibromooctadecane undergoes a double E2-elimination with the third equivalent of LDA needed to trap the acetylide ion before quenching with water to give **2.4** as a terminal alkyne (quant. yield). The alkyne is subsequently deprotonated using *n*-BuLi, with HMPA being used to selectively solvate the Li^+ ion, increasing the basicity of the *n*-Bu $^-$ anion and ensuring the formation of the acetylide ion. On addition of 1-bromohexadecane, the acetylide ion undergoes nucleophilic attack on the bromo-hexadecane forming the $\text{-C}_{16}\text{H}_{33}$ alkyne product **2.5** in moderate yields (41%).

Borylation of the alkyne **2.5** is undertaken using a stereospecific platinum catalyst. Great care must be taken to remove any residual moisture and oxygen from the reaction and de-gas all solvents, as the catalyst is easily poisoned. $\text{Pt}(\text{PPh}_3)_4$ has been shown to undergo stereospecific insertion of an alkyne during the catalytic cycle to produce the *Z*-isomer **2.6** with 99% isomeric purity^{73,74} (Figure 2.39).

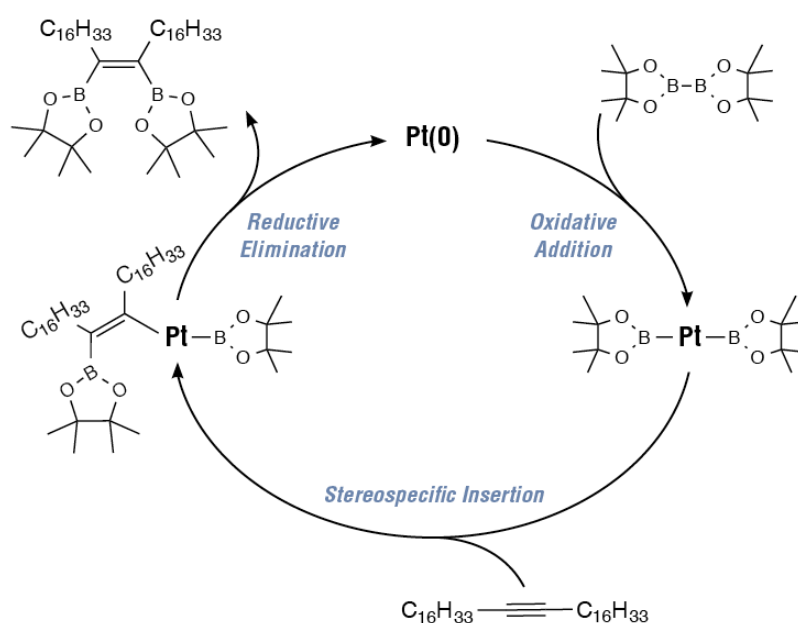


Figure 2.39 – Platinum cycle showing stereospecific insertion of alkyne

Only the *Z*-isomer is required, as any *E*-isomer would not be able to undergo ring closure in the next step due to the incorrect steric placement and non-rotational nature of the *E*-boronic ester.

2.2.3 Ring closure of the bi-thiazole unit

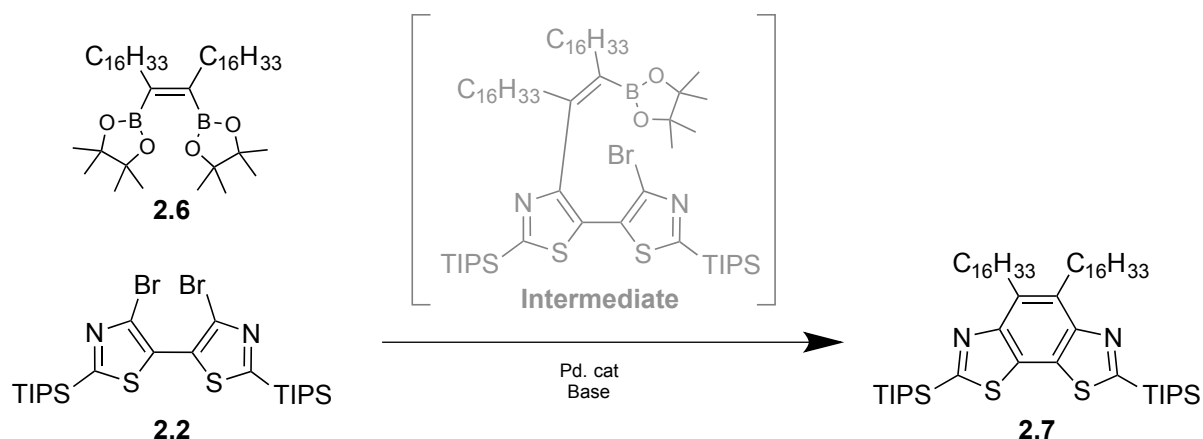


Figure 2.40 – Suzuki synthesis of bi-thiazole ring closure

The ring closure to form **2.7** (Figure 2.40) was performed via two step-wise palladium catalysed Suzuki coupling reactions adapted from the literature.⁵⁷ A number of conditions were tested including the catalyst, ligand and equivalents of water as demonstrated in the table below (Table 2.1).

Reaction	Catalyst	Ligand	H ₂ O Eq.	Time	Outcome ^a
1	Pd(PPh ₃) ₄	–	50	24 hours	0% (NMR)
2	Pd(OAc) ₂	(^t Bu ₃)P	50	24 hours	0% (NMR)
3	Pd(dppf)Cl ₂	–	100	24 hours	<5% yield (NMR)
4	Pd(OAc) ₂	SPhos	100	24 hours	13% yield (isolated)

Table 2.1 – Suzuki conditions for the ring closure of bi-thiazole. Fixed conditions were: THF (20 ml/mmol) / 5% cat. loading / 6 equiv. base. (K₂CO₃) / 60 °C on a 100 mg scale. a) Percentage of desirable product after 100% consumption of starting material

The highest yield for the ring-closure was achieved using the SPhos ligand. In 2004 Walker et al. reported the SPhos Buchwald ligand⁷⁵ – a palladium ligand designed specifically for use in Suzuki cross-coupling reactions. The bulky nature of the electron-donating ligand with OMe groups (creating even more steric bulk) promotes the formation and stabilisation of the

$L_1Pd(0)$ species.^{76–78} This species is smaller than the equivalent $L_2Pd(0)$ species, allowing the substrate to approach more closely and hence increase the rate of oxidative addition.

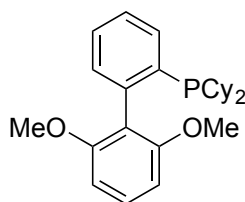


Figure 2.41 – Sphos Ligand

With the bulky size of the thiazole unit **2.2** (especially at the point the intermediate forms – Figure 2.40), it could be argued that the higher the concentration of the $L_1Pd(0)$ species, the faster one would expect oxidative addition to occur. SPhos style ligands have also been reported to have a higher rate of reductive elimination from the $L_1Pd(0)$ species than the equivalent $L_2Pd(0)$ species.^{79,80} The combination of these electronic and steric effects around the palladium centre result in a higher likelihood of the bi-thiazole species to undergo the two carbon-carbon bond forming reactions required prior to suspected decomposition in the reaction media – this is why a higher yield is seen when the SPhos ligand is used compared with other conditions. Unsatisfied with a yield of 13% and the possibility of continued Suzuki optimisations on synthetically expensive materials, another ring closure route was tested with the aim of achieving higher yields.

Literature procedures^{81,82} for the thiophene equivalent had shown successful yields (60–70%)⁸³ for similar ring closure reactions, but required the halogen on the substrate to be iodine as opposed to bromine. Therefore, the iodinated thiazole derivative was synthesised by reacting **2.2** (**X=TIPS**) with two equivalents of *n*-BuLi and quenching with a solution of iodine in THF to form the iodinated bi-thiazole **2.8** in high yields. Along with an alkyne, **2.8** could then be used to ring close as per the literature conditions adapted from various sources.^{81,83,84}

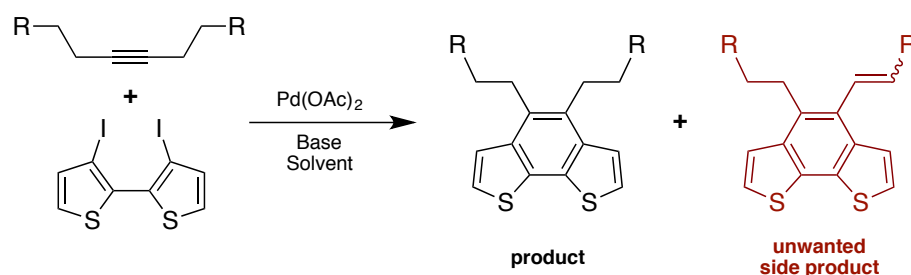


Figure 2.42 – Generic alkyne ring closure using 3,3'-diiodo-2,2'-bithiophene and alkyne showing alkene side product (red)

The use of an inorganic base such as M_2CO_3 (where $\text{M} = \text{Na}, \text{K}$ or Ag) for the reduction of Pd(II)I_2 to Pd(0) during the catalytic cycle can cause the unwanted side product seen in Figure 2.42 to form. Therefore the sterically bulky amine base⁸⁴ N,N -Dicyclohexylmethylamine (Cy_2NMe)⁸⁵ was used to retard the formation of the allene intermediate which goes on to form the unwanted alkene side product.

Due to the large amount of viscous/tacky black material and low yields obtained when purifying the ring closed **TzBTz** unit **2.7** via the boronic ester route, it was assumed there was significant degradation of the thiazole occurring during the reaction. It was deduced that there must be a trade-off between the temperature (energy) and time needed for the reaction to proceed against the decomposition that was clearly occurring at the high reaction temperature. To investigate this further, a smaller commercially available alkyne (6-dodecyne) was chosen so that the ring closure reaction could be monitored via GCMS throughout the reaction to determine at what point there was no longer any starting material remaining (Figure 2.43).

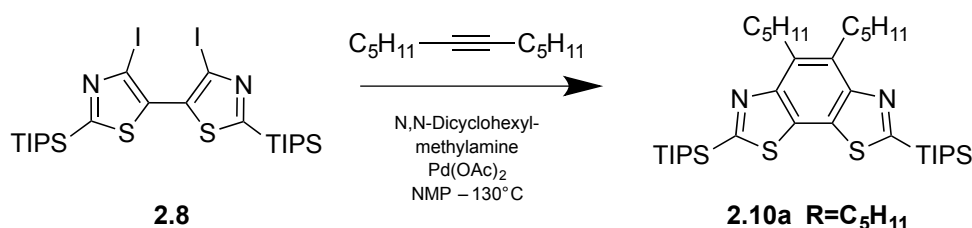


Figure 2.43 – Test reaction ring closure using iodation route and commercial alkyne

To improve on the previous routes yield (Figure 2.40– 13% max. isolated yield) throughout the reaction (Figure 2.43), hourly aliquots of the sample were taken before working them up and running GCMS analysis.

In an oil bath at 130 °C, the reaction had proceeded to approximately 80:20 **2.8:2.10a** within 2 hours and to completion within 3-4 hours. Past this point, the lack of starting material **2.8** meant the only process occurring was that of decomposition, impacting yield. Through this optimisation, the yield was pushed to 21% (average), which although not as high as hoped was still considerably better than the previous route.

Confirmation of the fully ring-closed product free from either of the potential alkene side products (Figure 2.44) required a number of different NMR experiments.

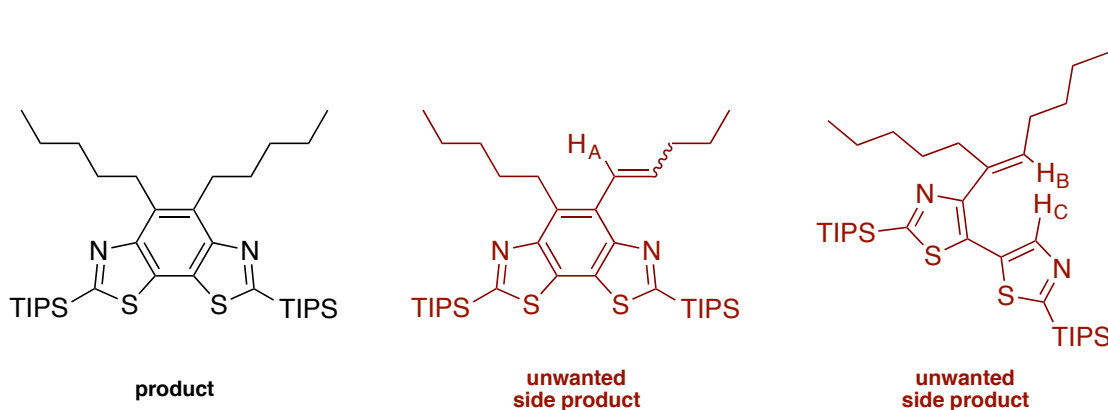


Figure 2.44 – Potentially unwanted side products from the ring closure reaction

A simple ¹H NMR (Figure 2.45) showed a clean spectrum with the visible peaks being at the correct chemical shifts and with the correct integrations, implying a highly pure main product. Had either of the unwanted side-products been present post-purification, then a characteristic peak would be present in the 4-7 ppm region corresponding to an alkene proton either within the ring-closed alkyl chain (H_A) or the partially attached alkyl chain (H_B). The partially ring-closed product would also have an additional proton present in the aromatic region (H_C). The lack of such peaks confirms neither of the side products were present.

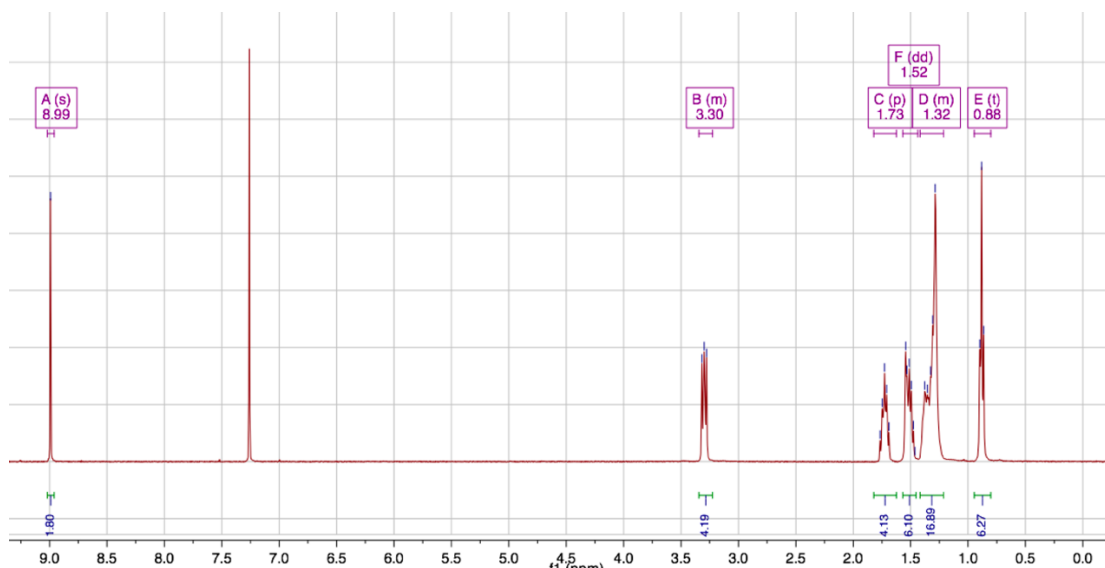


Figure 2.45 – NMR of 2.10a showing lack of alkene peak

An incredibly useful NMR technique called heteronuclear multiple-bond correlation spectroscopy (HMBC) was also used. HMBC shows the through bond correlation (2-4 bonds) between two different nuclei (in this case, ^1H and ^{13}C) – specifically, between the newly aromatic carbon (C_1) and the protons on the alkyl chain (H_1) – Figure 2.46. C_1 would appear in the aromatic region of the ^{13}C NMR (120-160 ppm) post ring closure, whereas before it would have been in the alkyne region (70-80 ppm). In addition, before the reaction H_1 is found at around 2 ppm in the ^1H NMR, whereas after the reaction it shifts up to 3.3 ppm due to its proximity to the newly electronegative environment of the aromatic ring.

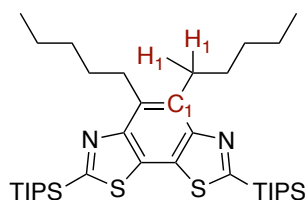


Figure 2.46 – Atom numbering of 2.10a to show HMBC between H_1 and C_1

Therefore, a direct through bond correlation between these two peaks with an alkene free proton NMR would indicate the ring closure and hence product **2.10a** had formed as expected. This can be seen in Figure 2.47 below by the two labelled peaks at ‘3.3, 133.4’ and ‘3.3, 154.8’ – directly correlating a through bond link between H_1 and C_1 .

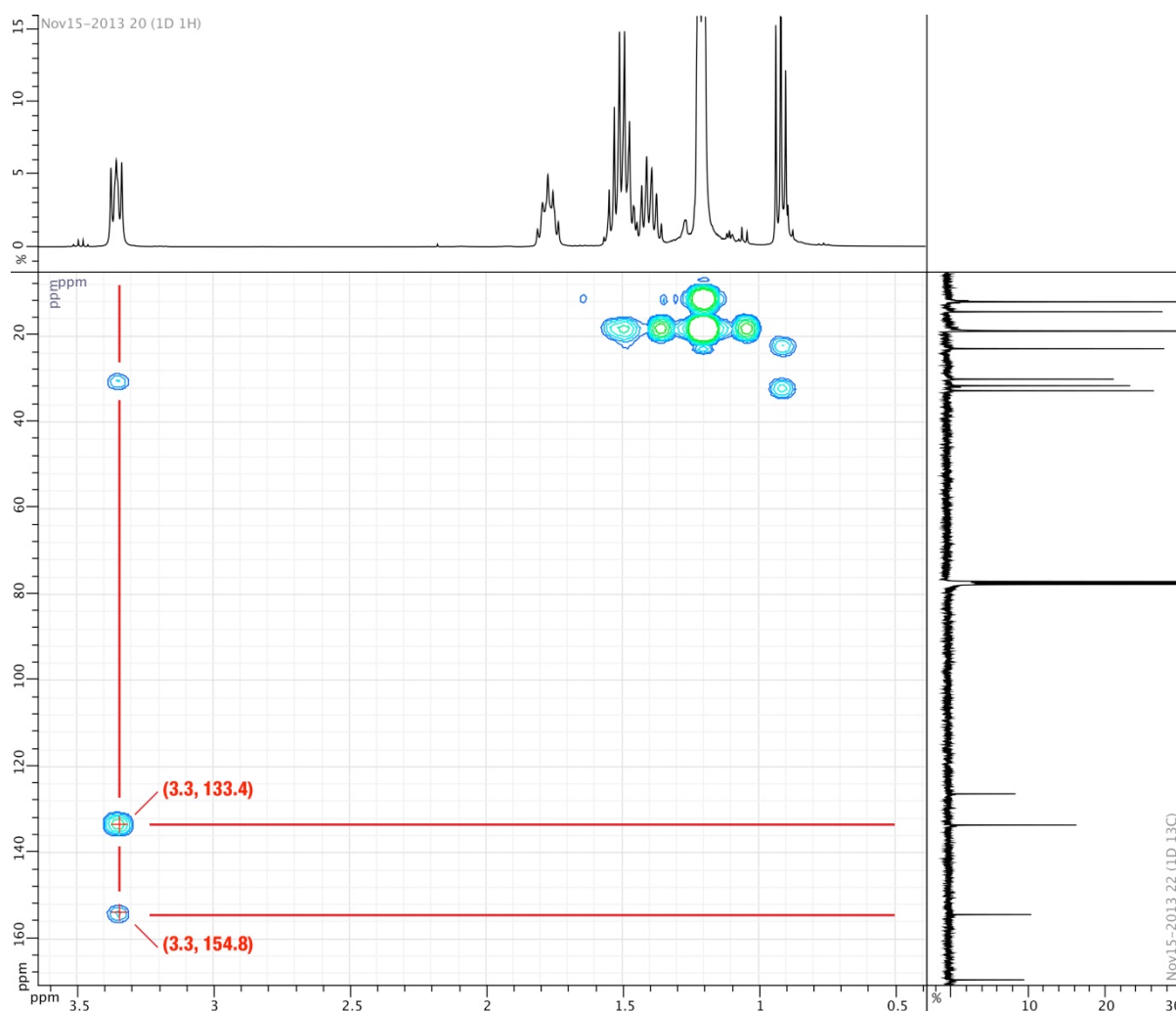


Figure 2.47 – HMBC showing through bond CH_2 proton linked with aromatic carbon

Using the knowledge gained during the investigations of the $-\text{C}_5\text{H}_{11}$ ring closure, successfully forming **2.10a**, formation of the $-\text{C}_{16}\text{H}_{33}$ derivative was attempted but unfortunately proved fruitless. Although there was a small percentage of product formed according to the NMR spectra, this was incredibly hard to isolate, with sub-1% yields. A possible reason for this could be to do with the tetratriacont-17-yne, in which the active alkyne site needed to perform the insertion sits in the middle of the $\text{C}_{34}\text{H}_{66}$ chain. The greasy nature of this alkyl chain means that the alkyne functional group is most likely extremely closed off and sterically blocked by the wrapping of the chains, hindering insertion into the active palladium centre. Due to this slowed reaction rate, the thiazole decomposition pathway would come to

dominate over periods at such high temperatures, meaning that the starting materials would have decomposed before forming the ring-closed product.

2.2.4 Longer alkyl chains, scale up and bromination

Originally, the $-C_{16}H_{33}$ alkyl chains were chosen as a way to increase the solubility of the **DTBTBT** polymer originally synthesised by Biniek et al. (Figure 2.31).⁵⁷ The solubility issues stemmed from the exceptionally rigid ring system consisting of 6 conjoined aromatic rings, requiring the extra-long solubilising groups to enable polymerisation with the un-alkylated co-monomers (thiophene, thienothiophene and benzothiadiazole).

The new smaller thiazole-based ring system, although planar, consists of only 3 conjoined rings, negating this need for such long solubilising $-C_{16}H_{33}$ alkyl chains, especially if polymerised with an alkylated co-monomer. Therefore, by choosing a co-monomer which is also alkylated, the balance between alkyl chains long enough to achieve high molecular weight and good processability, and short enough to not hinder π - π -stacking between the conjugated backbone can be achieved.

It was decided that an interesting concept would be to explore the backbone asymmetry of the **TzBTz-TBT** repeating unit in Figure 2.36. The aim was to enabling a degree of orbital hybridisation between the electron rich **TBT** unit and the more electron deficient **TzBTz**. Due to the relatively small difference between the electron density of the two monomers, the material would be expected to have a wide band gap whilst still performing well in ambipolar transistors. By using the **TBT** co-monomer as opposed to **CPDT**, the alkyl chains on both monomers will be of an in-plane sp^2 nature, with the aim of creating a crystalline structure with strong π - π -stacking between the polymer chains (aiding charge transport).

The choice of alkyl chain length therefore comes down to a combination of literature surveys and chemical intuition to choose a length which finds the balance between solubility and

molecular order. A multitude of polymers such as **pBTTT**,⁸⁶ **PQT**⁸⁷ and **PheDOT**⁸⁸ have used the $-C_{12}H_{25}$ alkyl chain with high degrees of success. Müllen et al.⁶¹ have shown that an increase in curvature along the backbone can aid in solubility and therefore it could be possible to use an even shorter chain than $-C_{12}H_{25}$. **PFO** (poly(9,9-dioctylfluorene)) is one of the most famous materials in the field of plastic electronics⁸⁹ and has adequate solubility using only two $-C_8H_{17}$ alkyl chains protruding from the bridging carbon at the 9-position in an sp^3 manner. Although **TzBTz** and **TBT** have sp^2 alkyl chains attached to the bridging carbons, the increase in backbone curvature compared with **PFO** should be enough for a $-C_8H_{17}$ chain to provide adequate solubility in the final polymer whilst allowing good backbone packing.

Having chosen the $-C_8H_{17}$ length, the required alkyne was then synthesised as per the previous method by taking the commercially available 1-decyne, deprotonating with *n*-BuLi in THF/HMPA before quenching with 1-bromooctane to form octadec-9-yne (**2.9b**). This was then ring-closed as per Figure 2.48 with **2.8** to form **2.10b**.

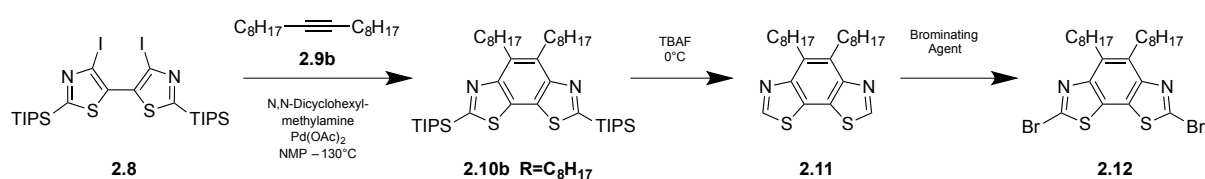


Figure 2.48 – Synthetic route to final C8-TzBTz monomer 2.12

Palladium residue was removed by passing **2.10b** through a pad of silica in hexane before the crude reaction mixture was reacted directly with a solution of TBAF to remove the protecting TIPS group and yield **2.11** with an inclusive yield of 30% for both the ring-closure and de-protection steps.

Bromination of **2.11** was initially attempted according to the literature method for the **TBT** monomer using NBS in DMF,⁸³ but no reaction occurred. It is likely that the α -position on **2.11** was too deactivated for electrophilic addition to occur due to the adjacent in-plane

nitrogen atom which – being more electron poor than carbon – would not favour the positive intermediate (at the 3 position) being formed during the reaction. Therefore, progressively harsher conditions were attempted with: i) NBS in chloroform/acetic acid, ii) bromine and iii) heating with bromine; with none of these conditions resulting in any bromination. Hence, much harsher conditions were used in which the α -protons were removed using *n*-BuLi and the lithiated species was quenched with 1,2-dibromo-1,1,2,2-tetrachloroethane as the brominating agent. Purification by column chromatography yielded the final monomer **2.12** in good yield (89%), ready for polymerisation.

2.3 Synthesis of TBT co-monomer

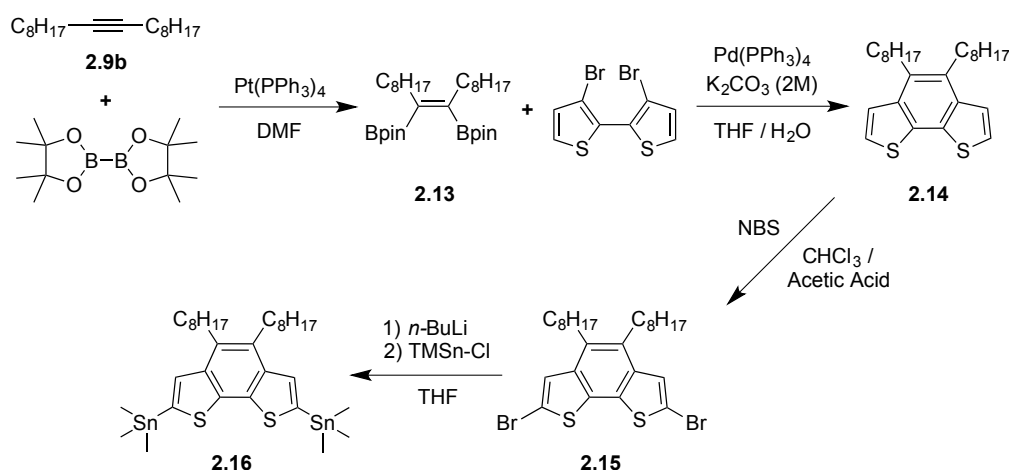


Figure 2.49 – Synthetic route to final C8-TBT monomer 2.16

The synthesis of the **TBT** co-monomer was adapted from the literature procedure given by Biniek et al.⁵⁷ among others.^{90,91} The boronic ester **2.13** was synthesised using the Z-selective platinum catalyst as before, and then **2.13** was used to perform a Suzuki ring closure with the commercially available 3,3'-dibromo-2,2'-bithiophene to give **2.14** in moderate yields. The bromination of **2.14** at the α -position was a simple acetic acid-catalysed NBS bromination to yield **2.15**.⁸³ The bromines were removed with *n*-BuLi via a metal-halogen exchange to form the lithiated species that was quenched with trimethyltin chloride to yield the **TBT**-tin

monomer **2.16** as a clear oil. The NMR showed approximately 15% of the mono-tin species was present in the product, which if used 'as is' would drastically affect the polymer molecular weight by acting as an end-capper (see Carothers' equation – Chapter 1 – equation 1.9). This mono-stannylated product therefore had to be removed. Due to the instability of electron rich tin monomers on silica, preparative GPC (which uses the minor size differences between the mono- and di-tin species to separate them out) was selected as the purification method. Due to the size difference between the mono- and di-tin being so small compared to the size of the whole molecule, each successive purification cycle resulted in a loss of yield, albeit resulting in the exceptionally pure product (**TBT – 2.16**) suitable for step-growth polymerisation.

2.4 Polymerisation

There are few other Stille polymerisations of thiazole-based polymers with a bromine in the 2-position performed in literature. The majority of thiazole-based monomers for use in organic electronics use an electron rich flanking group at the 2-position of the thiazole as these are often easier to work with synthetically.^{92,93} They are also easier to use in terms of predictability: as already shown, there can be problems with the deactivated nature of the carbon at the 2-position. Therefore, without literature precedent the first system that was tested was based on the conditions regularly used in the laboratory by Schroeder et al.⁹⁴ for Si-IDT thiophene copolymers. This was a standard microwave-assisted coupling using an exact one-to-one ratio of the two monomers (**2.12** & **2.16**) with Pd(PPh₃)₄ in *o*-xylene (Figure 2.50).

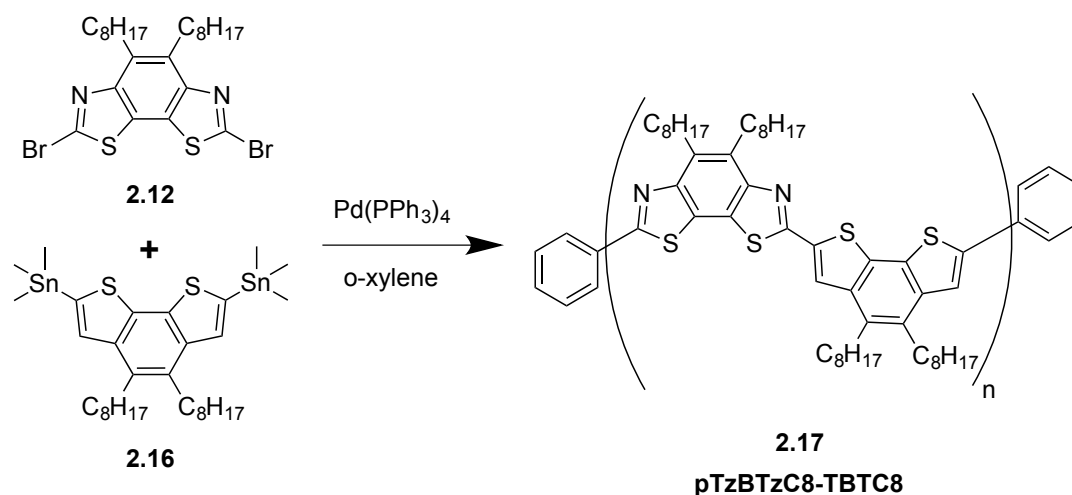


Figure 2.50 – Polymerisation of TzBTzC8 (2.12) and TBTC8 (2.16)

Exceptionally high purity and careful weighing of the exact mass of each monomer is required to gain high molecular weights in step growth polymerisation, especially when performed on such a small scale (100 mg) compared with the accuracy of the balance (0.1 mg). Therefore, an approximate quantity of the oily tin monomer **2.16** was dissolved in diethyl ether (1-2 mL) and added into an accurately pre-weighed microwave vial. The ether was removed under reduced vacuum and then left to dry for 24 h on a high-vacuum line to remove any residual ether. The vial/monomer was then weighed again to give an accurate weight and therefore number of moles of **2.16**, after which the calculated weight of solid **2.12** was added. As per the literature, Pd(PPh₃)₄ was then added before the vial was evacuated and filled with argon, and previously de-gassed *o*-xylene was added. The mixture was then heated in the microwave for 30 min at 180 °C before being end-capped with the addition of trimethyl(phenyl)tin followed by bromo-benzene.

On removal from the microwave, the resultant crude polymer (**pTzBTzC8-TBTC8 – 2.17**) was bright orange/yellow in colour. It was precipitated in HCl-acidified methanol before being Soxhlet extracted in acetone, hexane and chloroform, from which little polymer was extracted. The material was removed from the Soxhlet thimble to conduct solubility tests and it was found the polymer was insoluble in hot chlorobenzene and di-chlorobenzene.

The lack of polymer solubility even in the harshest of boiling solvents was most likely due to the length of the alkyl chains being too short combined with the fact they are bonded in an sp^2 fashion to the already extremely planar backbone. Although it was expected that the four chains and curved backbone across the monomer units would provide adequate solubility, this was clearly not the case. Another possibility was that some kind of cross-linking reaction had occurred that resulted in an insoluble mesh. Although unlikely, this could easily be tested by co-polymerisation of **TzBTzC8** – **2.12** with a commonly used highly soluble monomer. This would rule out any side reactions and, if successful, suggest that the lack of solubility was solely due to the short alkyl chain length rather than a thiazole cross-linking side reaction.

CPDTC16 (Figure 2.51) was previously synthesised by Dr. Miquel Planells in the laboratory according to a published literature procedure,^{95,96} and this was used directly for polymerisation with **TzBTzC8**. The same polymerisation conditions were used as for **TzBTzC8-TBTC8**, with the hypothesis being that the longer $-C_{16}H_{33}$ chains of the CPDT protruding from the backbone in an sp^3 manner from the central carbon should confer excellent solubility to the polymer, proving that the **TzBTz** monomer could undergo Stille polymerisation successfully.

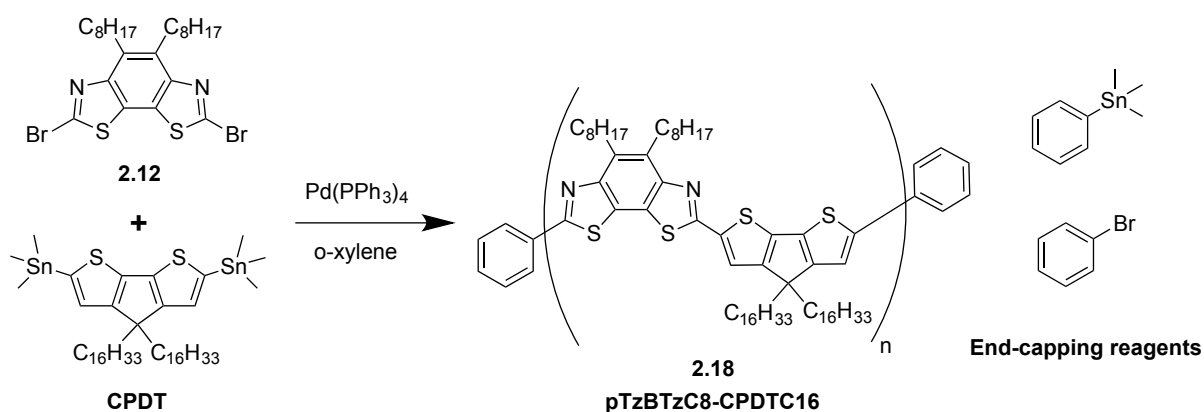


Figure 2.51 – Polymerisation of TzBTzC8 (2.12) and CPDTC16

The resultant polymer (Figure 2.51) was dark red in colour and after washing with methanol and acetone via Soxhlet extraction, the polymer was found to dissolve mostly in the hexane Soxhlet fraction, suggesting a very high degree of solubility. The low molecular weight ($M_n = 7.6$ kg/mol, $M_w = 15$ kg/mol) could account for this increased solubility compared with the **TzBTzC8-TBTC8** polymer, although it was promising that the polymerisation was successful and it proved that monomer **2.12** could be polymerised without undergoing detrimental side reactions.

During investigation of polymer **2.17** and the monomers used, the GCMS of monomer **TzBTzC8 (2.12)** showed that the purified materials contained approximately 3% of the mono-bromo, mono-chloro moiety (Figure 2.52) due to use of 1,2-dibromo-1,1,2,2-tetrachloroethane as the quenching agent during the bromination step.

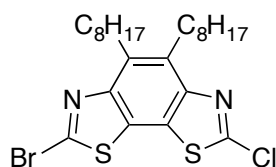


Figure 2.52 – Mono-bromo, mono-chloro impurity in 2.12 monomer

This was missed initially due to the lack of obvious differentiation between the bromo- and chloro-moieties in the ^1H , ^{13}C , or MALDI-TOF data, combined with the fact that separation via column chromatography is impossible due to their highly similar R_f values. The chloro-moieties presence would therefore mean that there was effectively 3% of an end-capping reagent within the polymer reaction mixture, which would have potentially devastating effects on the molecular weight (according to Carothers' equation). Simply changing the quenching reagent from 1,2-dibromo-1,1,2,2-tetrachloroethane to tetrabromo-methane would be expected to solve this issue. The 3% impurity could explain the low molecular weight for the **TzBTzC8-CPDT** polymer, and also suggests that the $-\text{C}_8\text{H}_{17}$ chains were such poor

solubilising alkyl chains that even at low molecular weight, the **TzBTzC8-TBTC8** polymer was still insoluble.

Having determined the length of alkyl chain and bromination quench step to be the most likely issues with the previous insoluble polymerisation, a new synthetic pathway was deduced.

2.5 Alkyl chains – increasing solubility

2.5.1 Choosing the right length

Having previously discussed the plethora of polymers that have successfully used $-C_{12}H_{25}$ linear side chains, and the issues previously seen with increasing the length to $-C_{16}H_{33}$, it is a logical choice to go directly between $-C_8H_{17}$ and $-C_{16}H_{33}$, and use a $-C_{12}H_{25}$ chain. The reasoning for this is that a median length should be effective in transistor configurations, giving enough solubility to allow the final polymer to be processed, but not so much as to interfere with the packing arrangement, allowing high mobilities to be achieved.

The second thought was to synthesise a branched alkyl chain to sit on the co-monomer. This would increase solubility without significantly increasing the overall chain length, although this could have an effect on the packing due to the introduction of a branching point close to the backbone. It was expected that a polymer with branched chains would be high performing in photovoltaic devices compared with the all-linear polymer.

Bredas et al. performed an interesting computational study that looked into the impact of linear and branched side-chain placement on the polymer backbone in a bulk-heterojunction device with PCBM.⁹⁷ They concluded that the closer the PCBM sits to the electron poor ‘acceptor’ moiety on the backbone, the less charge recombination occurs, and that the addition of branched side chains on the electron rich ‘donor’ monomer increases the probability that the PCBM will be located thusly.

Donor	Acceptor	
Linear	Branched	↓ Increase in probability that PCBM is located on the acceptor moiety
Linear	Linear	
Branched	Linear	

Table 2.2 – Table showing the effect of linear vs. branched alkyl chains on the donor / acceptor moieties in relation to PCBM placement in a BHJ device⁹⁷

Therefore, it was concluded that the location of the branched chains should be on the electron rich **TBT** “donor” monomer, with the linear chains attached to the more electron poor **TzBTz** “acceptor” monomer with the aim of enhancing solar cell performance.

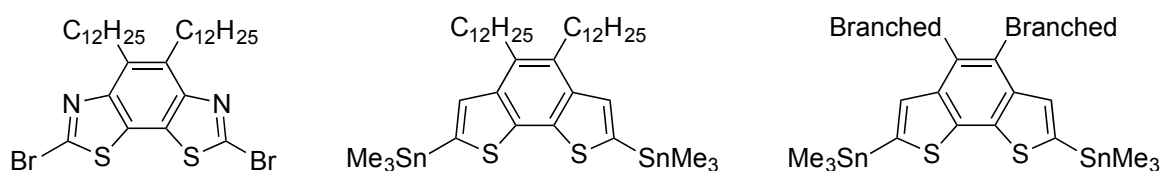


Figure 2.53 – Theorised TzBTzC12, TBTC12 and TBTCbranch monomers

2.5.2 Alkyl chain synthesis

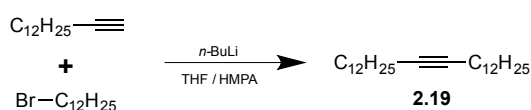


Figure 2.54 – Synthesis of C12 alkyne 2.19

The synthesis of the -C₁₂H₂₅ alkyne (**2.19** – Figure 2.54) followed the same procedure as **2.9b**. Commercially available 1-tetradecyne was lithiated with *n*-BuLi/HMPA and quenched under heat with 1-bromododecane to yield hexacos-13-yne (**2.19**) in good yield.

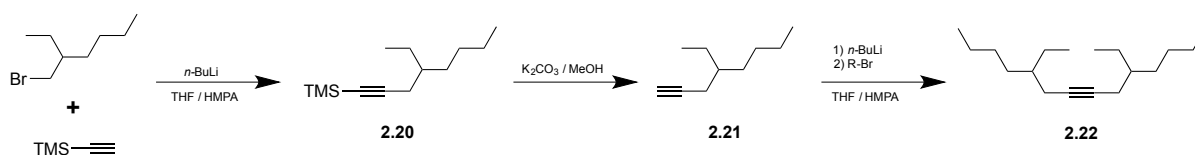


Figure 2.55 – Synthesis of branched alkyne 2.22

The initial synthetic strategy to synthesise the branched chain (**2.22**) followed that of Luscombe et al.,⁸³ although it was found that the reaction did not proceed with HMPT as directed, with the harsher HMPA⁹⁸ being required for any reaction to occur (**2.20**). Even using HMPA as a cation selective co-solvent, the nature of the reaction was temperamental, meaning it regularly did not proceed at all (possibly due to E2-elimination), prompting a different synthetic route to be sought to increase both yield and utilise less toxic reagents.

The Nobel Prize-winning Sonogashira reaction, first reported in 1975,⁹⁹ is a widely studied and highly effective carbon-carbon bond forming reaction that proceeds via cross-coupling of alkynes and aryl-/vinyl- -halides/-triflates. This being the case, the coupling of more de-activated alkyl-alkynes with alkyl-electrophiles has always been difficult due to their lack of reactivity (difficult oxidative addition)¹⁰⁰ and the tendency of the electrophile to undergo β -elimination. Eckhardt et al.¹⁰¹ were some of the first to use an *N*-heterocyclic carbene with bulky tert-butyl substituents to afford high yields in Sonogashira couplings of de-activated alkynes and alkyl-electrophiles.

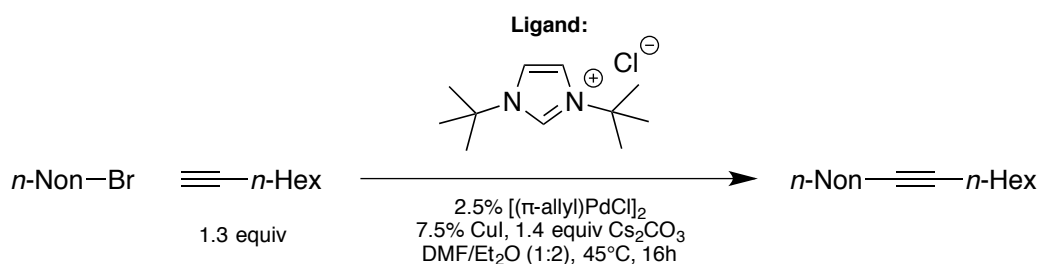
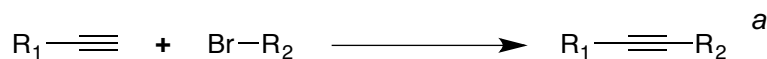
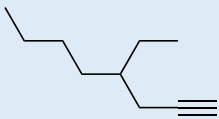
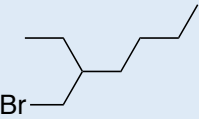
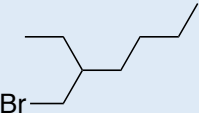
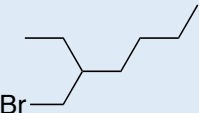


Figure 2.56 – Successful Sonogashira reaction between deactivated aryl-bromides and aryl-alkynes as reported by Eckhardt et al.

In an attempt to use this procedure (Figure 2.56) to synthesise the branched alkyne **2.22**, a number of different test reactions were performed in which various combinations of branched bromides and alkynes were tested.



Reaction	R ₁	R ₂	Outcome
1	 ^b		No product
2	TMS—C≡C		No product
3 ^c	C ₆ H ₁₃ —C≡C	Br—C ₈ H ₁₇	Successful
4	C ₆ H ₁₃ —C≡C		No product

a) 1.3 equiv. alkyne, 2.5% [(π -allyl)PdCl]₂, 7.5% CuI, 1.4 equiv. Cs₂CO₃, DMF/Et₂O (1:2), 45 °C, 16 h; b) Synthesised from previous low yielding HMPA procedure; c) Literature conditions¹⁰¹

Table 2.3 – Sonogashira test reactions

As can be seen from Table 2.3, the only successful reaction was the repeat of literature conditions (reaction 3) using *n*-alkyl chains without any branching points. Reactions 1, 3 and 4, in which commercially sourced 2-ethylhexyl bromide was used, proved to be unsuccessful, showing no product even when analysed using quantitatively sensitive GCMS. One possible explanation for this outcome is that the branching point sits at the β -position to the bromine, causing enhanced β -elimination to the corresponding alkene.

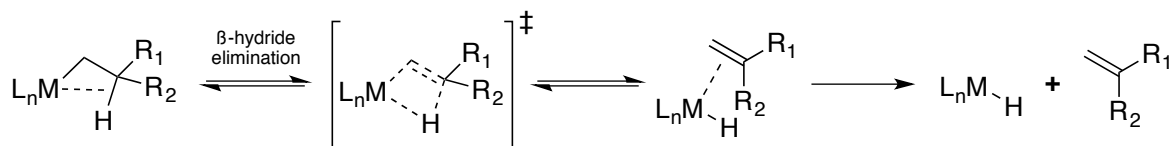


Figure 2.57 – β -hydride mechanism enhanced through electron donating R groups¹⁰²

Bonding from the C-H σ -orbital of the β -hydride to the metal centre is suppressed when R₁ and R₂ are electron withdrawing,¹⁰³ reducing the agostic donating effect and therefore β -

hydride elimination. Consequently, when R_1 and R_2 are electron donating as in the case of the branched alkyl chains, the agostic donating effect is potentially enhanced, which would result in increased β -elimination.¹⁰⁴

Isolating the proposed β -elimination alkene side product proved problematic, and as the hypothesised problem was the location of the branching point on the β -carbon, a branched alkyl chain with a different branching location was sought as an alternative way to test this elimination theory. Therefore, the synthesis of an ‘extended branching point’ alkyl bromide (**2.26**) was undertaken.

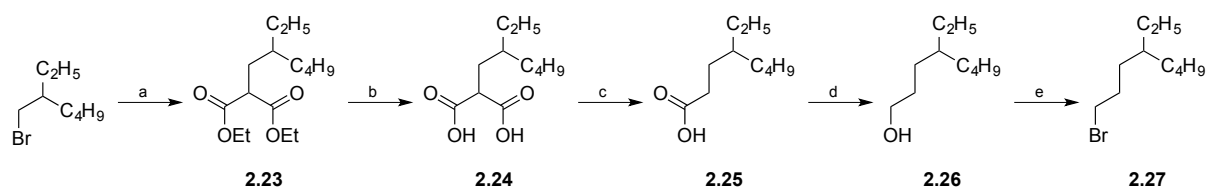


Figure 2.58 – Synthesis of extended branching point alkyl chain precursor

a) NaOEt/EtOH/50 °C/[EtOC(O)]₂C b) KOH/HCl c) 180 °C d) LiAlH₄/Et₂O e) NBS/PPh₃/DCM

Using the method used by Chen et al.¹⁰⁵ and Meager et al.,¹⁰⁶ an extended branching point alkyl chain was synthesised as in Figure 2.58 to add two additional CH₂ units between the bromine and the branching point of 2-ethylhexyl bromide (**2.27**). Diethyl malonate is deprotonated at the α -carbon to the carboxylate group ([EtOC(O)]CH₂) using the equivalent sodium ethoxide base (to minimise trans-esterification) to form the α -carbanion which undergoes enolate formation. The enolate carbanion then attacks the 2-ethylhexyl bromide starting material to form the mono-alkylated malonic ester – a single equivalent of the NaOEt base is required to stop di-alkylation through re-formation of a second enolate carbanion¹⁰⁷. Vacuum distillation of the malonic ester yields **2.23** as an oil. Further ester hydrolysis of **2.23** with KOH forms the di-acid, which when quenched with HCl forms **2.24** as a white solid. The solid **2.24** is then heated at 180 °C for 1 h to allow mono-decarboxylation to occur – melting occurs at ~140 °C with decarboxylation starting slowly at ~150 °C. This forms the

carboxylic acid **2.25** as a colourless oil. A simple reduction using two equivalents of lithium aluminium hydride yields the alcohol **2.26** as another colourless oil that was used crude in the next step. A classic Appel reaction of alcohol **2.26** in DCM with PPh_3 and NBS occurs via the oxyphosphonium intermediate to yield the final ‘extended branching point’ bromide alkyl chain **2.27**, which was again purified under vacuum distillation.

On successful completion of the synthesis of the new branched alkyl-bromide (**2.27**), a Sonogashira reaction with TMS-acetylene was once again attempted (Figure 2.59), providing **2.28** albeit in low yields (<20%).

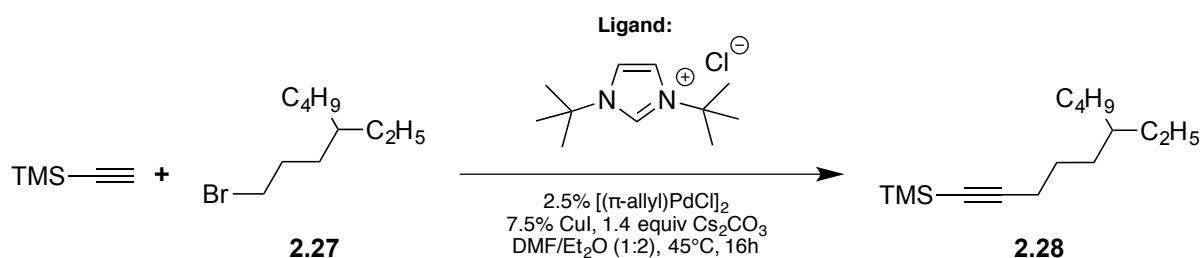


Figure 2.59 – Sonogashira coupling of 2.27 and TMS-acetylene

The low yield was most likely due to the labile Si-C bond forming ethylene gas under basic conditions, which would promptly escape from the reaction. A large excess of TMS-acetylene added into the reaction over time could be used to try to minimise this side reaction, or alternatively a stronger protecting group such as TIPS could be used.

Another option was to use the $n\text{-BuLi}$ /HMPA route (Figure 2.55) that had been successful before for n -alkyl chains, but was very low yielding (<10%) for the previous branched chains (due to the theorised E2-elimination). Lithiation of the TMS-acetylene with $n\text{-BuLi}$ in the presence of HMPA followed by quenching with **2.27** produced the product **2.28** in high yields (72%), thus confirming and solving the problem of the β -hydride being adjacent to the branching point causing E2-elimination ($n\text{-BuLi}$ route) or β -elimination (Sonogashira route). Although the Sonogashira reaction could have been further optimised, the successful HMPA route was used on scale-up due to time considerations and to move the project forward.

From here, **2.28** was de-protected with K_2CO_3 in MeOH to produce the terminal alkyne **2.29** in high yields. A repeat of the n -BuLi/HMPA lithiation followed by quenching with **2.27** resulted in the final branched alkyne **2.30** in large quantities (>10 g) and good yield.

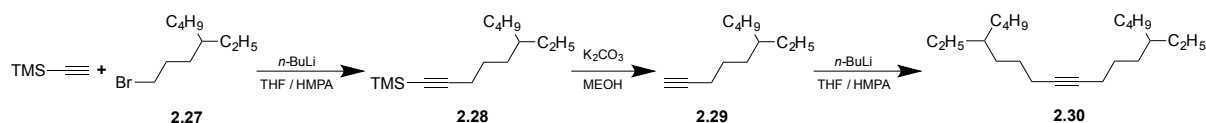


Figure 2.60 – Synthesis of final branched alkyl chain 2.3

With both the longer $-C_{12}H_{25}$ alkyne and the branched alkyne now having been synthesised, the new **TzBTz** and **TBT** monomers could be formed through a repeat of the ring closure steps as detailed in Sections 2.2.2 and 2.3.

2.6 Repeat of monomer ring closures

2.6.1 TzBTzC12 final monomer synthesis

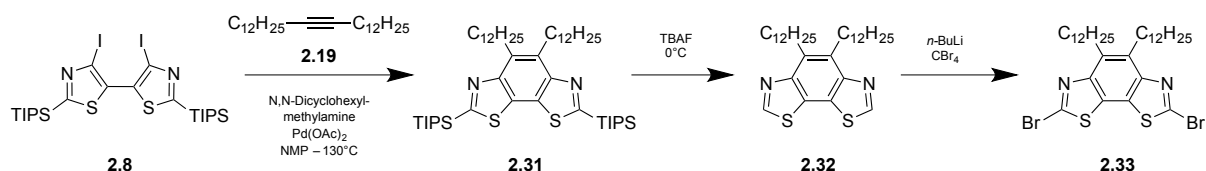


Figure 2.61 – Synthetic procedure for the synthesis of TzBTz(C₁₂) final monomer

As seen in Figure 2.61, the iodinated thiazole intermediate **2.8** underwent annulation with the newly synthesised symmetric alkyne **2.19** using the previously investigated procedure to give **2.31**. After a short plug through silica to remove palladium, this was directly deprotected in TBAF to yield **2.32** with a moderate 31% yield for the combined two steps. Previously, the brominating agent 1,2,2,2-tetrabromo-1,1-dichloroethane had produced a 3% mono-chloro adduct that could have affected the molecular weight of the final polymer, and therefore a new brominating agent, tetrabromomethane, was used to avoid this issue. Lithiation of **2.32** with n -BuLi and quenching with tetrabromomethane afforded the final monomer **2.33** as a white solid in low yields (28%), but high purity (>99% by GCMS).

2.6.2 TBTC12 and TBTCbranch co-monomer synthesis

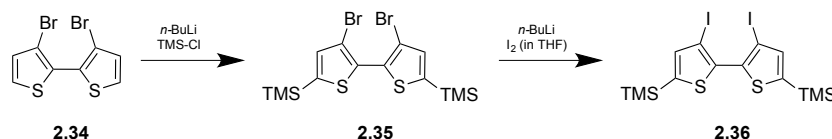


Figure 2.62 – Synthesis of the iodinated thiophene intermediate 2.36

The iodinated thiophene intermediate (2.36) was synthesised as shown in Figure 2.62, first through lithiation with LDA and protection of the thiophene α -protons with TMS chloride to give the protected 2.35, followed by metal-halogen exchange using n -BuLi and quenching with a solution of iodine in THF to give 2.36. The benefit of this was to capitalise on the reliability of the alkyne ring closure reaction with the synthetically expensive branched alkyl-alkyne, which otherwise would have to be Pt-coupled to yield the *Z*-alkene boronic ester before using the temperamental Suzuki annulation. The ‘synthetically cheap’ iodinated intermediate 2.36 can be made on large scales and easily purified, negating the need for further synthetic procedures on the ‘expensive’ alkyl-alkynes.

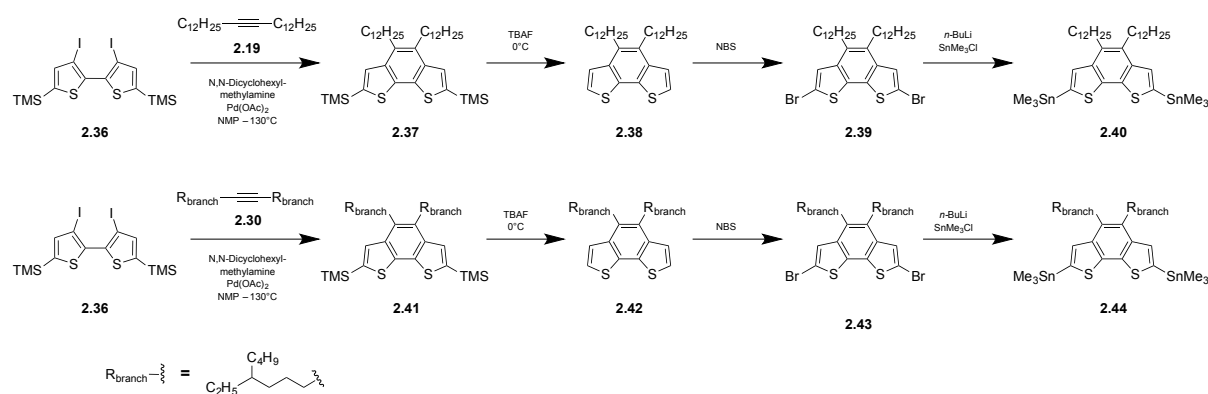


Figure 2.63 – Synthetic procedures for the synthesis of TBTC12 and TBTCbranch final co-monomers 2.40 and 2.44

As shown in Figure 2.63, intermediate 2.36 underwent a ring closure with both the linear $\text{-C}_{12}\text{H}_{25}$ and branched alkyl-alkynes to form 2.37 and 2.41, respectively, in good yields (55–60%). These both underwent deprotection in TBAF before bromination with NBS, yielding 2.39 and 2.43. Lithiation followed by quenching with trimethyltin chloride afforded

the crude monomers, which were individually passed through the recycling GPC to separate the mono- and di-tin adducts and afford monomers **2.40** and **2.44** in high purity, both as clear oils.

2.7 Polymerisation repeat

The previous polymerisation of the shorter $-C_8H_{17}$ chained monomers yielded **pTzBTzC8-TBTC8 – 2.17**, and although the polymer was insoluble, the catalyst/solvent system was deemed successful in terms of reactivity after further testing with the **pTzBTzC8-CPDTC16** polymerisation. As before, the two tin monomers **2.40** and **2.44** were oils, meaning that to get an accurate mass for polymerisation, their separate dissolution in ether before transferring to their respective reaction vials followed by the removal of the solvent was required prior to weighing. Once accurate masses had been attained, the exact molar quantity of monomer **2.33** could be calculated, weighed and added into the reaction vessel for each polymerisation, along with the $Pd(PPh_3)_4$ and degassed *o*-xylene, followed by polymerisation in the microwave (Figure 2.64) as before (Section 2.4). An end-capping procedure was then followed in which an excess of trimethyl(phenyl)tin was added to each reaction mixture and heated for 3 min at 180 °C to react with any remaining bromo-end groups. Then, a larger excess of 1-bromobenzene was added to each and the solutions heated for a further 3 min to react with any residual tin monomer end-groups and excess trimethyl(phenyl)tin.

End capping is an important procedure, as there is literature precedent that links it to large increases in performance. Kuwabara et al.¹⁰⁸ have shown that end-capping can reduced the sensitivity of devices to active layer thickness and thermal degradation, while Koldemir et al.¹⁰⁹ have shown that transistor mobility can be increased by an order of magnitude by end-capping due to a perceived improvement in polymer organisation (increasing charge transport).

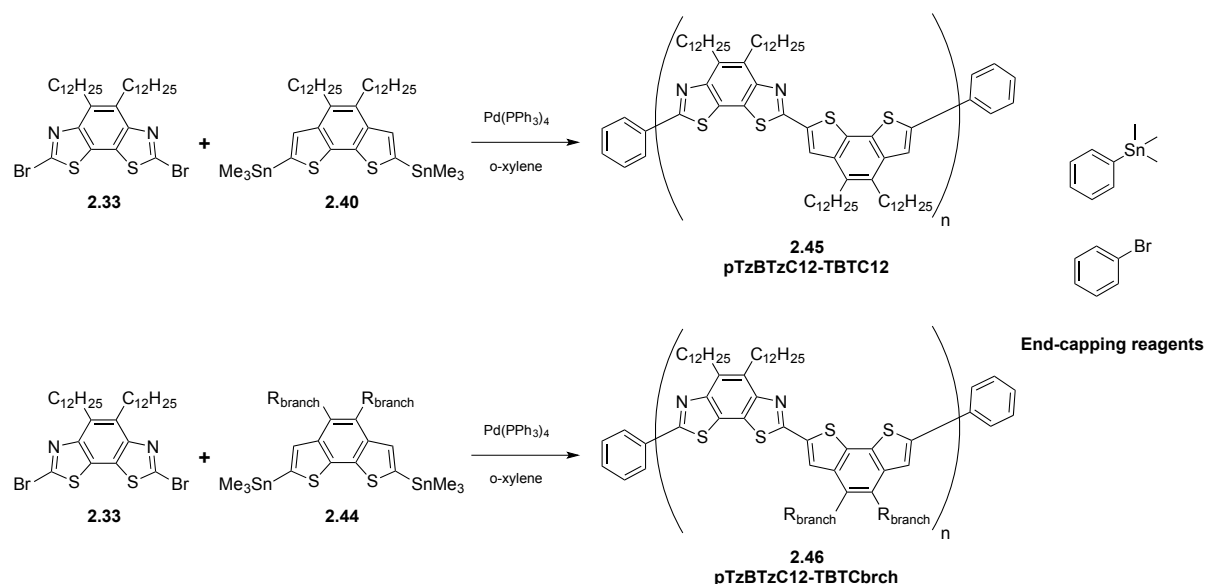


Figure 2.64 – Polymerisation of TzBTzC12 with TBTC12 and TBTCbranch

After the end-capping procedure, both polymers were the same bright orange colour seen for the -C₈H₁₇ polymer on removal from the microwave. The polymers were precipitated in acidified MeOH before being Soxhlet extracted in methanol, acetone, hexane and chloroform. Although some low molecular weight polymer was observed in the hexane fractions (which were discarded), the majority of both polymers dissolved into their respective chloroform fractions. These fractions were washed with diethyldithiocarbamate as a palladium scavenger¹¹⁰ before the solvent was removed completely in vacuo. The polymers were then each dissolved in a minimum volume of chlorobenzene before being precipitated in MeOH and filtered on a fine sinter to yield both polymers with reasonably large and suitably comparable molecular weights:

TzBTzC12-TBTC12 (55 mg, GPC: $M_n = 63$ kg/mol, $M_w = 105$ kg/mol, $\bar{D} = 1.66$).

TzBTzC12-TBTCbranch (77 mg, GPC: $M_n = 61$ kg/mol, $M_w = 117$ kg/mol, $\bar{D} = 1.91$).

2.8 Chapter conclusions

This chapter has reported on the successful synthesis on a new series of thiazole-based polymers for use in OPV and OFET devices and a new annulation method for thiazole-based aromatic compounds. After theorising and choosing a new thiazole-based monomer system to focus on, the initial synthesis involved attempted annulation using a $-C_{16}H_{33}$ alkyl chain. These long chains proved to be problematic, and therefore an investigation was undertaken to understand, confirm, and optimise the annulation reaction further using shorter $-C_5H_{11}$ alkyl chains.

The annulated product was successfully confirmed via HMBC-NMR and the reaction time optimised via GMCS. On considering the optimal alkyl chains length, a $-C_8H_{17}$ alkyl chain was chosen, synthesised (**2.9b**) and used in the annulation of the thiazole and thiophene precursors to yield the **TzBT (2.12)** and **TBT (2.16)** monomers respectively. On polymerisation to form **TzBTzC8-TBTC8**, the linear alkyl chains were too short to solubilise the polymer despite being present on both monomers, and hence a new set of alkyl chains were required.

To aid in the solubility, a longer linear chain (**2.19**) and a branched chain (**2.22**) were theorised. The synthesis of the linear $-C_{12}H_{25}$ alkyne precursor (**2.19**) was a repeat of the $-C_8H_{17}$ alkyne precursor synthesis (**2.9b**) that once successfully completed was used in the ring closures to yield the new monomers **TzBTzC12 (2.33)** and **TBTC12 (2.40)**.

The synthesis of the branched alkyl chain precursor (**2.22**) using the commercially available 2-ethylhexyl bromide proved to be problematic due to apparent E2- or β -elimination, and thus the product could not be obtained. A new somewhat protracted additional five-step synthesis was undertaken to move the branching point away from the β -position, giving a new branched alkyl-bromide starting material (**2.27**) with an 'extended branching point'. This

successfully solved the E2-/β-elimination issue during the alkyne precursor synthesis, allowing **2.30** to be synthesised and used for annulation to form the new monomer **TBTCbranch (2.44)**.

Once the monomers had been synthesised, the polymerisation resulted in two novel wide band gap polymers: **pTzBTzC12-TBTC12 (2.45)** and **pTzBTzC12-TBTCbranch (2.46)**. Their similarly high molecular weights allow an interesting comparison to be made between them without having to consider molecular weight effects. This comparison will allow observation of the effect of changing the alkyl chains from linear to branched on this new polymer series. This further analysis can be seen in the next chapter.

Due to the extended length of the synthesis and low yielding nature of the optimised thiazole ring closures, the initially theorised **DTzBTBTz** monomer requiring a double thiazole ring closure was not taken forward.

Chapter 3

Characterisation and analysis of TzBTzC12-TBTC12 and TzBTzC12-TBTCbranch

3.1 Background

As discussed in the introduction to Chapter 2, the main aim of the project was to synthesise a new set of polymers with improved properties compared to **CPDT** and **BDT** (Figure 2.35).

This was carried out using the synthetic strategy of including in-plane alkyl chains to allow closer π - π -stacking of the polymer backbones to improve charge transport, and the use of the electron poor **TzBTz** unit to enable orbital hybridisation with the **TBT** monomer to reduce the band gap and increase the absorption overlap with the AM1.5 solar spectrum. This orbital hybridisation also aimed to tune the energy levels to improve charge injection and extraction, and therefore increase the ambipolar properties of the polymers in OFET devices.

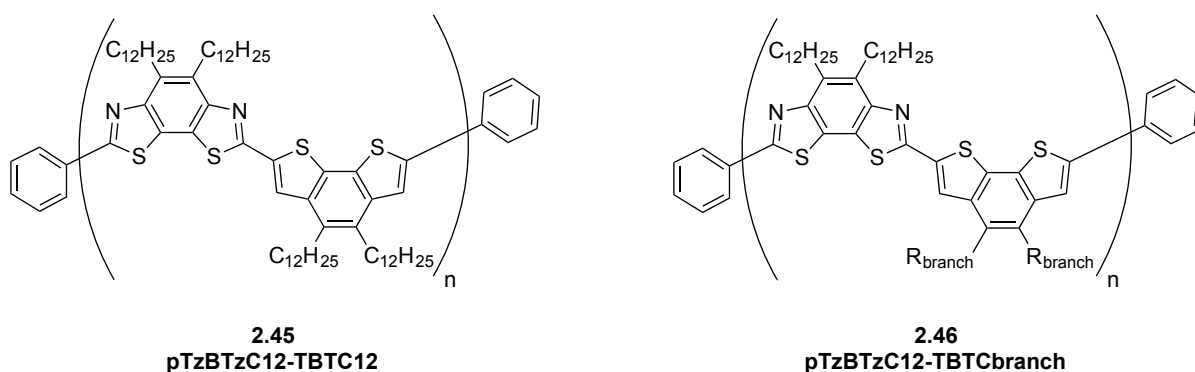


Figure 3.65 – Polymers pTzBTzC12-TBTC12 and pTzBTzC12-TBTCbranch

The following chapter focusses on the optical, morphological and device analysis of the two polymers successfully synthesised and discussed in Chapter 2, namely **pTzBTzC12-TBTC12 (2.45)** and **pTzBTzC12-TBTCbranch (2.46)**.

Polymer	M_n (kg/mol) ^a	M_w (kg/mol) ^b	$\mathcal{D}$ ^c	DP_n ^d
2.45	63	105	1.66	59
2.46	61	117	1.91	61

a) Number average molecular weight (M_n); b) Weight average molecular weight (M_w);
c) Polydispersity index ($\mathcal{D} = M_w/M_n$); d) Degree of polymerisation ($DP_n = M_n/m_r$) giving average number of repeat units

Table 3.4 – Summary of molecular weights for polymers 2.45 and 2.46 as determined using GPC (eluent: chlorobenzene, 80 °C)

To understand the likely organisation of the polymer, the minimum energy confirmation of a pentamer of the **TzBTz-TBT** backbone was calculated using Gaussian with the ω B97XD/6-31G* functional/basis set (Figure 3.66). The pentamer unit with methyl alkyl chains was chosen to maximise the understanding of the long-range order across the polymer backbone whilst also minimising the computational time required.

Molecular modelling can be a useful tool to understand the geometry and energetics along a single strand of a polymer backbone – as the number of monomer units within the model increases, the calculation comes closer to resembling a ‘polymer-like’ structure. As alkyl chains often affect intermolecular packing as opposed to backbone conformation, their addition to molecular models is computationally expensive for relatively little increase in accuracy.

Density functional theory (DFT) calculations based on the B3LYP (Becke 3-parameter; Lee, Yang, Parr)^{111–113} functional are common in organic electronics, with this particular modelling parameter being one of the most commonly used by chemists in the literature. However, B3LYP has a significant self-interaction error that tends to over-delocalise the electronic orbitals, an error that is extenuated in moieties with planar conformations such as the **TzBTz-TBT** unit. These issues can be somewhat mitigated by using a method which balances the local DFT exchange with the non-local Hartree-Fock (HF) exchanges, which tend to over-localise, suppressing the electron self-interaction error and giving a truer picture of the localisation or delocalisation of the molecular orbitals. Once such method that has been proven to have greater accuracy when predicting polymer electronic properties is using the ω B97XD functional – a long-range-corrected functional with tuned range-separation parameters.^{114,115} By comparing the difference between the calculated HOMO energy level and the calculated ionisation potential of a molecule (Koopman’s theorem),^{114,116} an iterative approach to finding a specific omega ‘ ω ’ function can be taken for each molecule to give a

more accurate trade-off between the HF and DFT functionals used. This increase in accuracy allows a fairer comparison between the calculated and observed energetic properties of the **TzBTz-TBT** system, and is the reason that the ω B97XD/6-31G* functional/basis set will be used for molecular modelling calculations.

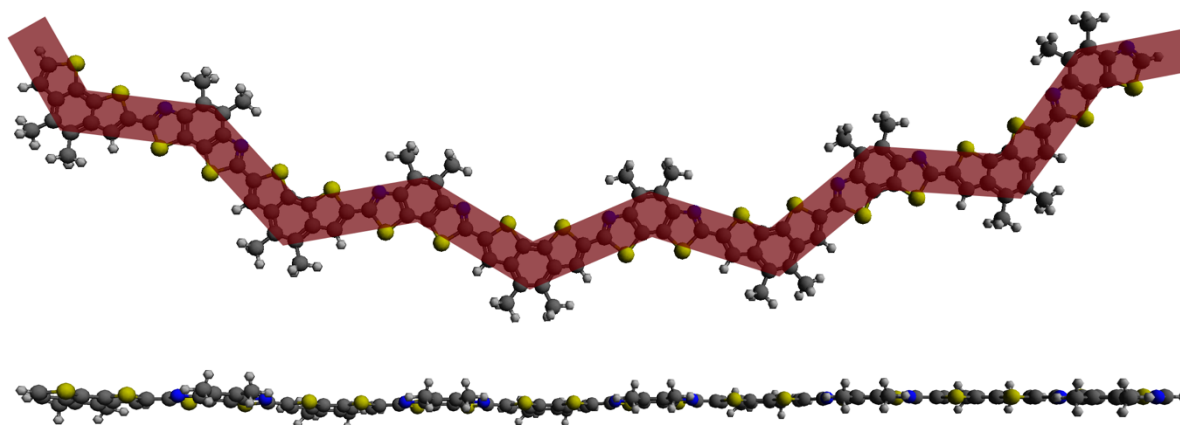


Figure 3.66 – Minimum energy conformations of a pentamer of the TzBTz-TBT backbone calculated using Gaussian with the ω B97XD/6-31G* functional/basis set

Figure 3.66 (bottom) shows the highly planar nature of the backbone, with the co-monomer dihedral angle being less than 2° throughout. This results in no twisting along the polymer backbone either between the units or across the pentamer as a whole – allowing for strong π - π interactions between polymer chains. It has been theorised by Bronstein et al. that such planarity occurs when thiophene and thiazole units are adjacent to each other due to nitrogen lone pair donation into the sulphur antibonding orbitals (Figure 3.67).¹¹⁷

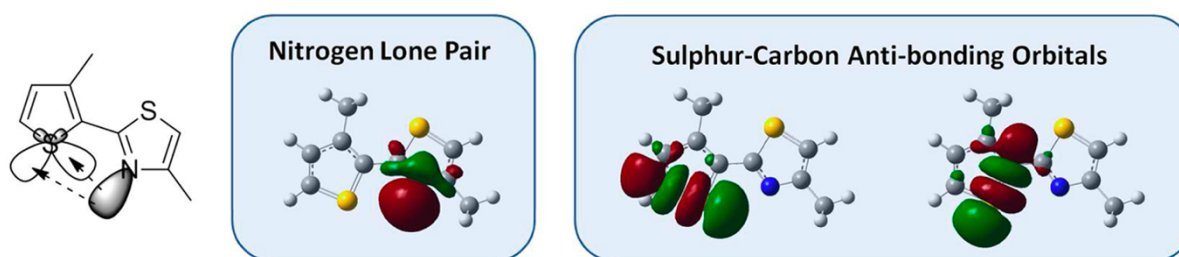


Figure 3.67 – Modelling by Bronstein et al.¹¹⁷ showing nitrogen lone pair donation from the thiazole nitrogen lone pair to the thiophene sulphur anti-bonding orbitals.

This ‘conformational lock’, in which the S–S dihedral angle between the **TzBTz** and **TBT** units is set at 180° , can be seen in the potential energy curve (Figure 3.68).¹¹⁸ It shows a large energy barrier must be overcome for any torsional twisting to occur between units, leading to a highly planar and stable confirmation across the molecule. The potential energy curve quantifies this stabilising interaction when looking at the S–S dihedral, where an angle of 0° is ~ 0.1 eV less stable than an angle of 180° .

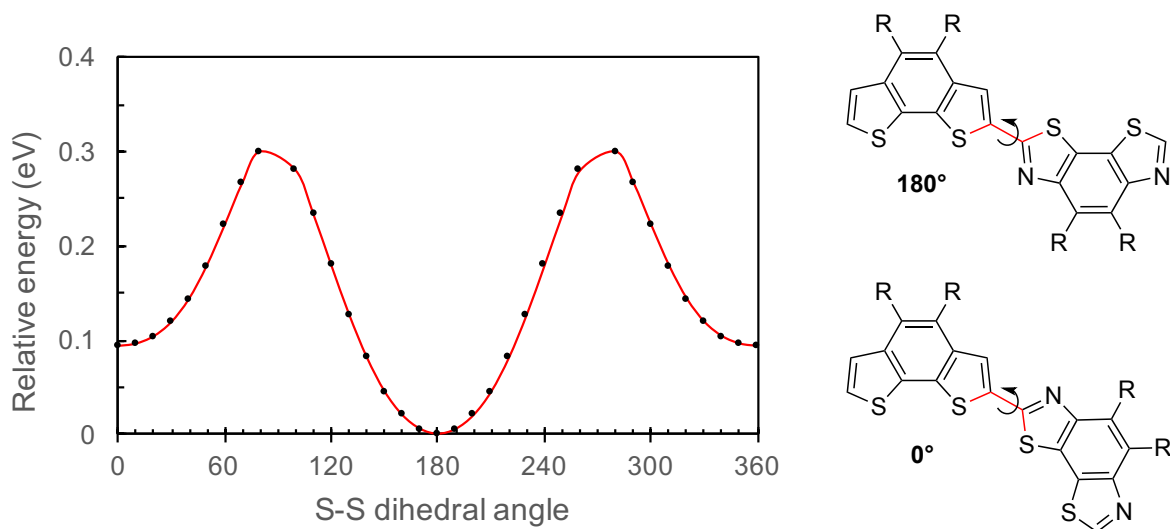


Figure 3.68 – Torsional strain around the S–S dihedral within a TzBTz-TBT dimer

The molecular model in Figure 3.66 (top) also illustrates a short zig-zag pattern between monomer units along the polymer chain, with a slight curvature in the long-range order over a number of repeat units. This could potentially limit the regularity of stacking between polymer chains, inhibiting charge transport. This said, Müllen et al. found that curvature along the backbone can help to increase solubility,^{61,62} which could be a possible reason for the good solubility observed for both polymers **2.45** and **2.46** in non-chlorinated solvents (*o*-xylene) even at high molecular weights.

With the linear (**2.45**) and branched (**2.46**) polymers having molecularly identical backbones, the only differences between the properties and performances of the two polymers should

originate from the differences in the side chains and the intermolecular polymer interactions and packing effects resulting from said differences.

3.2 Optical properties

The absorption properties of polymers **2.45** and **2.46** were studied via UV-Vis spectrometry (normalised) in dilute chlorobenzene solutions and as thin films spun from chlorobenzene (5 mg/mL) onto glass substrates (Figure 3.69).

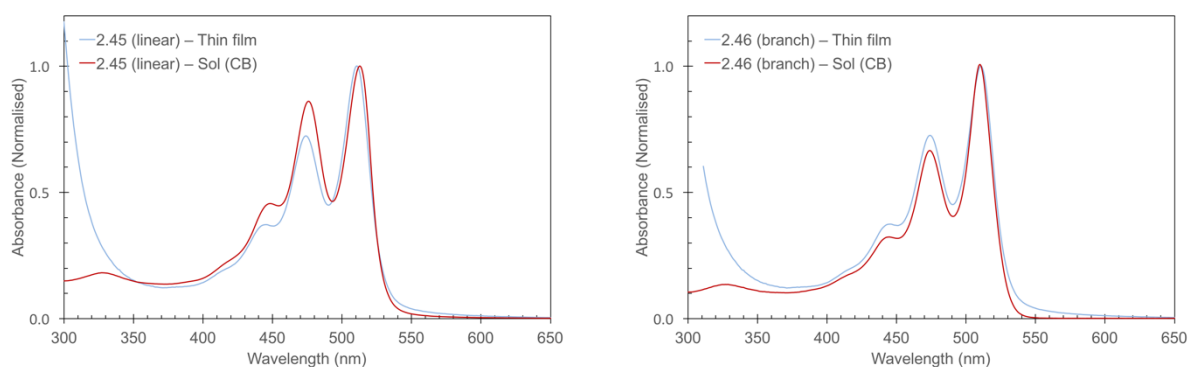


Figure 3.69 – UV-Vis spectra of TzBTzC12-TBTC12 (2.45 – left) and TzBTzC12-TBTCbranch (2.46 – right) both in solution (CB) and as thin films

The similarity of the UV-Vis spectra of **2.45** and **2.46** can be accounted for by the aforementioned identical nature of the polymer backbones. Both exhibit exceptionally defined spectra with a solution and thin-film λ_{max} at 510 nm, another strong peak at 473 nm, and a small secondary peak at 444 nm. Both of the solution spectra also show a small peak at 327 nm. All spectra (solution and thin film) show an on-set of absorption at 540 nm (within experimental error), giving optical band gaps (E_{opt}) of 2.3 eV. It could be argued that there is less donor-acceptor orbital mixing between the two monomers along the polymer backbone than expected, resulting in the wide band gap and discrete optical transitions.

Most polymers exhibit broad absorption profiles, often due to twisting along the backbone, which changes the conjugation length and therefore the absorption maximum. As the polymer chains move from free movement in solution to thin films, there is often a bathochromic shift

observed as the polymers pack closer together in the solid state, forming stronger π - π -interactions between the chains and lowering their energy – something not seen in Figure 3.69.

The uncharacteristically defined spectra of **2.45** and **2.46** suggest highly aggregated and exceptionally rigid polymers in both films and solutions with delocalisation of charges. There are also no obvious (usually broad) internal charge transfer peaks visible in the spectra. This peak often indicates donor-acceptor character along the polymer backbone, suggesting that the transitions are mostly π to π^* in nature.

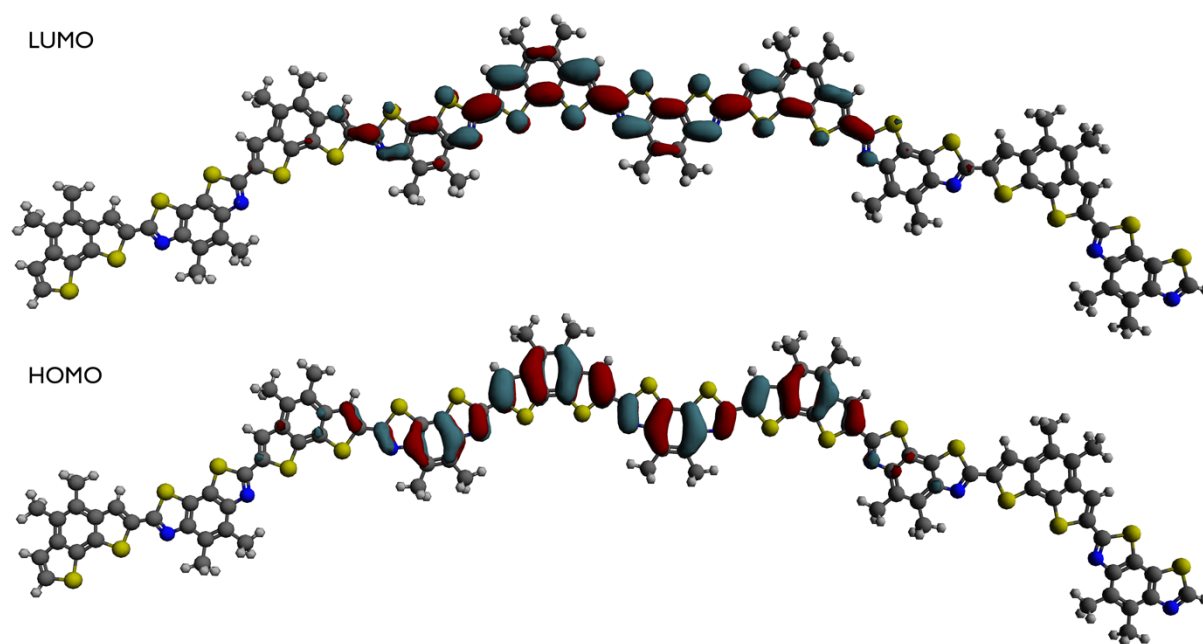


Figure 3.70 – DFT-HF calculation of HOMO (bottom) and LUMO (top) for the TzBTz-TBT pentamer using the ω B97XD/6-31G* method and basis set

DFT-HF calculations on the **TzBTz-TBT** pentamer using the ω B97XD/6-31G* method and basis set⁹⁷ were performed to give graphic representations of the HOMO and LUMO. These are illustrated in Figure 3.70, and show the expected delocalisations of both frontier orbitals. In many donor/acceptor polymers, the LUMO is often localised on the electron poor monomer and the HOMO is localised on the electron rich monomer – this is indicative of orbital hybridisation which is one method of lowering the band gap. The delocalisation

observed in the DFT-HF calculations therefore confirms the suspected lack of donor/acceptor character and the wider than predicted band gap.

To investigate the effects of aggregation in solution and the possibility that strong interchain interactions were responsible for the lack of shift seen between the solution and thin film spectra, temperature dependant UV-Vis spectroscopy was performed (Figure 3.71).

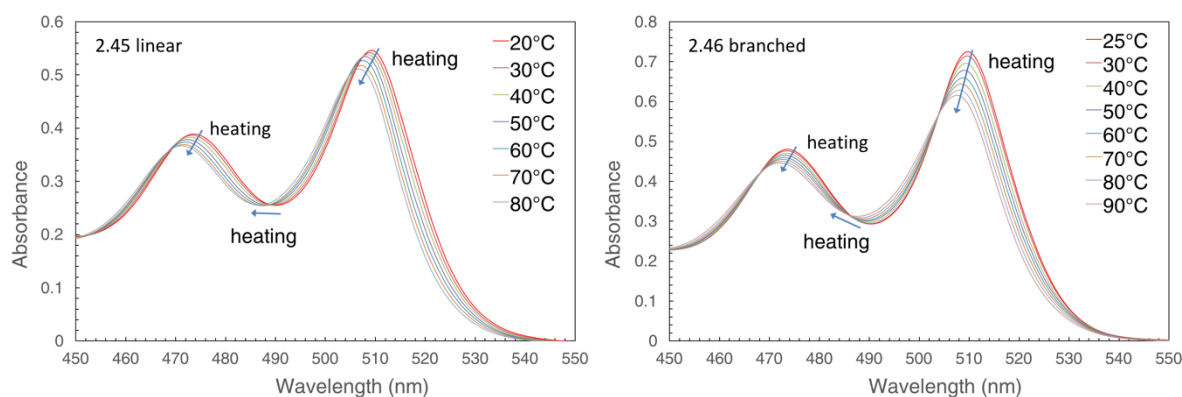


Figure 3.71 – Temperature dependant UV-Vis spectra for 2.45 (left) and 2.46 (right)

The two solutions were diluted down to as similar concentrations as experimental error would allow (approx. 7×10^{-5} mol/dm³) until their absorbance was less than 1. The two main observed effects for both of the polymers on heating in solution was a blue shift in wavelength of both the primary (510 nm) and secondary (475 nm) peaks, and a change in the absorbance ratio between the 510 and 475 nm peaks. The linear polymer (**2.45**) saw a shift in the λ_{max} of 4 nm (510 to 506 nm) on both the heating and cooling cycles, and the absorbance ratio of the primary (509 nm) to secondary (475 nm) peak decreased by around 3%.

The branched polymer (**2.46**) saw a smaller 2 nm shift (510 to 508 nm) in both the heating and cooling cycles, but the ratio between the 510 and 474 nm peaks saw the primary peak decrease 10% more than the secondary peak across the temperature range.

The weakness of the blue shifts and the small changes in the ratios of the two peaks in both materials is highly indicative that there is exceptionally strong aggregation in both materials,

with de-aggregation not occurring even at low concentrations, 80 °C and in the highly solvating solvent chlorobenzene.

The strong aggregation observed in the temperature dependent solution UV-Vis spectra is further corroborated by the lack of shift seen when moving from solution to thin film and the rigid planar structures seen in the DFT-HF calculations.

Polymer	$\lambda_{\max}$ (nm) ^a	E_{opt} (eV) ^b	ϵ ($10^3 \text{ M}^{-1}\text{cm}^{-1}$) ^c	$E_{\text{HOMO-CV}}$ (eV) ^d	$E_{\text{LUMO-CV}}$ (eV) ^d
2.45	510	2.3	74.1	– 5.6	– 3.4
2.46	510	2.3	93.6	– 5.6	– 3.4

a) Extracted from UV-Vis spectroscopy in thin film and solution; b) Estimated from optical absorption edge in thin films; c) Maximum molar extinction coefficient (per repeat unit); d) Extracted from CV onset of oxidation / reduction in 0.1 M $n\text{-Bu}_4\text{PF}_6$;

Table 3.5 – Polymer properties

A series of dilute solutions (in chlorobenzene) were used to calculate the maximum molar extinction coefficient per repeat unit for both polymers, giving values of $74,100 \text{ M}^{-1}\text{cm}^{-1}$ (**2.45**) and $93,600 \text{ M}^{-1}\text{cm}^{-1}$ (**2.46**) (Figure 3.72). This is over double the molar extinction coefficient of polymers that are considered to be highly absorbing, such as DPP-BDT ($31,400 \text{ M}^{-1}\text{cm}^{-1}$),¹¹⁹ and is therefore promising in terms of potential for solar cell applications.

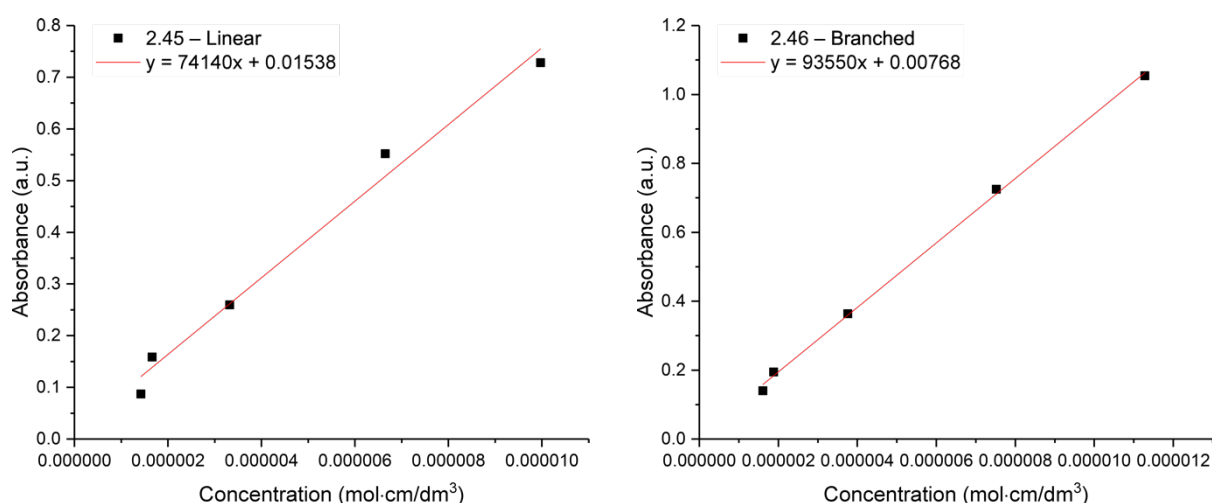


Figure 3.72 – Plots showing linear fits used to calculate the molar extinction coefficients of 2.45 (left) and 2.46 (right)

The ionisation potentials and electron affinities were measured via cyclic voltammetry (CV) to determine approximate values for the HOMO and LUMO levels, respectively (Table 3.5). The polymers were dissolved in chlorobenzene (10 mg/mL) before being spun on ITO coated films to act as the working electrodes. The scan rate was measured at 0.8 Vs^{-1} in a tetrabutylammonium hexafluorophosphate (0.3 M) electrolyte solution. The HOMO values were the same for both **2.45** and **2.46**, at -5.6 eV. With oxidative stability quoted as requiring a HOMO level below -5.2 eV,^{120,121} these polymers fall well within this stable regime – something qualitatively observed via a lack of tarnishing over time in air in the laboratory.

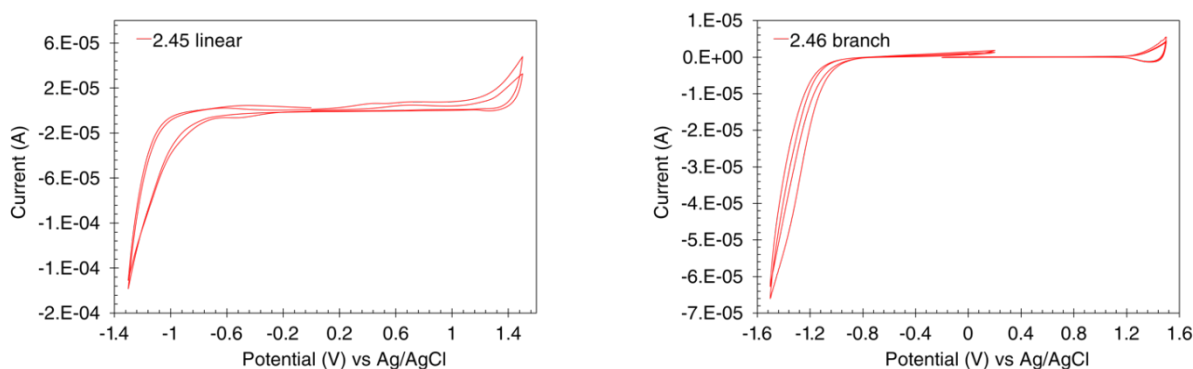


Figure 3.73 – Cyclic voltammograms of 2.45 (left) and 2.46 (right) spun as films from chlorobenzene (10 mg/mL) onto ITO substrates with tetrabutylammonium hexafluorophosphate electrolyte (0.3 M) at 0.8 Vs^{-1} ¹²²

The electrochemical band gaps of both polymers as determined by CV were 2.2 eV, similar to the optical band gap (2.3 eV). Although this wide band gap could potentially give rise to a large V_{OC} because of the deep HOMO, it also means a lack of overlap with the AM1.5 spectrum, which will severely limit light absorption and reduce photocurrent generation, consequently decreasing device current density.

3.3 Molecular packing

3.3.1 TGA and DSC

The two polymers proved to have exceptional thermal stability when tested using thermogravimetric analysis (TGA) at 25 to 700 °C, 10 °C / min. Decomposition of the materials, (defined by 5% weight loss) did not occur until 458 °C and 454 °C for **2.45** and **2.46**, respectively (Figure 3.74) – these are uncharacteristically high values for organic polymers.

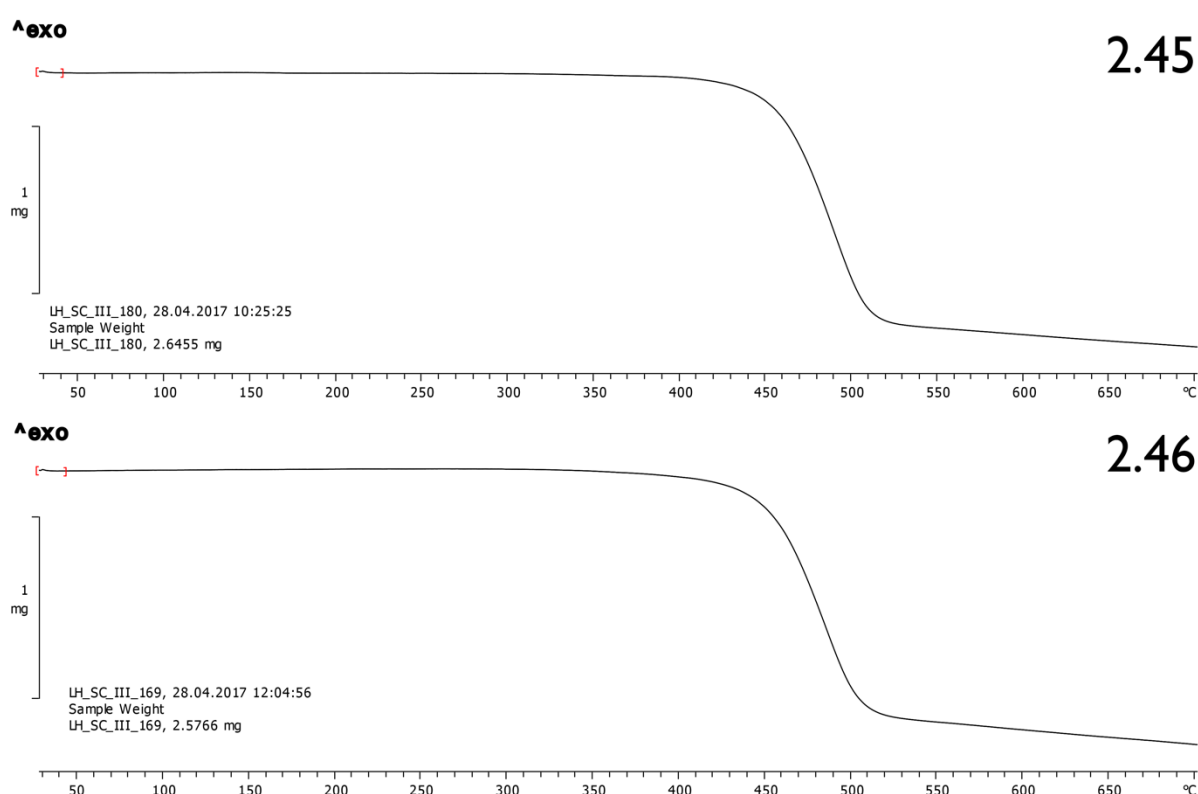


Figure 3.74 – TGA of polymers 2.45 and 2.46 under nitrogen atmosphere

The thermal properties were further probed using differential scanning calorimetry (DSC) – initially performed between -30 °C and 400 °C, post experimental review of the materials saw them degrade from an orange polymer to black carbonised material. This was most likely occurring due to sustained heating at the 400 °C during the 5-minute isotherm between each run, and therefore a lower ‘upper bound’ was chosen and the DSC performed between -30 °C

and 380 °C (both heating and cooling) at a rate of 10 °C / min to yield the DSC traces shown Figure 3.75).

The first cycle of each run is plotted on the top graph, with the second cycle below. The reason for this is that because often the fibrous nature of the materials stops the bottom of the DSC pan from being completely covered initially, potentially leading to different readings for the first cycle – this can be beneficial to see the polymer's initial state, but does not always give an accurate reproducible representation of the polymer's true melt/crystallisation characteristics. Once a full heating/cooling cycle has occurred, the polymer is assumed to have melted and cooled, therefore giving full coverage of the pan and removing any thermodynamically trapped state it may have been in previously. Both the first (top) and second (bottom) cycles of the DSC traces for heating (positive heat flow – red) and cooling (negative heat flow – blue) are therefore plotted in Figure 3.75 for polymers **2.45** (left) and **2.46** (right). The most common peak seen in DSC plots of organic polymers is the main backbone melt – this represents the energy required to break the intermolecular forces between the polymer chains, and if it is seen, it usually occurs above 150 °C. A second weaker transition often around 30-50°C can sometimes also be seen for the side chain melt, which occurs when side chains are ordered enough to crystallise. This thermal event is seen when there is enough energy in the system for the side chains to gain degrees of freedom, but not for the backbone stack to break apart.

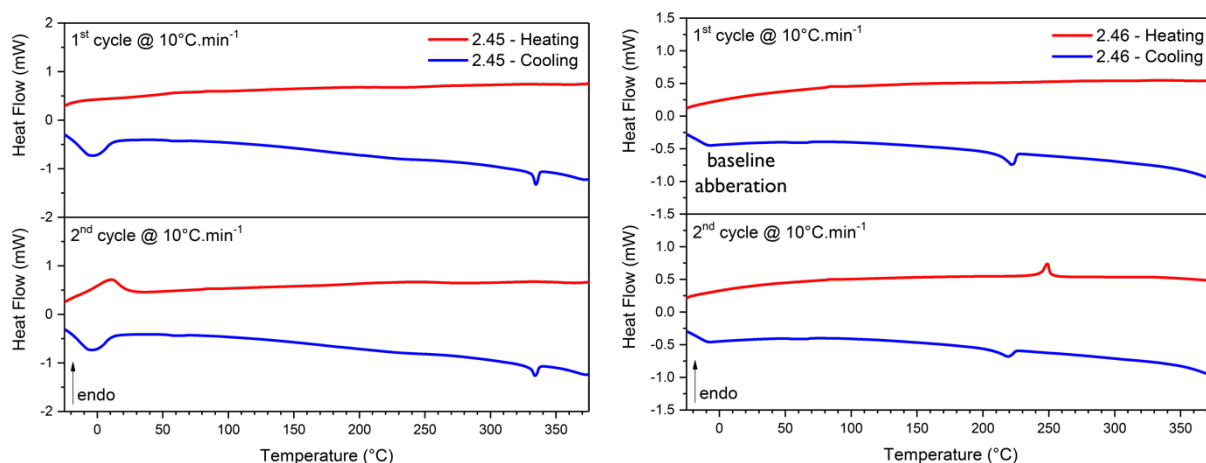


Figure 3.75 – DSC traces (under N_2) of 2.45 (left) and 2.46 (right) under heating and cooling cycles between $-25\text{ }^{\circ}\text{C}$ and $375\text{ }^{\circ}\text{C}$ ($10\text{ }^{\circ}\text{C} / \text{min}$). 1st cycle top, 2nd cycle bottom

Polymer	Cycle	Temp ($^{\circ}\text{C}$)	Integral (mW. $^{\circ}\text{C}$)	Enthalpy (J/g)
2.45	Cooling 1	- 4	-7.088	-13.3
2.45	Cooling 1	334	-1.772	-3.3
2.45	Heating 2	11	8.393	15.8
2.45	Cooling 2	- 5	-8.082	-15.2
2.45	Cooling 2	334	-1.4704	-2.8
2.46	Cooling 1	222	-1.937	-5.6
2.46	Heating 2	249	1.401	4.0
2.46	Cooling 2	219	-1.322	-3.8

Table 3.6 – DSC exo- and endothermic events for 2.45 and 2.46

The linear chained polymer **2.45** clearly shows a definitive backbone crystallisation at $334\text{ }^{\circ}\text{C}$ ($\sim 3\text{ J/g}$) on both the first cooling and subsequent cooling cycles with the event being reproducible over 4 heating and cooling cycles. No clear backbone melt is seen on the DSC, which due to the reproducibility of the crystallisation event, suggests the melt occurs over a long range and is a broad peak which is masked by the baseline and hence cannot be measured with this particular set-up. The linear polymer also clearly shows a definitively clear side chain melt at $11\text{ }^{\circ}\text{C}$ ($\sim 16\text{ J/g}$) and a crystallisation at $-4\text{ }^{\circ}\text{C}$ ($\sim 14\text{ J/g}$). The large

enthalpy associated with these events suggests a strong interaction between the polymer side-chains, but the unusually low temperature the event occurs at would mean the chains would be in a non-crystalline state at room temperature (for example during device fabrication).

The branched chained polymer **2.46** like the linear polymer shows a clear reproducible backbone crystallisation at 220 °C (~4.5 J/g), but unlike the linear polymer there is also a clear backbone melt at 250 °C (~4 J/g). No side chain melt is seen for the ethyl-hexyl chain, which is expected seeing as their bulky nature would be expected to inhibit crystallisation compared to the conformity of the linear chains.

Although the term crystallisation is used, kinetics play a significant role on the degrees of freedom the polymer has and therefore, there is a possibility that with the speed of cooling, the polymer can get kinetically trapped in a non-crystalline, glassy state as opposed to the true thermodynamic minimum. However, the presence of heating and cooling events in both polymers suggests a degree of molecular order corroborating with the aggregation between polymer chains observed in the temperature dependent UV-Vis spectra.

3.3.2 XRD

The molecular packing of the polymers was further investigated using X-ray diffraction (XRD) by drop casting thick films of polymers **2.45** and **2.46** on Silicon (100) substrates from a chlorobenzene solution (10 mg / mL) – Figure 3.76.

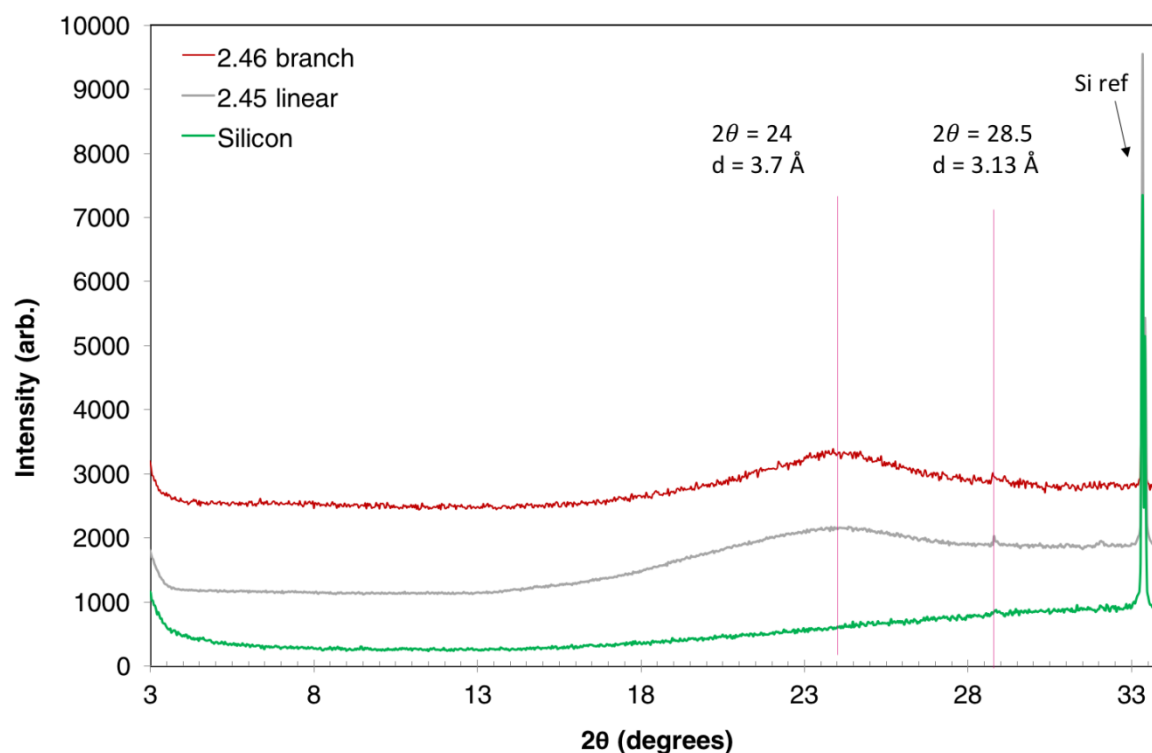


Figure 3.76 – XRD spectra of 2.45 and 2.46 films – films drop casted from chlorobenzene solutions onto Si (100) wafers. Films were measured as cast

The XRD spectra primarily shows a broad peak at a $2\theta = 24^\circ$ ($d \sim 3.7 \text{ \AA}$) when compared to the silicon background reference, most likely corresponding to some form of π - π -stacking. The broad nature of the peak indicates that this stacking was inhomogeneous in nature, and the peak does not correlate to a precise angstrom distance between polymer backbones. A small, sharp peak can be observed at $2\theta = 28.5^\circ$ ($d \sim 3.13 \text{ \AA}$) in both polymers, which could correspond to a slightly more ordered polycrystalline structure. However, the peak is exceptionally small when compared to both the broad peak at 24° and the Si reference peak.

3.3.3 Morphological conclusions

Overall analysis of the morphological natures of the polymers using the temperature dependant UV-Vis, DSC, and XRD data suggests that both polymers show signs of strong aggregation. Unfortunately, the strong inter-molecular bonding between the polymer chains seen in the UV-Vis and DSC does not appear to translate into a regularly ordered structure, as

illustrated by the broad peaks seen in the XRD spectra. This lack of defined order could potentially affect the charge-transport and subsequently device performances of the materials.

3.4 Devices

3.4.1 OFET results

The materials were tested for their suitability as hole transport materials through fabrication of OFET devices. Initially, devices were fabricated in a bottom-contact, top-gate configuration using a CYTOP dielectric,⁴¹ with the best devices being those that were annealed for 1 h at 100 °C. The transfer curves and output characteristics obtained under these conditions can be seen in Figure 3.77.

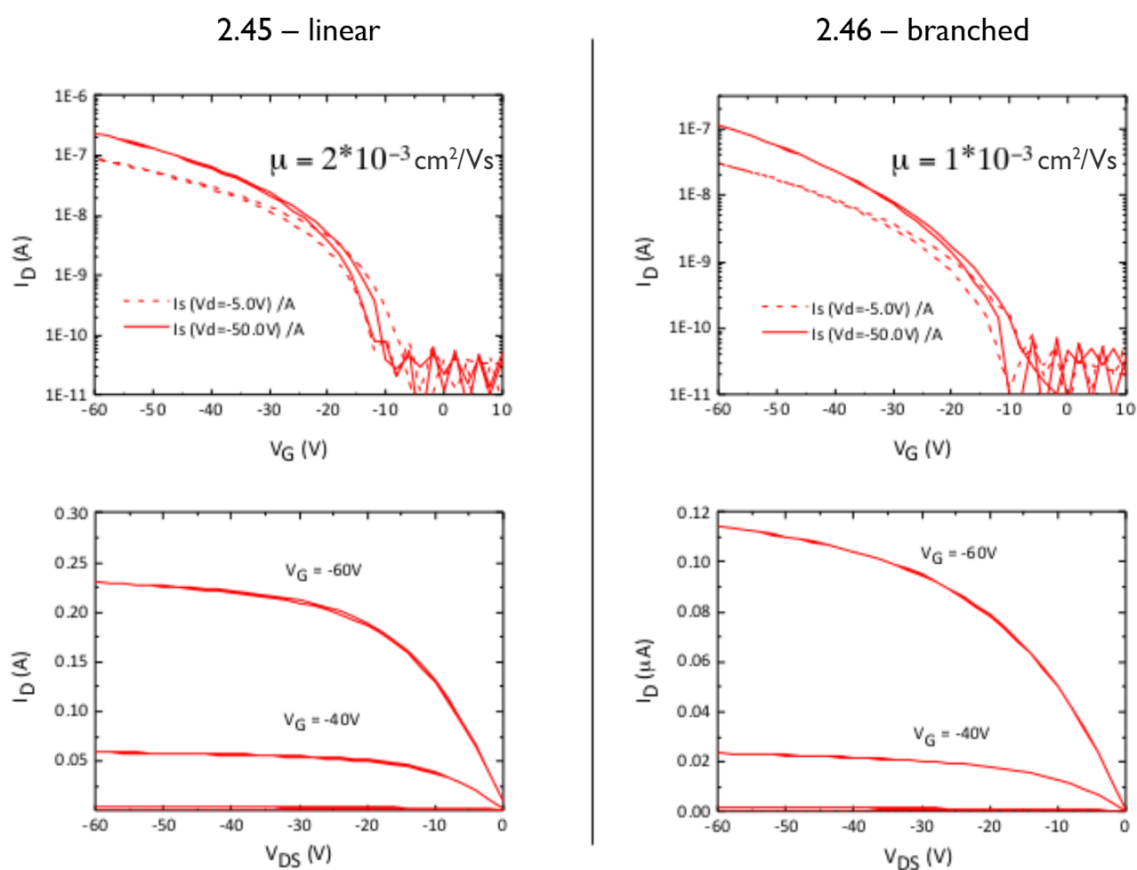


Figure 3.77 – OFET transfer curves (top) and output characteristics (bottom) for polymers 2.45 (left) and 2.46 (right)

The linear polymer **2.45** performed slightly better than the branched **2.46**, with their mobilities being $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and $1 \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively. However, neither values were as high as would be expected if the inferred aggregation was a product of strong π - π -intermolecular bonding (inducing charge transport). The increase in mobility for the linear polymer fits with the original hypothesis that the linear chains should allow for closer packing of the polymer chains and hence an increase in charge mobility compared with the branched polymer. Both polymers exhibited moderate threshold voltages of 10-15 V, with trap sites within the polymer the most likely cause.

Polymer	Dielectric	Anneal (°C)	μ_{sat} (cm^2/Vs)	V_T (V)	$I_{\text{ON}}/I_{\text{OFF}}$
2.45	CYTOP	100	0.002	-15	$\sim 10^3$
2.46	CYTOP	100	0.001	-11	$\sim 10^3$
2.45	CYTOP	200	N/A	-33	$\sim 10^3$
2.45	PMMA	200	0.03	-	$\sim 10^4 - 10^5$

Table 3.7 – OFET device characteristics for polymers 2.45 and 2.46

With **2.45** being the higher performing of the two polymers, further optimisation was performed on this material to investigate the effects of annealing and use of different dielectrics on device performance. Figure 3.78 – **a** (over) shows the notable decrease in performance in the OFET transfer curves for CYTOP dielectric devices when the annealing temperature was raised from 100 °C to 200 °C. Considering the high TGA and this temperature being below the features in the DSC, such a dramatic change in performance as a product of annealing was unexpected.

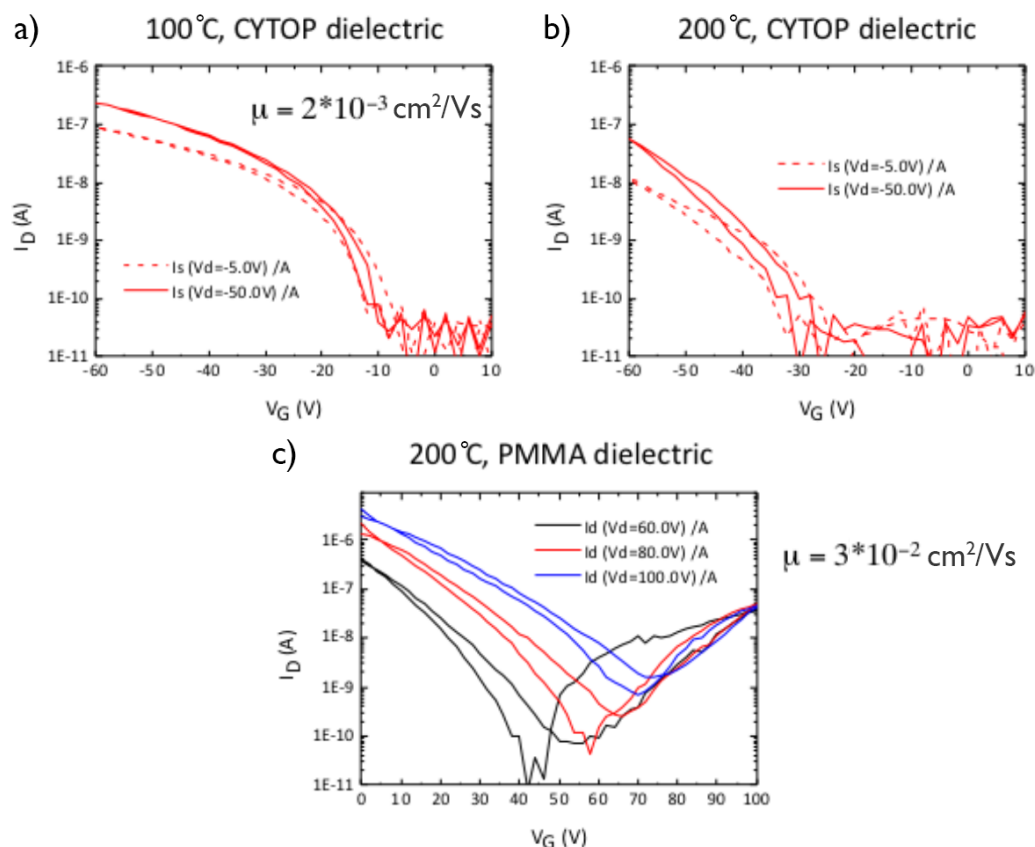


Figure 3.78 – OFET characteristics of optimised device for polymer 2.45

When the dielectric was changed to PMMA, the best performance was observed when annealing was performed at 200 °C, with the device also showing good ambipolar properties – something that was hypothesised to be likely due to the design of the molecule. The mobility of this device ($0.03 \text{ cm}^2/\text{Vs}$) had the best overall performance, although the higher gate voltages must be noted. With the high performance also coming from a device annealed at 200 °C, the decrease in the performance of the CYTOP devices annealed at 200 °C was likely to have been due to a change at the dielectric / polymer interface at this higher temperature.

The overall performance in OFET devices can be summarised in that the linear chained polymer (**2.45**) performed better than the branched polymer (**2.46**), as expected, with good matching of the polymer energetics with the gold contacts resulting in excellent charge injection into devices. However, the general lack of order within the polymers suggested by

the XRD fits with the overall lower than expected mobility values seen for the devices, and further suggests there is a distinct lack of molecular order within the polymer structure.

3.4.2 OPV results

The materials were further tested for their suitability as donor materials within inverted architecture solar cell devices (glass/ITO/ZnO/polymer:acceptor/MoO₃/Ag) using the non-fullerene acceptor ODFBR (Figure 3.79). Due to the wide band gaps of **2.45** and **2.46**, the use of a non-fullerene acceptor was intended to improve the overlap with the AM1.5 spectrum through the use of a smaller band gap unit whilst improving absorption through the ‘Channel-II’ absorption pathway seen in NFAs (Chapter 1 – Fig. 1.19)³⁸ compared with PCBM.

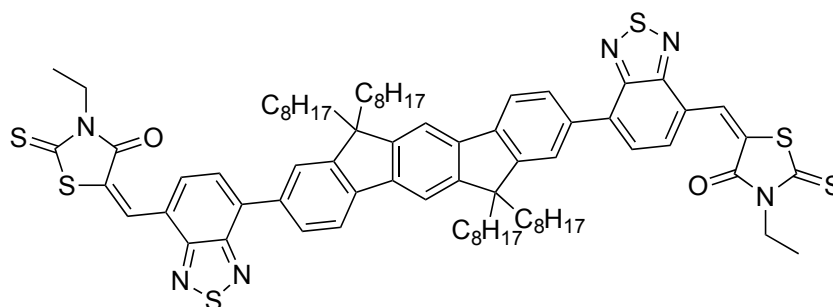


Figure 3.79 – ODFBR – Octylindenofluorene-benzothiazdiazole-rhodanine – NFA

The active layer blends (polymer:acceptor ratio 1:1) were spin-coated from chlorobenzene solutions without the use of additives. The current-density (J-V) curves and data for both polymers within OPV devices can be seen in Figure 3.80 and Table 3.8, respectively, where the area of each active device was 0.045 cm² and measurements were performed in a solar simulator using the AM1.5 spectrum at an intensity of 100 mWcm⁻².

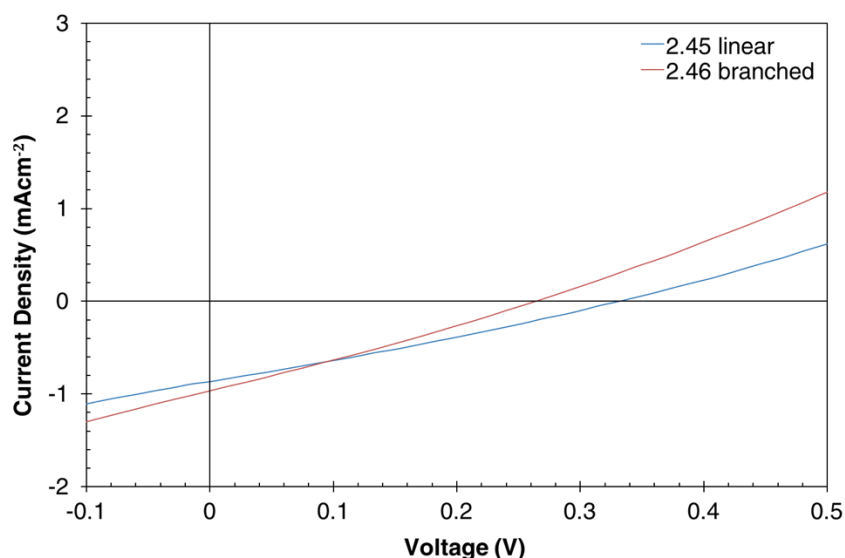


Figure 3.80 – J-V characteristics of OPV devices using polymers 2.45 and 2.46

Both polymers performed poorly in OPV devices, with the linear polymer (**2.45**) showing a slightly higher PCE of 0.08% compared to the branched material (**2.46**, 0.07%), with the increased performance coming from the 0.07 V increase in the V_{OC} of **2.45** to 0.33 V. The current density was higher for **2.46**, with a value of 0.97 mAcm^{-2} compared with 0.87 mAcm^{-2} for **2.45**, which fits with the hypothesis that the branched chains enhanced the morphology of the blend between the polymer and the acceptor, improving charge transport. Unfortunately, this increase in current comes with the loss in V_{OC} , reducing the overall PCE to similarly low levels for both polymers.

Polymer	$J_{SC} \text{ (mAcm}^{-2}\text{)}$	$V_{OC} \text{ (V)}$	Fill Factor	PCE (%)
2.45	0.87	0.33	0.28	0.08
2.46	0.97	0.26	0.27	0.07

Table 3.8 – J-V data for OPV devices of 2.45 and 2.46

Overall, the OPV performance was significantly poorer than expected, although it is in line with the poor transistor performance and the lack of morphological structure shown in the XRD spectra. This suggests the amorphous natures of the polymers inhibited charge transfer throughout the blends, therefore reducing the current density.

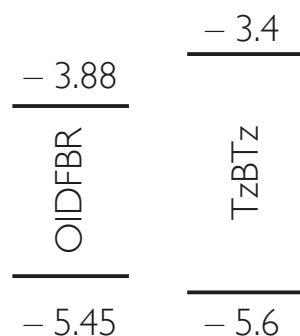


Figure 3.81 – EA and IP (CV) of OI DFBR relative to TzBTz

Another reason for the low performance could be the mismatch in the HOMO levels of **OI DFBR** and **TzBTz**, which likely resulted in no current coming from the Channel II pathway. This is because any holes formed in the **OI DFBR** due to absorption of an electron could not transfer to the **TzBTz** due to a lack of energy off-set between them, hindering charge separation. This lack of offset could even cause enhanced recombination, with excitons formed on **TzBTz** preferring to transfer directly from the **TzBTz** to the **OI DFBR** rather than undergoing charge separation at the interface.

3.5 Chapter conclusions

Analytical characterisation and device fabrication have presented an interesting perspective on two new polymers and how their morphological properties affected device performance. Molecular modelling initially gave an insight into the polymer structure, with a ‘conformational lock’ between the **TzBTz** and **TBT** units occurring as the nitrogen lone pair donates electron density into the sulphur anti-bonding orbitals. The result of this is a torsional twist of less than 2° along the polymer backbone, giving a rigid, highly defined π -core, which led to the expectation of strong inter-chain π - π -packing between units.

The defined structure and negligible shift in wavelength between the solution and thin film UV-Vis spectra indicated that this inter-chain packing was strong, with this being further corroborated by temperature dependant UV-Vis analysis, wherein little break-up of

aggregates was seen even at 80 °C in chlorobenzene. The UV-Vis also gave the onsets of absorption, wherein optical band gaps of 2.3 eV were estimated for both polymers. This was much wider than expected, with less ‘push-pull’ orbital hybridisation occurring between the **TzBTz** and **TBT** units than hypothesised, as visualised by the frontier orbital models in Figure 3.70.

TGA showed extreme stability for these organic polymers, with 5% weight loss not occurring until over 450 °C for both materials. Further thermal studies using DSC showed strong backbone crystallisation at 334 °C and 220 °C for **2.45** and **2.46** respectively, conforming the strong interchain forces observed in UV-Vis. A side-chain melt and crystallisation was also clearly observed for the linear chains in **2.45**, which was not seen for **2.46**. XRD analysis provided evidence that there were strong interchain interactions, as seen by the broad peak at around $2\theta = 24^\circ$, although the lack of definition suggested there was very little repetitive π - π -stacking within the material, suggesting a lack of long-range order within the materials.

OFET devices showed good charge injection for both polymers, but trap sites caused moderate threshold voltages of 10-15 V. As expected, the linear polymer (**2.45**) performed the best, with a hole mobility of $0.002 \text{ cm}^2/\text{Vs}$, and with further optimisation the material showed ambipolar properties with a maximum hole mobility of $0.03 \text{ cm}^2/\text{Vs}$. The high molar extinction coefficients of $74,000 \text{ M}^{-1}\text{cm}^{-1}$ (**2.45**) and $93,000 \text{ M}^{-1}\text{cm}^{-1}$ (**2.46**) were promising in terms of potential solar cell performance, but unfortunately the low currents of less than 1 mAcm^{-2} for both polymers resulted in extremely low PCEs of less than 0.1%.

In conclusion, the polymers performed similarly in most instances, showing the interactions between the rigid backbone cores had a much greater effect than the differing linear and branched alkyl chains. Although strong aggregation of the polymer backbones was clear from UV and DSC, the XRD and device performance gave confirmation this aggregation did not

form a defined enough structure to allow good charge transport, whether this was in OFET or OPV devices. Although this poor morphology along with the wide band gap resulted in low OFET and OPV outputs, this comprehensive set of data revealed interesting insights into two new polymers with a novel thiazole-based monomer unit.

Chapter 4

DTP-DPP-based polymers for OPV and OFET

4.1 Introduction

Diketopyrrolopyrrole, better known as **DPP**, has been used in the dye industry since the 1980s thanks to its high extinction coefficient and the vibrant colours it can produce. The most notable example is Pigment 254, better known as ‘Ferrari Red’ due to its vibrant red colour. Pigment 254 is exceptionally UV and heat stable, solving ‘chalking’ problems which had made previous red paints look dull over time. The optical properties of **DPP** can be easily tuned through small chemical modifications, such as changing the moiety on the flanking benzene unit. Here the difference between a chlorine atom and an amine will change the colour from red to blue/violet (Figure 4.82).¹²³

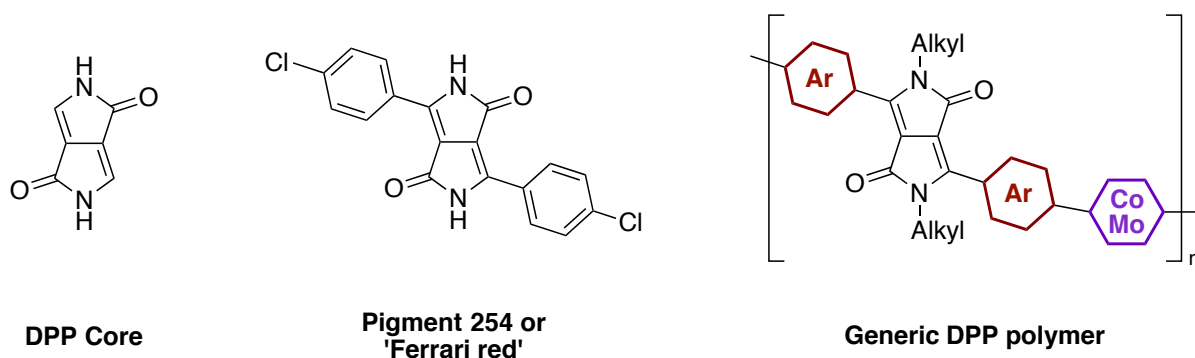


Figure 4.82 – Examples of DPP. Ar = Aromatic Unit. CoMo = Aromatic co-monomer

The strongly electron withdrawing nature, polarizability, and crystallinity of DPP all make it highly suitable for use in organic semiconducting polymers. Janssen et al. have synthesised a plethora of **DPP**-style monomers since 2008.¹²⁴ The changeability of the aromatic flanking units, co-monomer, and alkyl chains on the **DPP** core (Figure 4.82) result in a highly tuneable material that can display an array of optical absorptions up to 1000 nm, with high hole and electron mobilities and ultimately good charge transport properties.

DPP polymers have come a long way since the early days, where one of their first uses in a BHJ-OPV device gave a PCE of 4.0%.¹²⁴ Recent **DPP**-containing polymers have achieved

PCEs of >8% in BHJ devices,^{125–127} while in OFETs electron and hole mobilities have reached up to 6.3 and 17.8 cm²V⁻¹s⁻¹, respectively.^{128,129}

Although some semiconducting polymers have been synthesised with ultra-low bandgaps,^{130–133} few have reached wavelengths of above 900 nm, missing out a large part of the near-IR energy that makes up the AM1.5 spectrum. Synthesis of polymers with a small band gap, good oxidative stability (HOMO > -5.2 eV^{120,121}) and a defined HOMO/LUMO level matching the BHJ acceptor moiety is a tough problem which can be synthetically demanding.

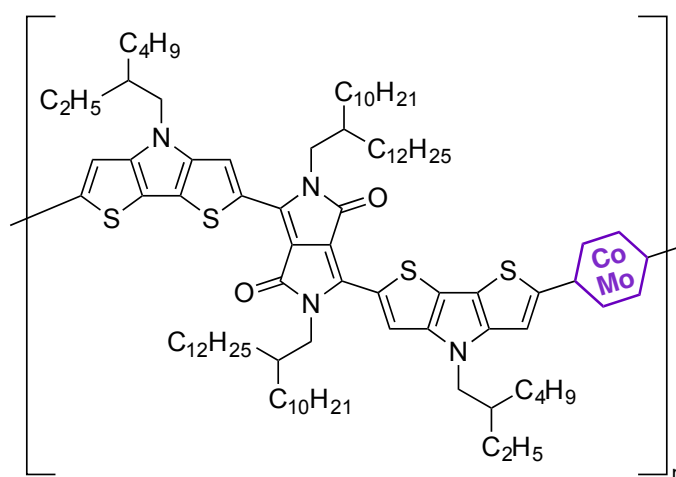


Figure 4.83 – DTP-DPP monomer in generic polymer

This section of the thesis aims to synthesise a small-band gap monomer with greater AM1.5 spectral overlap for use in BHJ OPV – namely the **DTP-DPP** unit (Figure 4.83), where the electron-poor central **DPP** unit will be flanked with two electron-rich alkylated dithienopyrrole (**DTP**) units. This serves two functions, with the first being intrinsic and the second synthetic. Firstly, the **DTP** unit is very electron rich – this is due to the two thiophene units being bridged with a nitrogen atom, which donates its own electron density into the π -cloud whilst also planarising the whole unit. The addition of a **DTP** group either side of the electron-poor **DPP** unit should create an exceptionally strong donor-acceptor effect across the moiety and bring the band gap down to ~1 eV. Secondly, the addition of the solubilising alkyl chains on the nitrogen atom of the **DTP** adds solubility during the **DPP** formation step

of the synthesis. Usually, on formation of the **DPP** unit via the succinic method¹³⁴ (Figure 4.84), strong hydrogen bonding interactions along with π - π -stacking between the units results in an insoluble compound that is difficult to work with. The addition of the alkyl chains onto the flanking aromatic **DTP** unit should break up these aggregates and resolve some of the solubility issues, allowing for more efficient alkylation of the **DPP** unit.

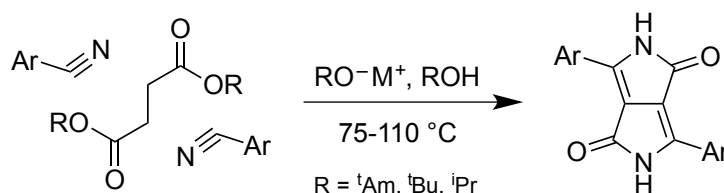


Figure 4.84 – Generic succinate ring closure method of DPP formation, forming a poorly soluble product when Ar is unalkylated

Another benefit of the strong orbital hybridisation already occurring across the central **DTP-DPP** unit is that the energy levels can then be fine-tuned by altering the co-monomer. For example, the addition of an electron rich thiophene unit should raise the HOMO, slightly reducing the band gap, whereas the addition of an electron poor benzothiadiazide unit should cause greater orbital hybridisation and therefore both raise the HOMO and lower the LUMO, decreasing the band gap further.

During the author's synthesis of the **DTP-DPP** monomer, Janssen et al. published a paper in which a thiophene flanked **DPP** core was co-polymerised with **DTP** to create a very similar polymer to the one discussed here.¹³⁵ Although similar, their polymer lacked the functionality to change co-monomer and therefore tailor their energy levels and band gap further. This was evident in the LUMO offset between the donor polymer and acceptor fullerene, which was >0.5 eV, reducing the V_{OC} when the polymer was used in OPV devices. By having the functionality to change the co-monomer, it should be possible to tune the HOMO/LUMO levels and band gap to improve PCE by increased the V_{OC} , resulting in sustained high current.

4.2 Monomer synthesis

Figure 4.85 shows the synthetic scheme for the synthesis of the **DTP-DPP** monomer (**4.6**).

Initially, the **DTP** precursor was synthesised before the mono-aldehyde was made and converted into the nitrile. This was used to form the **DTP-DPP(H)** (**4.4**) using diethyl succinate (similar to the Reformatsky method)¹³⁴ followed by alkylation and bromination to afford the final **DTP-DPP** monomer (**4.6**).

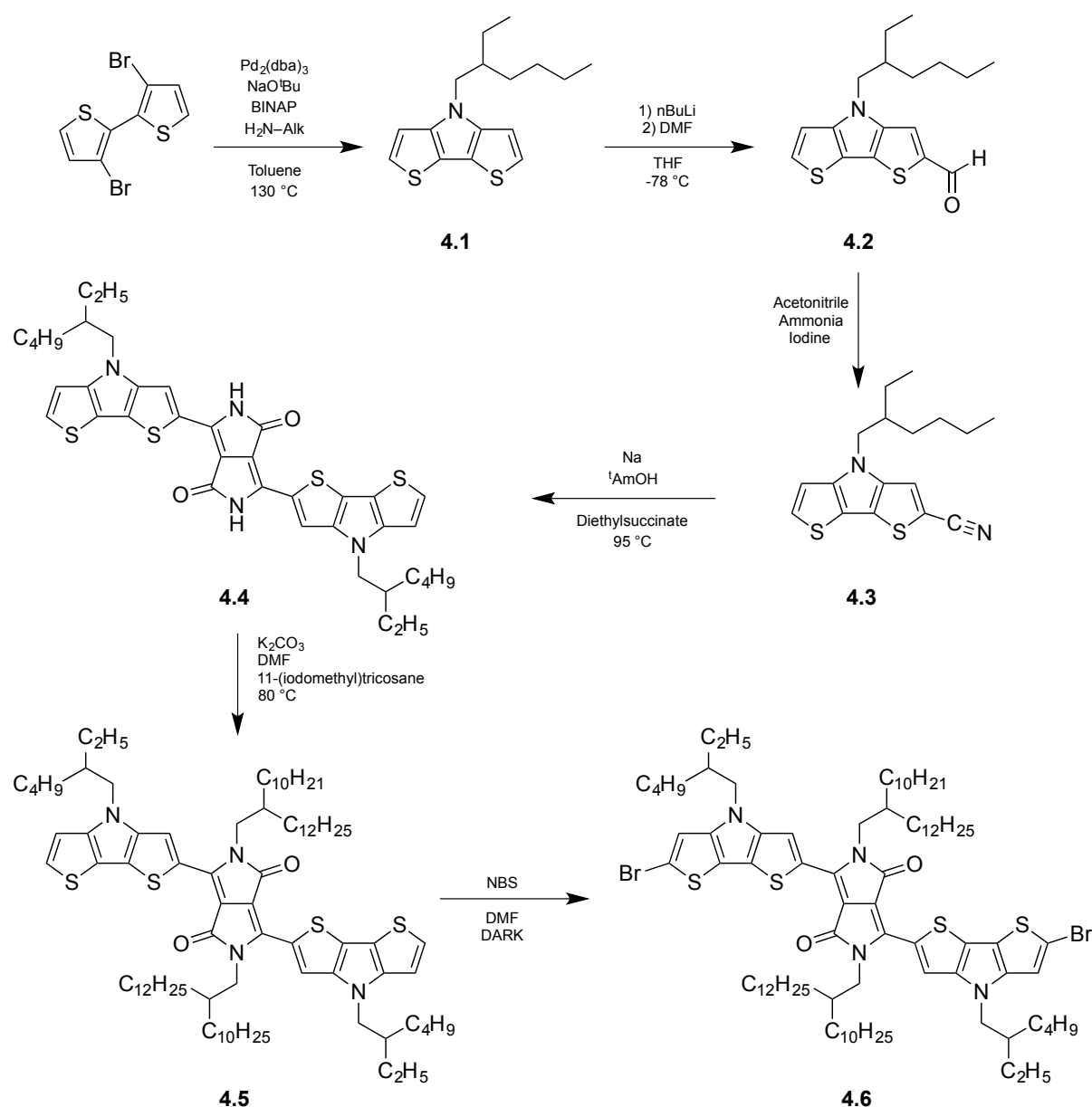


Figure 4.85 – Synthetic pathway toward the DTP-DPP monomer

4.2.1 Synthesis of DTP precursor

The alkylated dithienopyrrole (**4.1**) was synthesised from adapted literature sources.^{136,137}

The commercially available 3,3'-dibromo-2,2'-bithiophene underwent a Buchwald-Hartwig palladium-catalysed cross-coupling with the commercially available 2-ethylhexylamine. The reaction proceeds via a similar mechanism to that of a Suzuki-style palladium cycle, with oxidative addition of the aromatic halide, amine addition and deprotonation, followed by reductive elimination to form the new C-N bond.¹³⁸ This cycle must then occur a second time intramolecularly for the fully ring-closed species to form – hence high dilution is favourable. The use of a bulky bi-dente ligand such as BINAP aids in the reduction of β -elimination by blocking an open coordination site on the palladium complex.¹³⁹ Purification on silica chromatography left a visible oxidised red layer on the top of the column, most likely due to the contact the electron-rich DTP unit had with oxygen during the work-up proceedings causing oxidative degradation. The dark red / brown oil **4.1** was made in high purity on a large scale (>15 g) with excellent yields (98%).

The mono-formylation of **4.1** to yield **4.2** was performed under strict stoichiometric conditions using a 1:1 ratio of **4.1**:*n*-BuLi. The careful and slow addition of the lithiating agent into a dilute solution of **4.1** at -78 °C ensured a high yield of the mono-lithiated species. Quenching with an excess of DMF yielded **4.2** as a brown oil in good yield (84%).

The formation of the nitrile **4.3** directly from the aldehyde **4.2** was adapted from literature conditions.^{140–142} As the reaction was performed in a large volume of ammonia water, the water-miscible solvent acetonitrile was used to solubilise the DTP-aldehyde moiety enough for a reaction to take place. On addition of the ammonia and iodine to the aldehyde, oxidation occurred to form the *N*-iodo aldimine intermediate (Figure 4.86 – A) which in turn eliminates a hydrogen iodide molecule in the presence of the ammonia solution to yield the nitrile **4.3**.

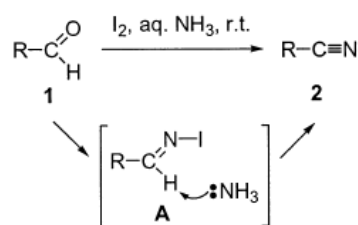


Figure 4.86 – Reaction intermediates in the formation of a nitrile from an aldehyde

4.2.2 DPP formation

The base-promoted condensation of nitriles with succinic esters has been the most common method of **DPP** formation since the reaction was invented at the Ciba-Geigy Chemical Corporation in the 1980s.¹⁴³ Although this is not the most efficient way of making DPP, the addition of pre-formed flanking aromatic groups via the nitrile has historically allows a plethora of interesting compounds to be synthesised.

Compound **4.3** was synthesised from adapted literature methods in which electron rich nitriles have been used as flanking aromatics in **DPP** formation.¹³⁵ The use of pre-optimised reaction conditions is important because the more electron-rich the nitrile, the more deactivated it is and the lower overall yield that is expected.^{143,144}

The tertiary-alcohol base is formed through addition of solid sodium to the *tert*-amyl alcohol solvent, whereupon it is heated at reflux. The use of a tertiary base is important because they are strong enough to deprotonate the succinate, yet too hindered to add to the cyano nitrile via nucleophilic addition. Combining a tertiary base with a tertiary alcohol solvent reduces the occurrence of dimerisation of the succinic ester via a Claisen condensation.¹⁴⁵

The **DTP-CN (4.2)** and succinate ester solution was then added dropwise to the heated base mixture. Elevated reaction temperatures were required due to the low electrophilicity of the nitriles, which will not undergo nucleophilic attack from the succinic anions at low temperatures. The quick formation of the succinic anion means it is not desirable in high

concentrations at high temperatures as it may undergo side reactions – therefore, it is kept at a low level in solution by adding to the reaction mixture dropwise.

The cyano nitriles add to the succinate in a stepwise manner, with mono ring closure being followed by di-ring closure. The solution was therefore left heating overnight to maximise the yield. Even with the alkylated **DTP** flanking groups, the strength of the bonding between the **DPP** units meant the material was insoluble enough to be worked up via methanol precipitation and filtration to yield **4.4** as a dark blue solid with a slight purple pearlescent hue. The yield of 41% was higher than expected considering the electron-rich nature of the **DTP** flanking group.

4.2.3 DTP-DPP(H) alkylation

Initially, the **DPP** alkylation was performed as per literature conditions: **4.4** was heated in DMF at 120 °C in the presence of NaO^tBu base before the slow addition of the bromo-alkyl chain, followed by heating overnight.¹⁰⁶ Yields for **DPP** alkylation vary with the flanking aromatic unit, with the electron density of the ring playing a role in the basicity of the nucleophilic nitrogen. Purification of the crude alkylated materials was problematic, with impurities still being present after column chromatography in multiple solvent systems, always running at the same R_f as the product.

On further inspection, it was suspected that the impurity was an *O*-alkylated derivative of the desired product, which could not be separated by chromatography due to the alkylated **DTP** unit causing the *N*-alkylated product and *O*-alkylated impurity to have very similar R_f values. Although *O*-alkylation occurs during this synthetic step for **DPP** with various flanking units, usually the difference between the moieties is significant enough that they can be separated via column chromatography. Literature precedence has shown this to be the case, with NMR

classifications of all three separate moieties (Figure 4.87) mimicking the NMR impurities seen in product **4.5**¹⁴⁶ (Figure 4.88).

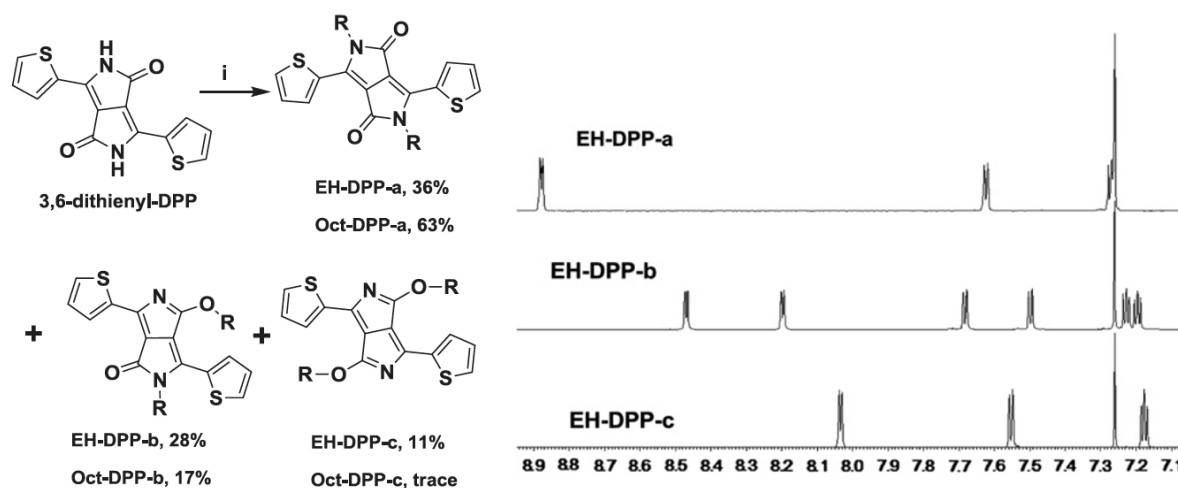


Figure 4.87 – Literature showing the difference in aromatic NMR signals (right) between *N*- and *O*-alkylated DPP core units (left)¹⁴⁶

With *O*-alkylation looking to be the majority impurity, an elegant purification technique was undertaken, performing a reverse etherification of the crude material. This reverts any mono- or di-*O*-alkylated product to the alcohol, significantly altering the *R_f* value of these impurities and allowing column chromatography to be used to separate the mixture. Figure 4.88 shows the ¹H NMR aromatic region of the impure **DPP-4.5** mix of isomers (top) compared with the NMR of the pure *N*-alkylated **DPP-4.5** (bottom) after heating with dioxane/HCl for 1 h at 120 °C before further column chromatography.

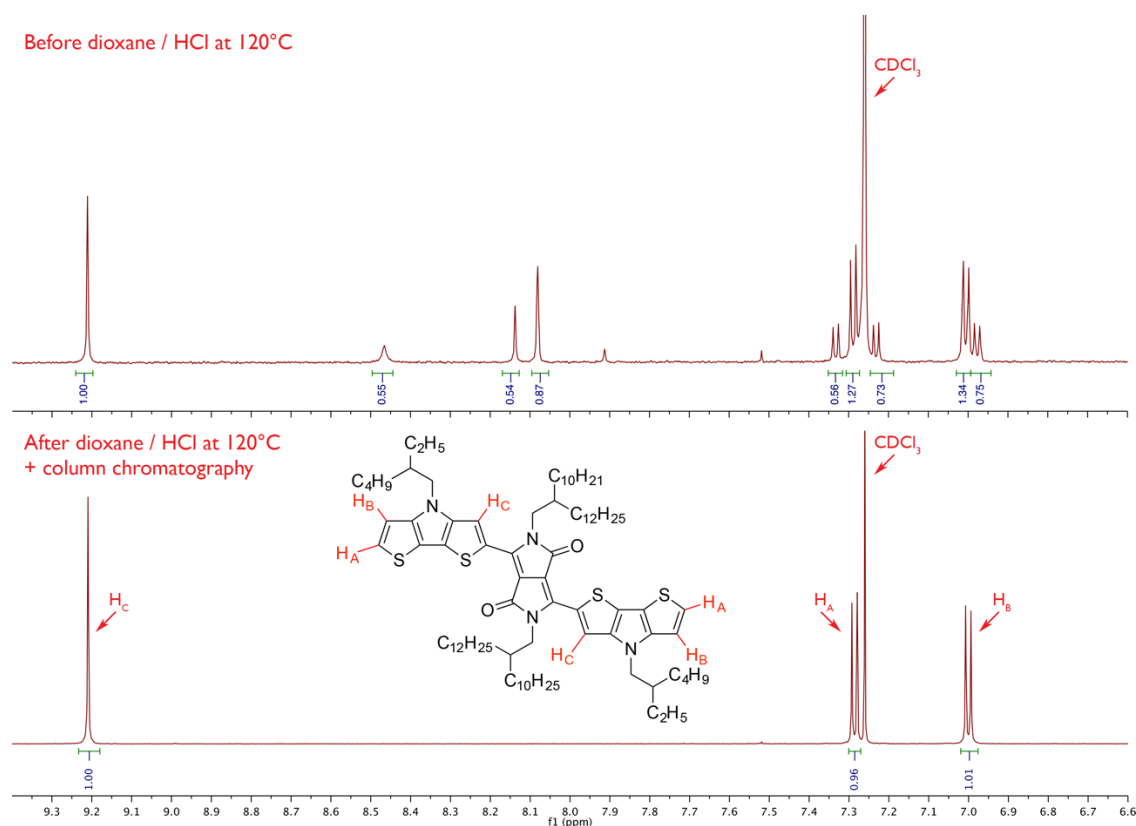


Figure 4.88 – NMR of impure DTP-DPP with additional aromatic peaks (top) and pure *N*-alkylated DTP-DPP with the expected three aromatic peaks (bottom)

The proton NMR clearly shows that the combination of dioxane/HCl reverse esterification and further column chromatography removed all impurities from the **DPP** alkylated product, leaving only *N*-alkylated **DPP-4.5**. Unfortunately, the partially or completely un-alkylated **DPP** could not be recovered as strong hydrogen bonding led to the product not moving on silica and being stuck on the baseline. Although the reverse esterification process was highly detrimental to the yield, this was a necessary route to take as purity is so important in the final polymerisation process.

Further confirmation that the impurities were some form of *O*-alkylated product can be seen by analysing the ^1H NMR of the alkyl chains attached at the NCH_2 or OCH_2 positions. Figure 4.89 shows additional peaks in the region at around 4.1 ppm, which occurred due to the

proximity of the CH₂ protons to the O–C bond, changing the de-shielding compared with the CH₂ protons in the equivalent NCH₂ position.

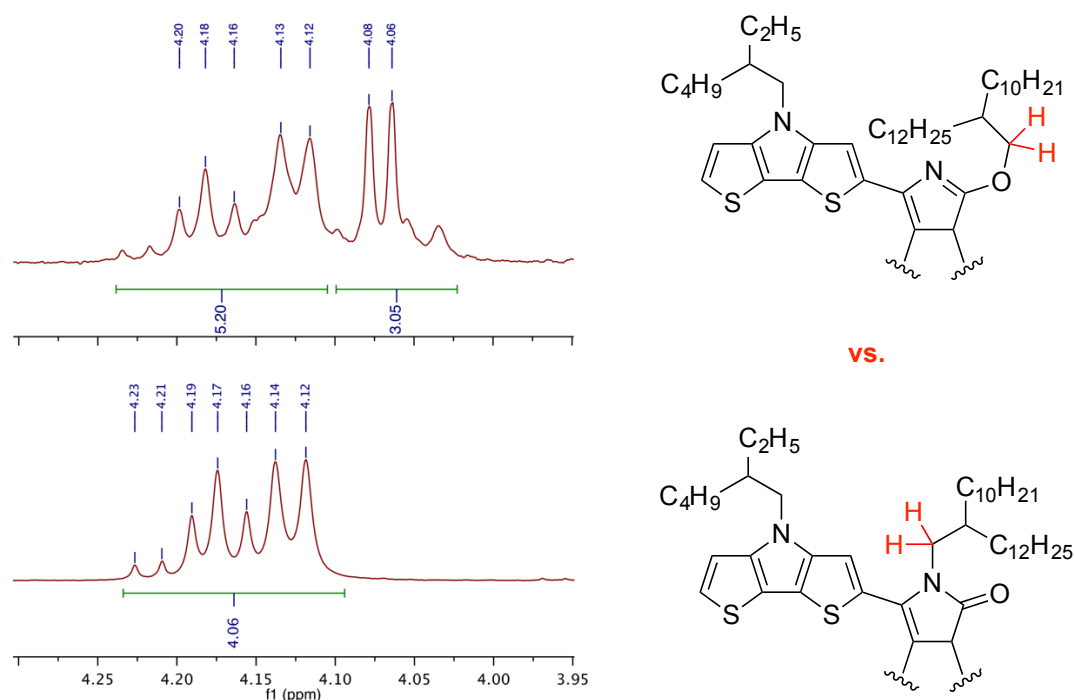


Figure 4.89 – Additional peaks around 4.1 ppm due to proximity of the CH₂ protons to the C–O bond (top). Pure N-alkylated product (bottom)

On further optimisation of the reaction, the use of iodo-alkyl chains instead of bromo-alkyl chains combined with a reduction in the reaction time to 4 h and a lower heat (80 °C) yielded less of the O-alkylated side product – although to what degree was difficult to quantify. The low yield achieved even after optimisation of the additional purification steps was an unfortunate necessity to ensure that the **DTP-DPP** alkylated product **4.5** was sufficiently pure for polymerisation.

4.2.4 DTP-DPP bromination

The bromination of **4.5** was initially attempted by following a literature protocol for electron-rich **DTP** type monomers that called for the use of NBS in chloroform at 0 °C.^{147,148} The solution turned a dark purple colour, and although a change in R_f was seen via TLC, no

aromatic peaks were observed in the proton NMR spectrum after working up the reaction and purifying the material by column chromatography, where it was found that although the final product was still a distinctive dark blue colour, a lot of dark blue material was retained on the silica. As analytical grade chloroform had been used, it was theorised that dissolved oxygen and the partially acidic nature of chloroform had caused the DTP-DPP to oxidise, dimerise, or decompose, and therefore the use of a completely aprotic anhydrous solvent such as THF would provide a more controlled environment for the bromination to proceed in (NBS in THF at 0 °C). After working up the reaction, there was no longer any purple residue (which would suggest no oxidation), however the proton NMR spectrum still lacked any aromatic peaks despite the fact that the material was the same deep dark blue as the starting material, which suggests that a strongly conjugated material was present. MALDI-mass-spectrometry revealed a peak at 1546.9, which was 4 a.u. higher than the expected mass at 1542.8.

The key to understanding what was occurring lay in the unusually broad signal at 4.2 ppm (Figure 4.90 – top). Broad NMR signals often occur when a labile proton is undergoing exchange with other protons in the NMR solution. As bromination with NBS occurs via an electrophilic pathway, it was theorised that protonation could have occurred at the **DTP**-flanking and **DPP**-core nitrogen atoms due to an excess of H^+ ions in the brominating solution. This would cause a broadening of the NCH_2 peaks to the extent observed, and a broadening of the aromatic peaks to such an extent that they would no longer be visible at a normal level of magnification. To assess the accuracy of this theory, a proton NMR spectrum of the material was run in a strong base, pyridine, with the idea being that the excess base would deprotonate any **DTP-H⁺** or **DPP-H⁺**, reducing the peak broadening and giving greater resolution to any proton peaks in proximity to the aromatic ring system. This exact effect can be seen in Figure 4.90 – bottom, with peaks H_A and H_B now being visible, while peaks H_C and H_D show a significant improvement in resolution.

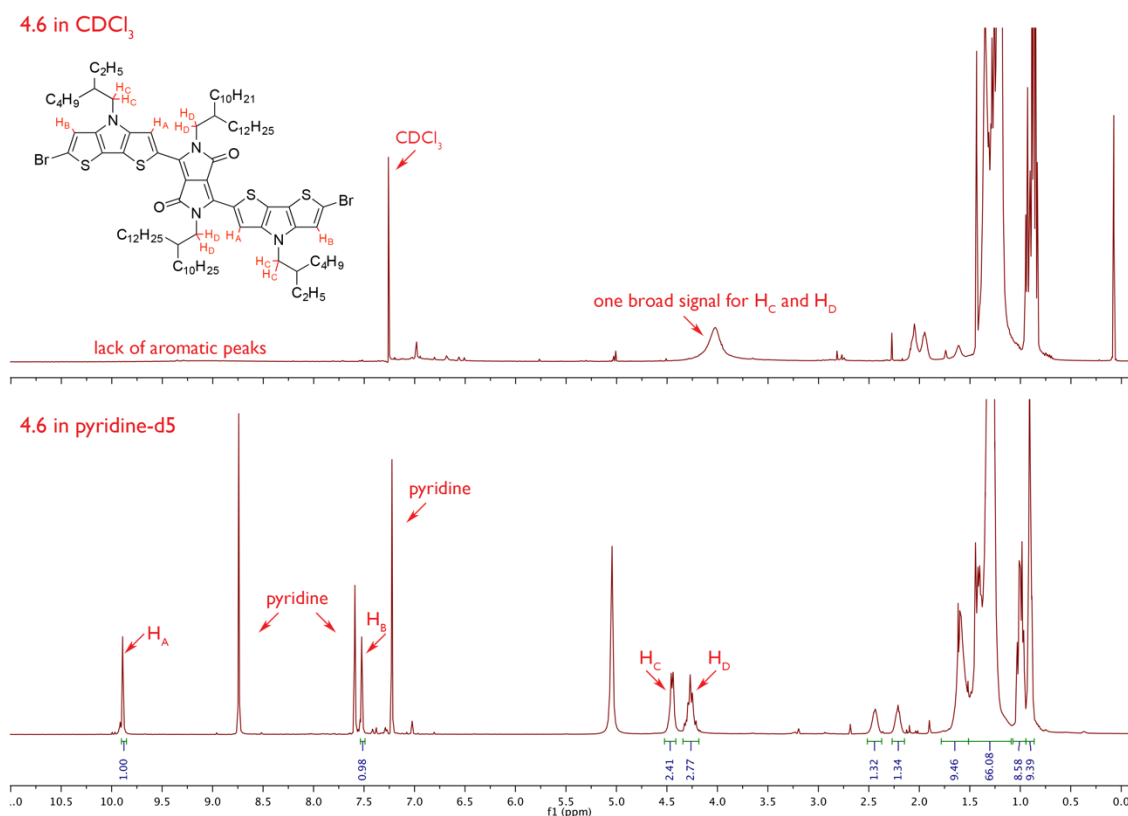


Figure 4.90 – Brominated DTP-DPP (4.6) in CDCl_3 (top) and pyridine-d_5 (bottom)

The NMR spectrum in pyridine confirmed that the bromination using NBS was working effectively, but was causing protonation that could be reversed by contact with base.

Therefore, the bromination was repeated using the previous conditions (NBS in THF at 0°C), this time washing the extracted product with a K_2CO_3 solution during the work-up procedure to de-protonate the **DTP-DPP**. Once de-protonation had occurred via the basic work-up, purification via column chromatography was facile and the NMR spectrum could even be run in CDCl_3 without a loss of resolution, yielding **4.6** as a dark blue highly viscous oil with a high purity that was ready for polymerisation.

4.3 Polymerisation

4.3.1 Monomer selection

As discussed in Section 4.1, the aim of this project was to create an ultra-low band gap polymer by using the strong push-pull orbital hybridisation across the **DTP-DPP** monomer while using the co-monomer to make small adjustments to the final HOMO/LUMO levels.

Therefore, the two co-monomers that were initially chosen were thieno[3,2-*b*]thiophene (**TT**) and benzo[*c*][1,2,5]thiadiazole (**BT**). The reasoning behind this choice was their small sizes and their rotational linearities. With the proton on the **DTP** unit closest to the **DPP** core giving rise to an unusually deshielded NMR signal at 9.2 ppm, it was clear that some form of planarising interaction was occurring between this proton and the oxygen on the **DPP** core unit. A computationally quick MM2 forces calculation on a trimer of the two units (**DTP-TT** and **DTP-BT**) confirmed that in this ‘twisted’ conformation (Figure 4.91), the rotationally linear co-monomers result in highly linear polymer chains, potentially aiding in π - π interactions.

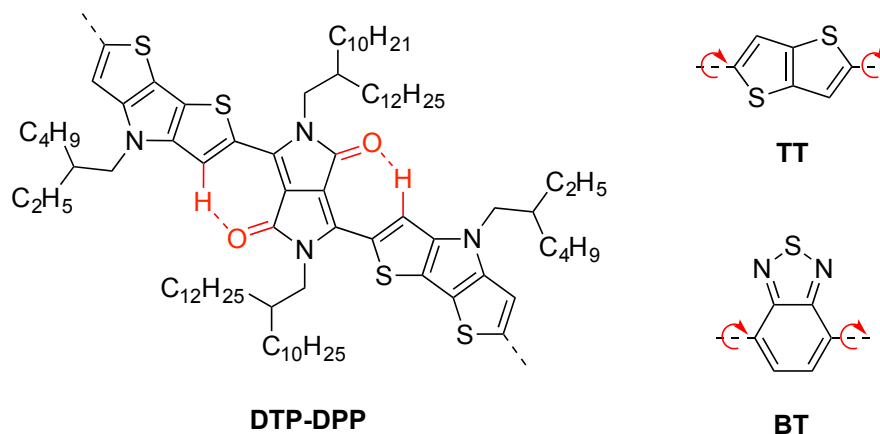


Figure 4.91 – Planarising interaction between DTP-H and DPP=O (left). Rotational linearity of both TT and BT co-monomers (right)

The other reason for choosing **TT** and **BT** as co-monomers is the difference between their energetics, with **TT** being electron rich and **BT** being electron poor. Using these two

materials should give an indication of the band gap range achievable using **DTP-DPP** polymers.

Due to the highly viscous, oily nature of the **DTP-DPP** monomer, an approximate quantity of monomer was dissolved in diethyl ether and transferred to a pre-weighed microwave vial. The ether was removed *in vacuo*, the vial was dried overnight under vacuum, and then the microwave vial was re-weighed to give an accurate mass of monomer present. Standard Stille^{126,135} and Suzuki^{59,149} polymerisations were then prepared following literature conditions.

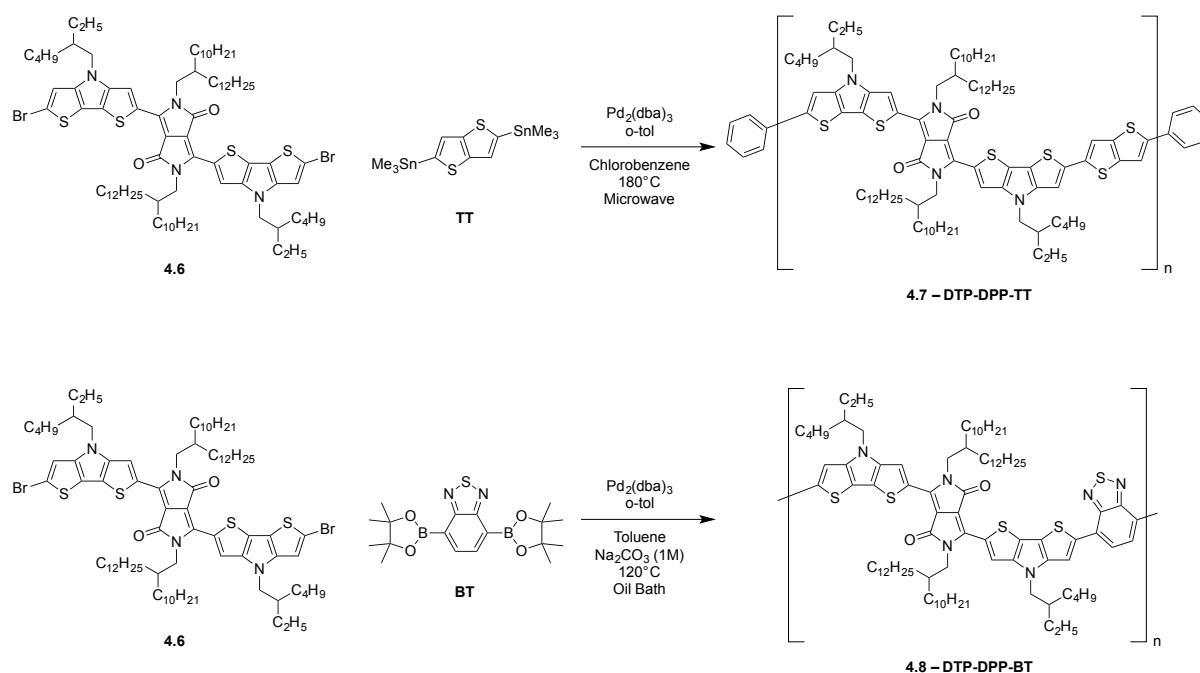


Figure 4.92 – Polymerisation of 4.6 with TT and BT to yield the polymers *pDTP-DPP-TT* (4.7) and *pDTP-DPP-BT* (4.8)

4.3.2 *pDTP-DPP-TT*

On precipitating the polymer **pDTP-DPP-TT** (4.7) in methanol, it was found that some of the polymer appeared to be caked onto the sides of the microwave vial and would not dissolve in additional boiling chlorobenzene (CB), suggesting its molecular weight was too high to be soluble in common chlorinated solvents. The precipitated polymer was then

filtered into a glass-fibre thimble and purified via Soxhlet extraction in methanol (overnight), acetone (overnight), hexane (overnight), and chlorobenzene (6 h). The methanol and acetone fractions appeared clear, while the hexane fraction showed a slight blue tinge, and the majority of polymer dissolved into CB. Some dark blue high molecular weight material was still visible in the Soxhlet thimble, suggesting that the stoichiometric ratio of the monomers had been highly accurate, resulting in the formation of some high molecular weight insoluble material.

The CB fraction was washed vigorously with an aqueous solution of sodium diethyldithiocarbamate to remove residual palladium metal,¹¹⁰ followed by washing twice with water to remove any residual salts from the polymer solution. The chlorobenzene was then concentrated to a minimum and the polymer was precipitated in methanol, wherein a slight yellow colour was seen in the solution – most likely due to sodium diethyldithiocarbamate still being present – before being filtered and washed further with methanol to remove any more salts. **pDTP-DPP-TT (4.7)** was collected as a dark green/black shiny plastic in fairly low yields (27%), but with high molecular weight (Table 4.9).

4.3.3 pDTP-DPP-BT

After methanol precipitation and filtration of the solid **pDTP-DPP-BT (4.8)** into a glass Soxhlet thimble, the methanol filtrate was a fairly dark green colour, suggesting some low molecular weight material was still present even after the two-day reaction time. Soxhlet extraction in methanol (overnight), acetone (overnight), and hexane (overnight) all yielded solutions with strong blue colours, although removing the solvent under vacuum showed that very little material was present in any of the samples. Performing a final extraction in chloroform yielded very little material and therefore the previous hexane fraction was taken and washed with an aqueous solution of sodium diethyldithiocarbamate followed by water. The hexane was removed *in vacuo* and the polymer was redissolved in a minimum volume of

CB before being precipitated in methanol, filtered, and further washed with methanol to yield **pDTP-DPP-BT (4.8)** as a dark green/black powder (21%) with a low molecular weight (Table 4.9).

4.4 Analysis

This section examines the optical, electronic, and physical properties of the two newly synthesised polymers **pDTP-DPP-TT (4.7)** and **pDTP-DPP-BT (4.8)**. The molecular weight properties as determined by analytical GPC are summarised in Table 4.9, and the first point to be noted is the exceptionally high molecular weight and incredibly low polydispersity index shown for **4.7**. The excessively high molecular weight provided by the GPC results was due to the extensive rigidity of the polymer backbone, which is known to lead to over-estimation of the degree of polymerisation because the GPC is calibrated using a flexible polystyrene standard. The rigid ‘rod-like’ behaviour of the polymer also results in poorer separation of differing polymer lengths on the GPC column, bringing the polydispersity index unrealistically close to unity for a step-growth polymerisation. However, although the results are somewhat skewed due to the rigid nature of the polymer, they still suggest a high molecular weight was achieved in the polymer (as opposed to oligomer) regime as a consequence of the efficient Stille polymerisation used.

Polymer	M_n (kg/mol) ^a	M_w (kg/mol) ^b	$\mathcal{D}$ ^c	DP_n ^d
4.7	170	184	1.06	111
4.8	4.3	7.1	1.6	3

a) Number average molecular weight (M_n); b) Weight average molecular weight (M_w); c) Polydispersity index ($\mathcal{D} = M_w/M_n$); d) Degree of polymerisation ($DP_n = M_n/m_r$), giving average number of repeat units

Table 4.9 – Summary of molecular weights for polymers 4.7 and 4.8 as determined using GPC (eluent: chlorobenzene, 80 °C)

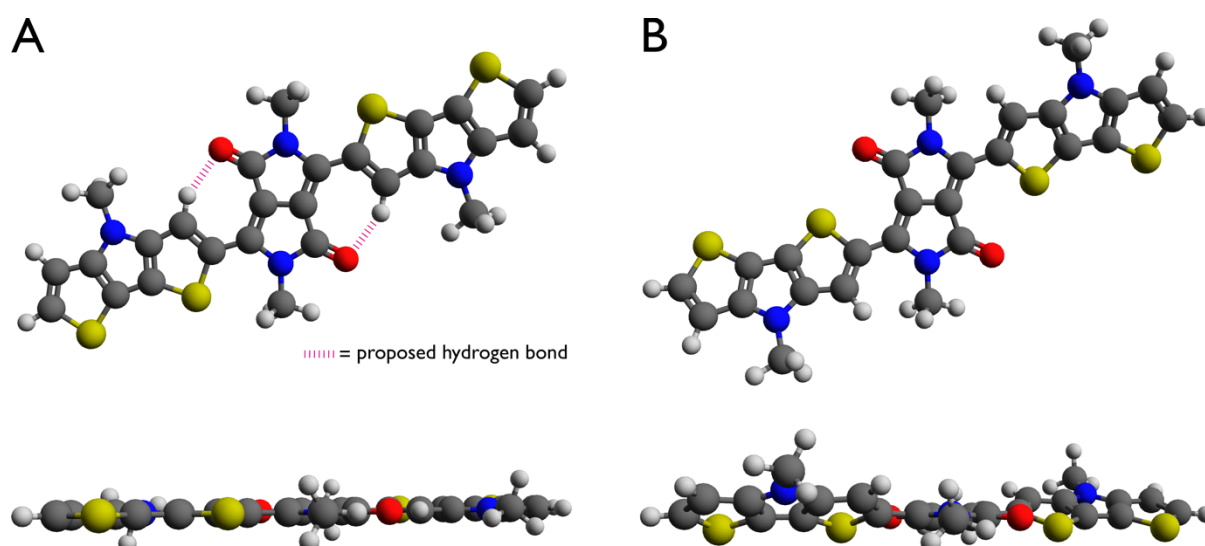
In contrast, Table 4.9 shows that **4.8** had a comparatively low molecular weight. Here, it can be seen that the Suzuki polymerisation conditions used were much less successful, resulting in molecular weights that correspond to short oligomers on the scale of dimers, trimers, and tetramers (although Soxhlet extraction would be expected to have removed the majority of dimers present). The reasoning behind the low molecular weight of **4.8** compared with **4.7** is simply that Stille polymerisation requires vastly less optimisation of the reaction conditions than Suzuki polymerisation due to the high reactivity of the C-Sn bond, allowing a much larger margin of error when choosing system conditions. On the other hand, Suzuki reactions have to be acutely tailored to each individual system (catalyst/ligand, base, solvent, concentration, water equivalents), and unless the conditions are close to the optimum the reaction tends not to go to completion, which is a huge problem for polymerisations as they require >99% conversion to achieve high molecular weights. Although close attention was paid to the literature conditions chosen for the Suzuki reaction, including the previously achieved molecular weights and the similarity of the monomer units, clearly the **DTP-DPP** system needed further refinement if more Suzuki polymerisations were to be performed.

As the molecular weight has a drastic effect on the overall physical and optoelectronic properties of materials (see Figure 1.5 – Chapter 1 Section 1.2.3), the substantial difference between **4.7** and **4.8** makes a direct comparison of the two polymers difficult. This is because one is a polymer and the other an oligomer, and therefore differing properties cannot be strictly attributed solely to their molecular differences (**TT** vs. **BT**). For ease of discussion, both **4.7** and **4.8** will be referred to as ‘polymers’ in the analysis below.

4.4.1 Modelling and geometry

Molecular modelling was performed to ascertain whether the expected geometry illustrated in Figure 4.91, in which the **DTP** proton points towards the **DPP** carbonyl, was indeed the lowest energy geometry. The two monomer units were modelled in Gaussian using the

ω B97XD/6-31G* functional/basis set, as shows in Figure 4.93. Conformer A (left) was 8.5 kcal/mol lower in energy than conformer B (right), leading to the hypothesis that there was indeed a hydrogen bonding interaction occurring between the **DTP** proton and the **DPP** carbonyl. This results in significant planarisation across conformer A compared with the twisted nature of conformer B, lowering its energy. This planarising interactions forces the unit into a kind of ‘conformational-lock’ similar to the one seen for **TzBTz-TBT** in Chapter 3, which would also explain the skewed nature of the high molecular weight GPC results due to an increase in the rigidity of the polymer backbone.



**Figure 4.93 –Modelling of two monomer geometries
of DTP-DPP: Conformer A (left) and Conformer B (right)**

This ‘hydrogen bond-like’ interaction is also corroborated by the unusually high shift observed for the **DTP** proton in the ^1H NMR spectrum (9.2 ppm, Figure 4.88), which could demonstrate the presence of a de-shielding interaction with a nearby oxygen.

Geometry modelling was performed for the three possible permutations of both **4.7** and **4.8** in order to calculate the lowest energy geometries of each monomer block (**DTP-DPP** core with either **TT** or **BT** as a co-monomer). DFT-HF calculations were then performed on dimers of both **4.7** and **4.8** to produce visualisations of the HOMOs and LUMOs (Figure 4.94).

The HOMOs in both **4.7** and **4.8** are similar in that they delocalise evenly across the whole backbone, rather than being focused on any particular unit. However, the LUMO of polymer **4.7**, where the co-monomer is the more electron-rich **TT**, is focused mainly on the central **DPP** unit, whereas the LUMO of **4.8** is spread out further and sits mostly on the electron poor **BT** units as well as the central **DPP** unit. This suggests more push-pull hybridisation is occurring across **4.8** compared with **4.7**, as originally hypothesised.

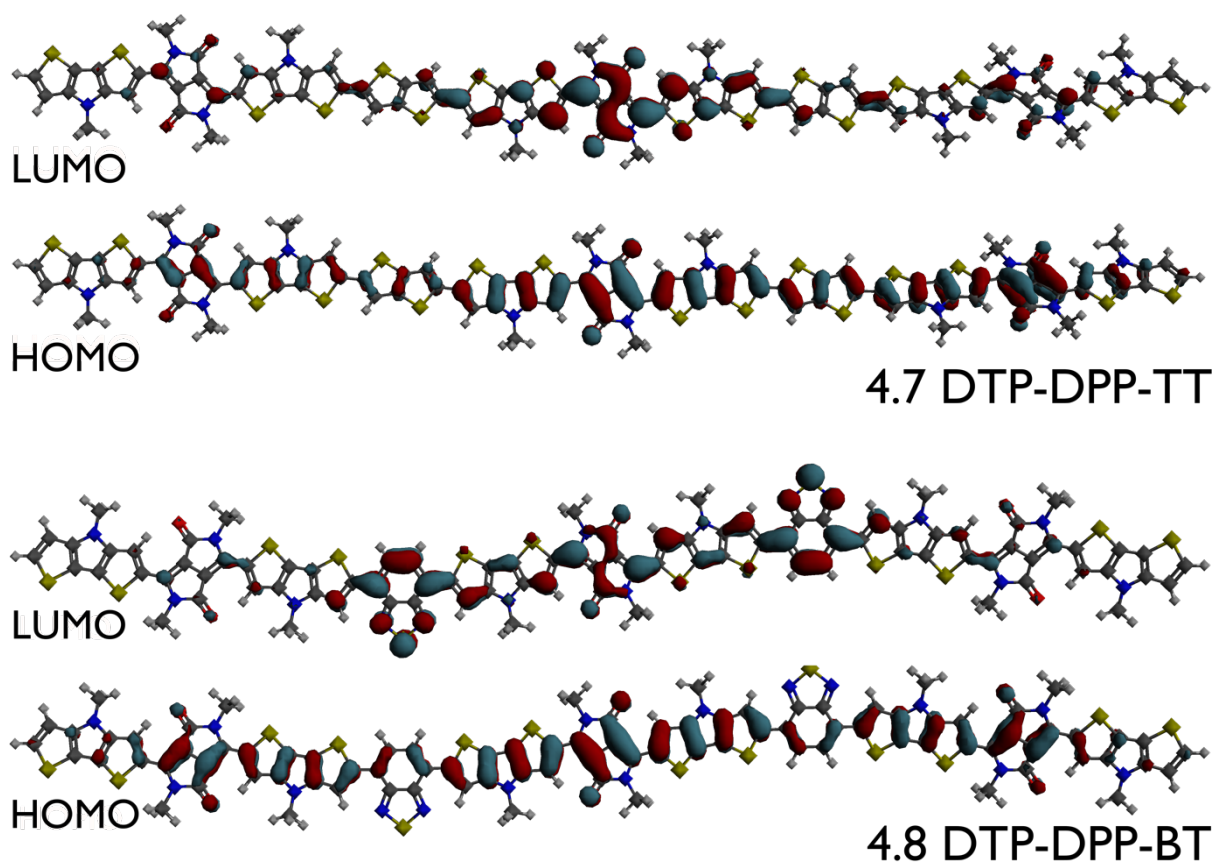


Figure 4.94 – HOMOs and LUMOs of **4.7** (top) and **4.8** (bottom) as calculated using DFT-HF with the ω B97XD/6-31G* method and basis

4.4.2 Optical and electronic properties

The optical properties of **4.7** and **4.8** were studied via UV-Vis spectrometry (normalised) in dilute chlorobenzene solutions and as thin films spun from chlorobenzene (5 mg/mL) onto glass substrates (Figure 4.95).

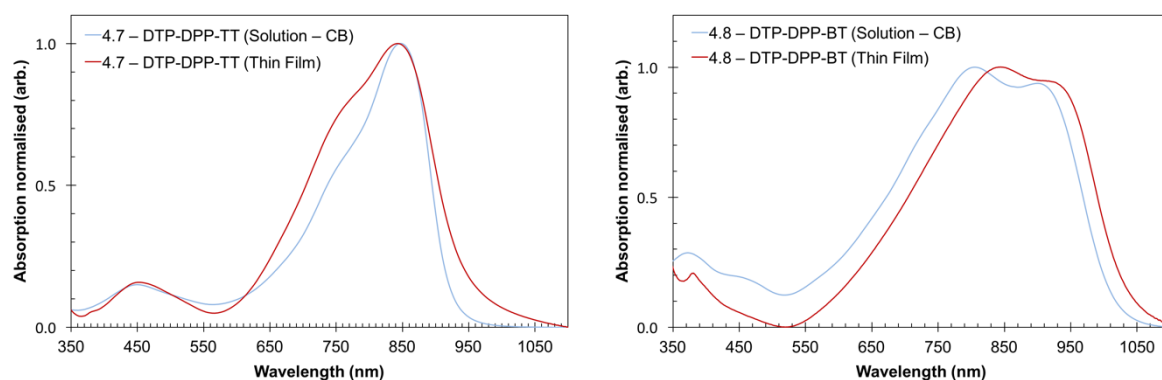


Figure 4.95 – UV-Vis spectra of 4.7 (left) and 4.8 (right) both in solution (CB) and as thin films

In solution, λ_{max} for polymer **4.7** is observed at 848 nm, with a slight shoulder on the main peak as well as a smaller absorption band at 450 nm. It is unclear whether this shoulder is due to a spectral feature of the polymer chain or a vibronic shoulder, although it is unlikely to be residual oligomer present due to the tight polydispersity and extensive Soxhlet processing of the material. On moving from solution to thin film, there is a very slight hypochromic shift in λ_{max} to 843 nm, although peak broadening is also observed, with a large increase seen in the intensity of the shoulder at 750 nm and a shift in the onset of absorption of around 50 nm. The onset shift can be attributed to solid state packing, but the intensity increase of the hypochromic shoulder is unusual, and although similar phenomena have been observed previously in **DPP** polymers with electron rich flanking groups,¹⁵⁰ it is not a common or well-studied occurrence. One possible explanation is that an increase in ‘H-type’ aggregation is sometimes seen for certain packing arrangements moving towards a more semi-crystalline structure,¹⁶ giving rise to a hypochromic shift.

Polymer **4.8** shows a lower wavelength peak as the dominant feature in its UV-Vis spectrum, with a solution λ_{max} at 805 nm along with another peak of almost equal intensity at 900 nm. This broad absorption profile with two peaks 100 nm apart likely occurs due to the mixture of low molecular weight oligomers present in the material, each of which would be expected to

have a different absorption profile. On moving to thin film, the whole spectrum red-shifts by approximately 30–40 nm due to an increase in planarisation as the molecules pack closer together in the solid state. No ‘H-type’ aggregation effects such as those seen for polymer **4.7** are seen for **4.8**, although this is most likely due to the degree of polymerisation being so low that longer-range polymer effects do not occur, therefore changing the molecular interaction between units.

The optical band gaps were estimated from the onsets of absorption in the thin-film UV-Vis spectra giving E_{opt} (**4.7** at 940 nm) = 1.32 eV and E_{opt} (**4.8** at 1036 nm) = 1.20 eV. Even considering molecular weight effects, the electron poor nature of the **BT** unit in polymer **4.8** can clearly be seen to have resulted in an increase in push-pull hybridisation between the **DTP-DPP** and the **BT** units, resulting in a lower observed band gap compared with polymer **4.7** which utilised the electron rich **TT** co-monomer unit.

A series of dilute chlorobenzene solutions were used to calculate the maximum molar extinction coefficient per repeat unit for both polymers, giving values of $118,700 \text{ M}^{-1}\text{cm}^{-1}$ (**4.7**) and $67,600 \text{ M}^{-1}\text{cm}^{-1}$ (**4.8**) (Figure 4.96).

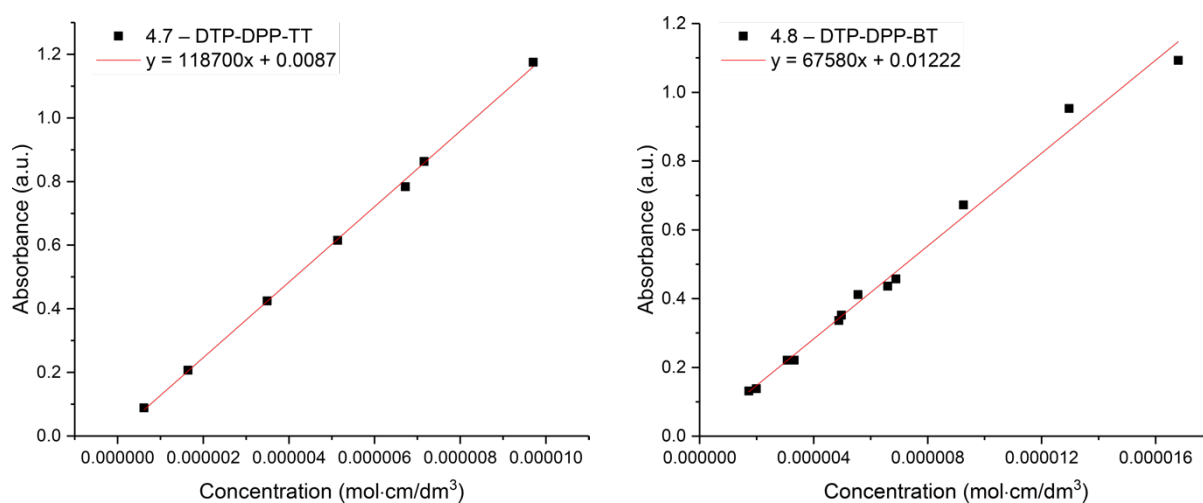


Figure 4.96 – Plots showing linear fits used to calculate the molar extinction coefficients for 4.7 (left) and 4.8 (right)

A higher extinction co-efficient can lead to higher photocurrent in OPV devices, and therefore the exceptionally large value for polymer **4.7** is promising in terms of photovoltaic performance. **DPP** polymers often have high molar extinction coefficients, which has been theorised to be due to their high persistence length (polymer stiffness), long monomer units, and excellent co-linearity combined with high oscillator strengths.¹⁴ The proposed ‘conformational lock’ of the DTP-proton being hydrogen bonding to the DPP carbonyl and the long central **DTP-DPP** monomer, which combine to lead to the linearity seen in the molecular modelling for polymer **4.7** would explain how the polymer structure relates directly to the high extinction co-efficient observed. This also fits with the substantially lower extinction coefficient observed for **4.8**, which could be due to the directionality of the **DPP** units either side of the **BT** unit (Figure 4.94), increasing curvature across the backbone and reducing co-linearity across the polymer. The lower molecular weight could also mean the material was below the extinction co-efficient saturation point, which occurs beyond a certain molecular weight (ϵ increases with M_w), meaning that a higher molecular weight could have resulted in a more comparable extinction coefficient value.

Polymer	$\lambda_{\max}^{\text{sol}}$ (nm) ^a	$\lambda_{\max}^{\text{TF}}$ (nm) ^a	E_{opt} (eV) ^b	ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ^c	$E_{\text{HOMO-CV}}$ (eV) ^d	$E_{\text{LUMO-CV}}$ (eV) ^e	E_{elec} (eV) ^f
4.7 – TT	848	843	1.32	118.7	-5.1	-3.7	1.4
4.8 – BT	805	845	1.20	67.6	-5.1	-3.9 ^g	–

a) Extracted from UV-Vis spectroscopy in thin film and solution; b) Estimated from optical absorption edge in thin films; c) Maximum molar extinction coefficient (per repeat unit); d) Extracted from CV onset of reduction in 0.3 M n-Bu₄PF₆; e) Extracted from CV onset of oxidation in 0.3 M n-Bu₄PF₆; f) Calculated electrical band gap from CV values; g) Calculated from E_{HOMO} (CV) + E_{opt} .

Table 4.10 – Optoelectronic properties of pDTP-DPP-TT (4.7) and pDTP-DPP-BT (4.8)

Cyclic voltammetry (CV) was performed to probe the electrochemical properties of **4.7** and **4.8**. The polymers were dissolved in chlorobenzene (10 mg/mL) before being spun on ITO-coated glass slides to act as the working electrodes. The spectra were measured at a scan rate

of 0.8 Vs^{-1} in 0.3 M tetrabutylammonium hexafluorophosphate electrolyte solutions. After multiple attempts, a full oxidation and reduction cycle was successfully measured for polymer **4.7**, but only a weak reduction peak could be measured for **4.8** due to instability and repeated de-lamination issues.

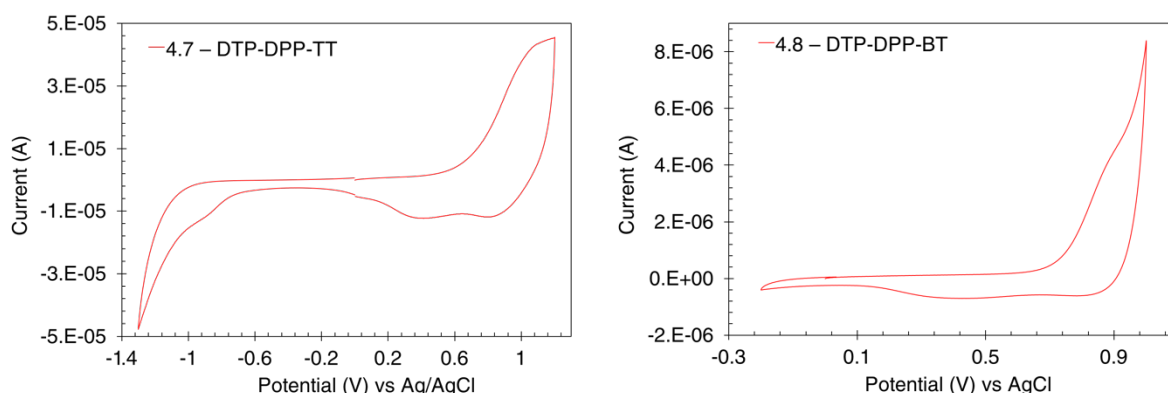


Figure 4.97 – Cyclic voltammograms of 4.7 and 4.8 spun as films from chlorobenzene (10 mg/mL) onto ITO substrates with tetrabutylammonium hexafluorophosphate electrolyte (0.3 M) at 0.8 Vs^{-1} ¹²²

Both polymers exhibited HOMO values of -5.1 eV, higher than the oxidative threshold of -5.2 eV, leading to potential issues with ambient air stability. As the HOMO levels were mostly dictated by the electron rich **DTP** unit and orbital delocalisation occurring across the backbone (Figure 4.94), it is unsurprising the HOMO levels were the same for both polymers. To compare the LUMO values fairly, E_{LUMO} for **4.7** was re-calculated using $E_{\text{HOMO}} + E_{\text{opt}}$ giving a slightly higher value of -3.78 eV. Even so, the LUMO for polymer **4.8** was lower at -3.9 eV compared with -3.78 eV for polymer **4.7** – fitting with the expected increase in push-pull orbital hybridisation in **4.8** occurring with the **BT** unit compared with the **TT** – shifting the LUMO value lower.

4.4.3 TGA and DSC

The thermal stabilities of **4.7** and **4.8** were examined using TGA from 25 to 700 °C at 10 °C/min in order to find their decomposition points (defined by 5% mass loss). Although the onset of decomposition was very similar for both, occurring at around 390 °C, there was almost no decomposition seen at all for **4.7** before 370 °C, whereas decomposition of **4.8** began at 295 °C. This could potentially again be a molecular weight issue or simply that the **BT** polymer is less stable.

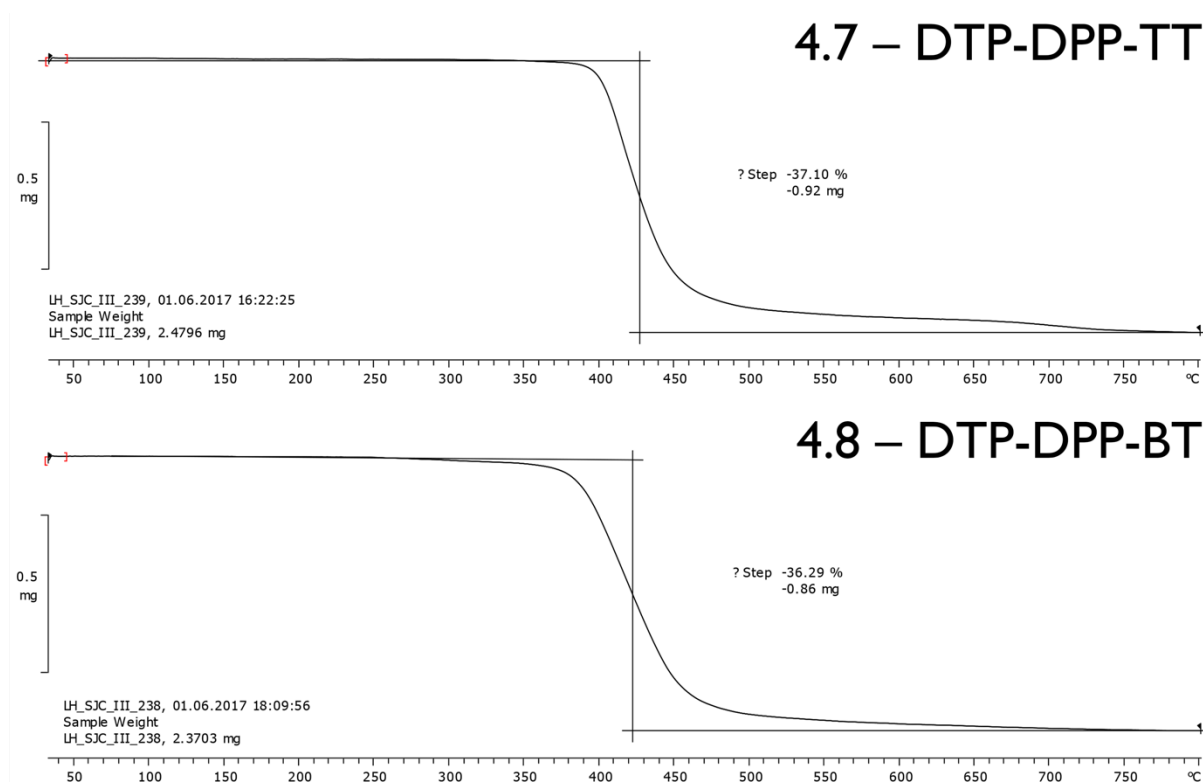


Figure 4.98 – TGA of polymers 4.7 and 4.8 under nitrogen atmosphere

The thermal properties were further probed using DSC performed from -30–340 °C and -30–280 °C for **4.7** and **4.8**, respectively, at a rate of 10 °C/min.

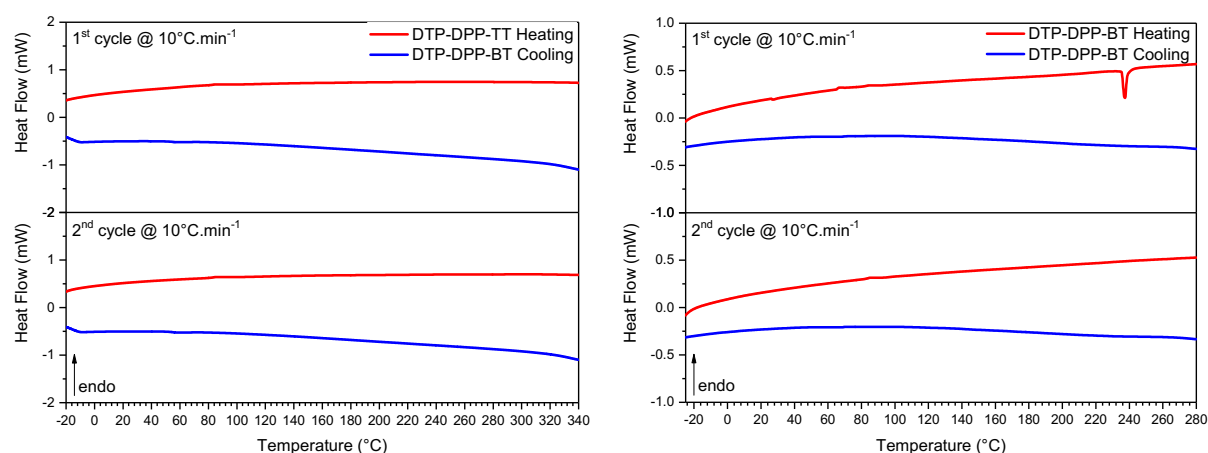


Figure 4.99 – DSC traces (under N_2) of 4.7 (left) and 4.8 (right) under heating and cooling cycles (10 °C/min). 1st cycle (top), 2nd cycle (bottom)

As with many other **DPP** polymers, the DSC traces are almost completely featureless for all cycles (**4.7**) and the second and subsequent cycles (**4.8**), suggesting that the polymers have low crystallisation tendencies. This is unsurprising given the high density of branched alkyl chains of different lengths. The first heating cycle of polymer **4.8** sees an unusual sharp exotherm at 237 °C, which although repeatable (always on the first cycle) is energetically small at 1.2 J/g. It is likely to be an artefact from the many oligomers with differing sizes present, which could re-arrange on heating into a more stable state compared to the highly glassy state formed after the final precipitation into methanol during polymer processing, resulting in a cold-crystallisation. Once this has occurred, the second and subsequent cycles are featureless, which is much more indicative of the true properties of the polymer.

4.4.4 XRD

The molecular packing of the polymers was further investigated using X-ray diffraction (XRD) by drop casting thick films of **4.7** and **4.8** onto silicon (100) substrates from chlorobenzene solutions (10 mg/mL). The resulting XRD patterns are shown in Figure 4.100.

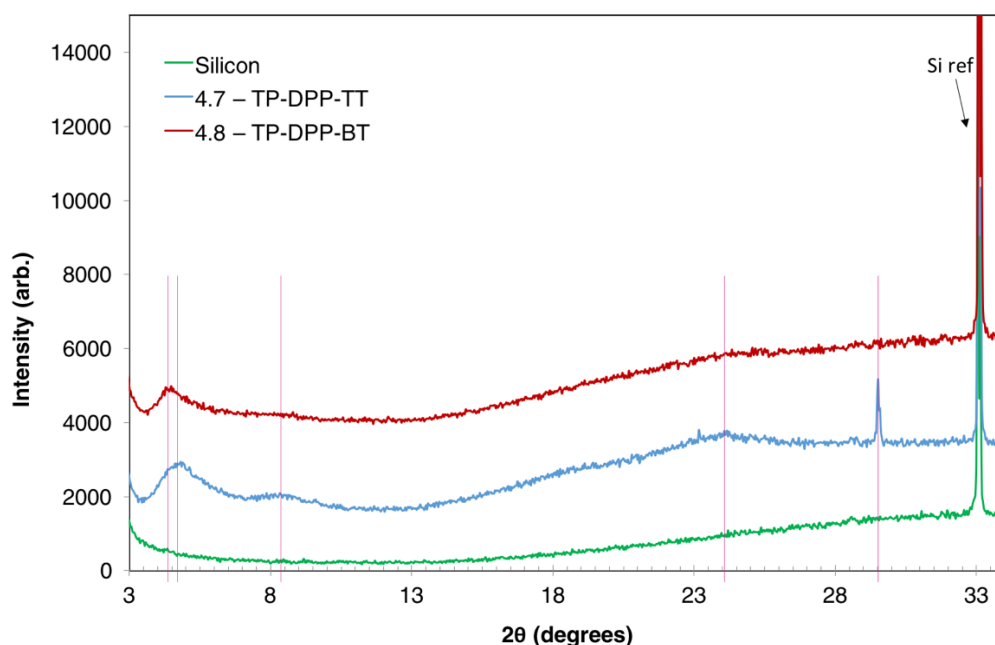


Figure 4.100 – XRD spectra of 4.7 and 4.8 – films were drop cast from chlorobenzene solutions onto Si (100) wafers. Films were measured as cast

Both polymers **4.7** and **4.8** show small, broad peaks at around $2\theta = 4.4^\circ$, which corresponds to a d-spacing of ~ 20 Å. This is within the region of lamellar packing, clearly indicating that some long-range order was observed within both polymer systems. Unlike polymer **4.8**, which has no further order, further peaks can be observed in the spectrum of polymer **4.7**, as summarised in Table 4.11. An additional small broad lamellar peak is seen at 10.5 Å, followed by a broad π - π -stacking peak with the summit at a d-spacing of 3.7 Å. There is then a final, sharp, and clearly defined peak corresponding to a d-spacing of 3.0 Å. This could be close π - π -stacking between the long polymer chains, which agrees with the very flat nature of the polymer indicated by the NMR spectra and the Gaussian calculations. It could also be the length of the repeat unit which being periodic in a rigid polymer could give rise to a peak.

Polymer	2 θ (degrees)	d-spacing (Å)
4.7	4.6	19.19
4.7	8.3	10.64
4.7	24.0	3.70
4.7	29.4	3.04
4.8	4.3	20.53

Table 4.11 – Summary of peaks observed in the XRD spectra of 4.7 and 4.8, and their corresponding d-spacings

4.5 Chapter conclusions

In conclusion, this chapter has reported a new pathway to the synthesis of a complex **DPP**-based monomer incorporating electron-rich **DTP** units on the flank of the **DPP**. The limited oxidative stability of the **DTP** unit added complexity to the synthesis at a number of points, including the initial **DTP** formation and the final monomer bromination. As the purity of the final monomer is highly important, keeping the products of each step as pure as possible was of paramount importance. Hence, extra steps were taken to remove the *O*-alkylated product, to the detriment of the yield but with the benefit of exceptional purity. Bromination in acidic media caused protonation issues requiring basification for the isolation of the final product, which could then be purified and polymerised accordingly.

Two new polymers, **pDTP-DPP-TT (4.7)** and **pDTP-DPP-BT (4.8)** were successfully synthesised with a high molecular weight achieved for the Stille polymerisation product, **4.7**. Although it had a lower molecular weight, polymer **4.8** was still successfully made, and further optimisation of the Suzuki polymerisation may yield higher molecular weights.

The **DTP-DPP** core was shown to arrange in a conformation in which a sort of ‘hydrogen-bond’ was formed between **DTP** protons and the **DPP**-carbonyl oxygen atoms, resulting in an exceptionally planar geometry. Combining this material with the rotationally linear **TT**

and **BT** units gave two highly planar polymers with high persistence lengths and strong push-pull orbital hybridisation, resulting in broad absorption profiles and low band gaps. The **DTP-DPP** central core unit appeared to dictate the position of the HOMOs (-5.1 eV), with the LUMO of **4.8** being brought down in comparison with **4.7** due to the presence of the **BT** unit. The long persistence length of **4.7** was theorised to be responsible for the exceptionally high extinction co-efficient of this polymer, which could lead to high currents in BHJ-OPV.

Both polymers also exhibited good thermal stabilities and fairly featureless DSCs (from the 2nd cycles) that are typical for DPP polymers due to the multitude of branched chains along the backbones. Some lamellar-type order was seen in the XRD patterns of both polymers, but the high molecular weight **4.7** saw a higher degree of order, with a π - π -stacking distance of only 3.0 Å, which could be beneficial for OFET charge transport.

Fabrication into OPV and OFET devices is currently on-going for both of the new materials, with the optical and physical data promising high PCEs and mobilities, especially for **4.7**.

Chapter 5

Carbazole-based non-fullerene acceptors for use in OPV

5.1 Introduction

As discussed in Section 1.4.4, the majority of acceptor materials used in BHJ-OPV devices for the last decade have been **PCBM**-based, with **PC[60]BM** and **PC[70]BM** being the most commonly used materials (Figure 5.101). One of the main driving forces away from the use of these fullerene acceptors has been their cost, with **PC[60]BM** currently costing around \$800/g from commercial sources.¹⁵¹ The reality is that OPV can only be realised with cheap, mass producible materials such as **P3HT**, which can be made for below \$40/g,¹⁵² as opposed to synthetically costly but high efficiency materials such as **PCE10**^{153,154} or **Y4**.¹⁵⁵ With maximum efficiencies in **P3HT/PC[60]BM** cells usually being below 5%,¹⁵⁶ new non-fullerene acceptor materials (NFAs) are required that energetically match with cheaper donor materials such as **P3HT**, ultimately allowing improvements in both price and performance.

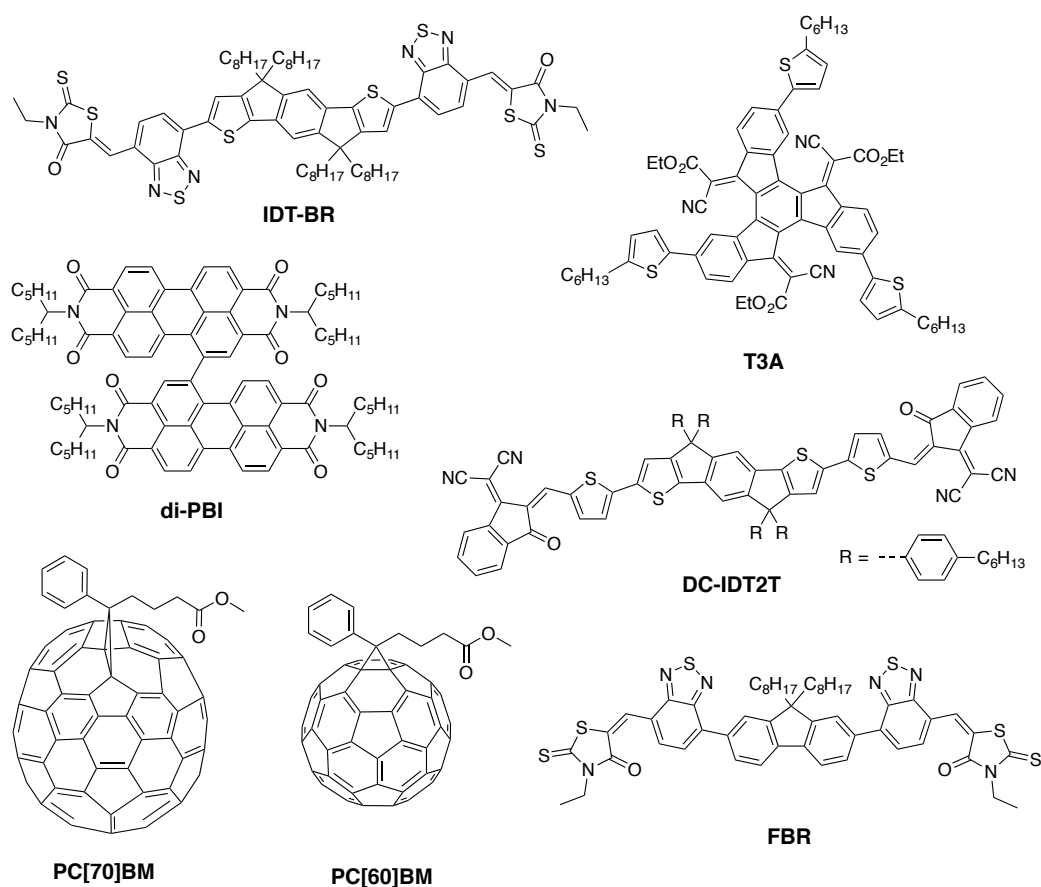


Figure 5.101 – Commonly used fullerene acceptors **PC[60]BM and **PC[70]BM** (bottom left) as well as newer NFAs **IDTBR**,³⁷ **T3A**,¹⁵⁷ **di-PBI**,¹⁵⁸ **DC-IDT2T**, and **FBR**¹¹⁹**

Although a number of different NFA structures have been proposed – often incorporating electron-poor structures such as truxenones,¹⁵⁷ diketopyrrolopyrroles,¹⁵⁹ and perylene diimides¹⁵⁸ – it is the calamitic molecules such as **DC-IDT2T**,¹⁶⁰ **FBR**,¹¹⁹ and **IDTBR**³⁷ that have begun to surpass the PCEs achieved in **PCBM**-based BHJ-OPVs. Their effectiveness as **PCBM** alternatives stems from a number of design principles based around an electron rich rigid ‘donor’ core flanked by either a donor or acceptor unit (D/A), followed by an acceptor moiety (A) that is often attached via a vinyl linkage (Figure 5.102).



Figure 5.102 – Schematic illustrating a calamitic NFA with a rigid donor core and flanking acceptor units³⁸

The combination of multiple electron rich or poor units in a symmetrical pattern allows exact tuning of the energetics through orbital hybridisation whilst also simplifying the synthetic pathway. As well as allowing electronic tuning, each unit also plays a role in the morphological and charge-transport properties within the BHJ-OPV device.

The rigid donor core aids crystallinity, whilst also providing a point for the attachment of solubilising alkyl chains. Some of the most efficient NFAs have utilized central cores previously seen as monomer units in well-known high performing polymers such as indacenodithiophene (**IDT**),^{59,160} fluorene,¹⁶¹ and indacenodithieno[3,2-b]thiophene (**IDT2T**).¹⁶² Attaching the bulky solubilising chains to the central core also provides steric freedom to the flanking acceptor units, making them sterically available for electron transfer and therefore improving charge transfer at the polymer/NFA interface.¹⁶³ This steric availability of the acceptors is necessary as these units are often where the LUMO is spatially

localised in NFAs, and it has been hypothesised that improving the ‘steric registry’ between the NFA LUMO and the donor polymer LUMO in donor/acceptor BHJ-OPVs is beneficial to device performance.³⁸

The building blocks between the rigid donor core and the flanking acceptors in calamitic NFAs mainly act as tuning parameters for increasing or decreasing the band gap, allowing adjustment of the spectral overlap and the LUMO-LUMO offset between the NFA and donor polymer. In the case of **IDTBR**, the use of the electron-poor benzothiadiazole unit helps to extend the LUMO, thereby providing a larger area with steric access to the donor polymer for efficient electron transfer.

The aim of this project was to synthesise and analyse a series of new non-fullerene acceptors through modification of the central rigid donor core. The rationale was to base the design on the successful **FBR** acceptor (4.1% in OPV with **P3HT**), changing the central fluorene unit to a carbazole with the same length alkyl chains (Figure 5.103).

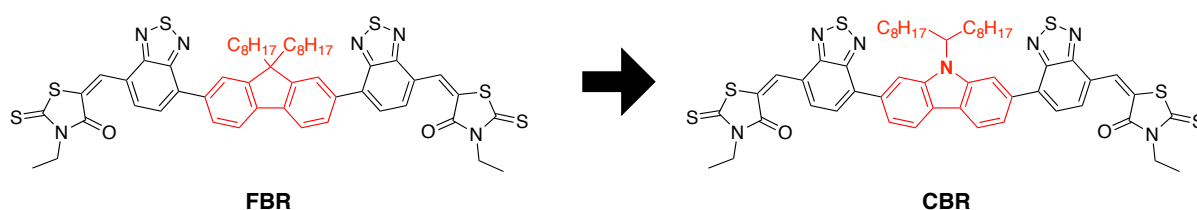


Figure 5.103 – Design rationale of modification of the successful FBR unit (left) by changing the central fluorene core to a new carbazole moiety (CBR – right)

The potential benefits of this modification are two-fold. Firstly, the carbazole unit is more electron rich than the fluorene derivative, therefore increasing the ‘push-pull’ orbital hybridisation effect across the NFA. By solely changing the electron rich unit, the HOMO level should be raised, resulting in a lower bandgap than **FBR** whilst keeping the LUMO level intact (with an offset large enough to enable charge separation). This raising of the HOMO should effectively red-shift the absorption and reduce the absorption overlap with the

P3HT donor polymer, potentially increasing the overlap with the AM 1.5 spectrum and increasing efficiency.

Secondly, the alkyl chains on **FBR** protrude out of the plane of the molecule from the sp^3 -bridging carbon, whereas the bridging nitrogen atom within the carbazole sits within the plane of the backbone with the branching point sitting one carbon away. This could potentially aid the packing of the **CBR** unit in the solid state, improving charge transport in devices. Although structurally different, Meager et al. have shown that through alkyl chain branching point manipulation on **DPP** units, the addition of a single carbon between the nitrogen and the alkyl chain can significantly improve PCE.¹⁰⁶

As well as making the **CBR** analogue to **FBR**, new flanking electron accepting groups such as indandione and thiobarbituric acid will be explored to tune the energy levels of the new carbazole-based molecule further.

5.2 Synthesis

The synthesis was carried out according to modified literature procedures.¹¹⁹

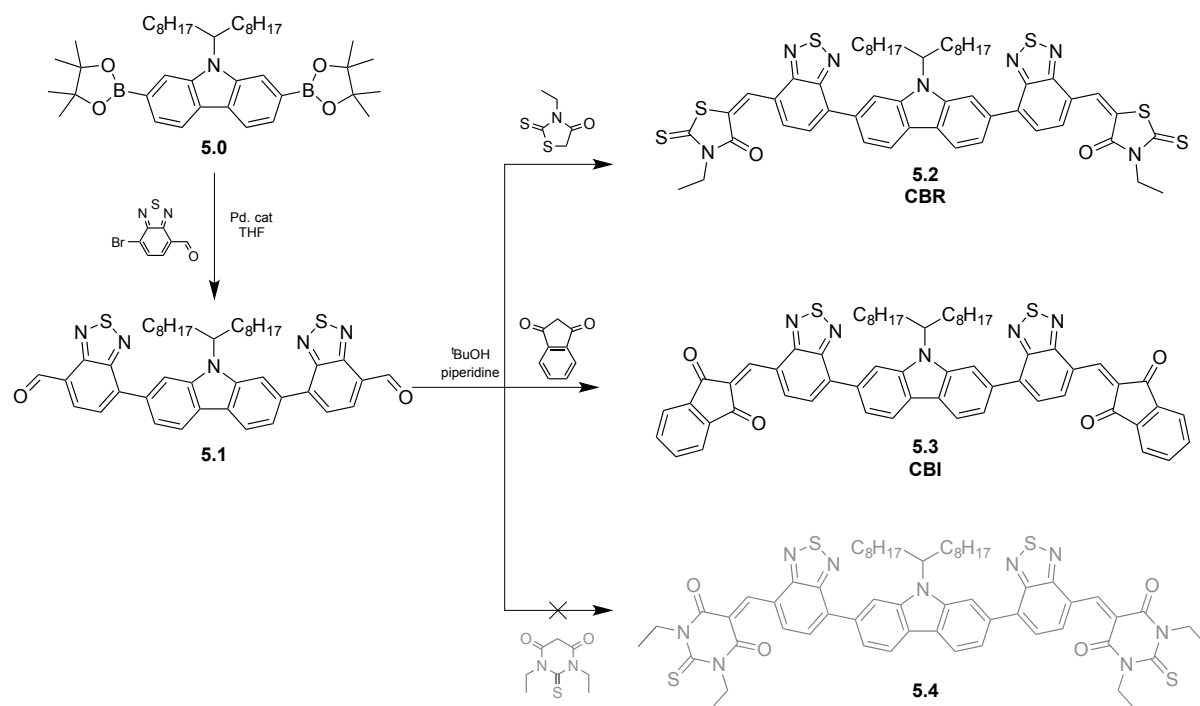


Figure 5.104 – Synthesis of carbazole-based NFA acceptors

Initially, the commercially available carbazole-diboronic acid-bis(pinacol) ester (**5.0**) was coupled to the commercially available benzothiadiazole unit via a palladium-catalysed Suzuki cross coupling reaction to form **5.1** as a bright orange solid. Although column chromatography in 1:1 DCM:Hex (+2% EtOAc) yielded a highly pure product, streaking of material on the column suggested it was sticking to the silica (most likely due to the two polar aldehyde groups), reducing separation and resulting in the lower-than-expected yield (62%). As expected, the proton NMR shows a highly deshielded singlet at 10.83 ppm corresponding to the aldehyde proton. Although the integrations of the aromatic peaks between 7.8 and 8.5 ppm were correct (5 protons), the expected splitting patterns (4 doublets and 1 singlet) were not observed, with 3 broad signals and 2 doublets being seen (Figure 5.105).

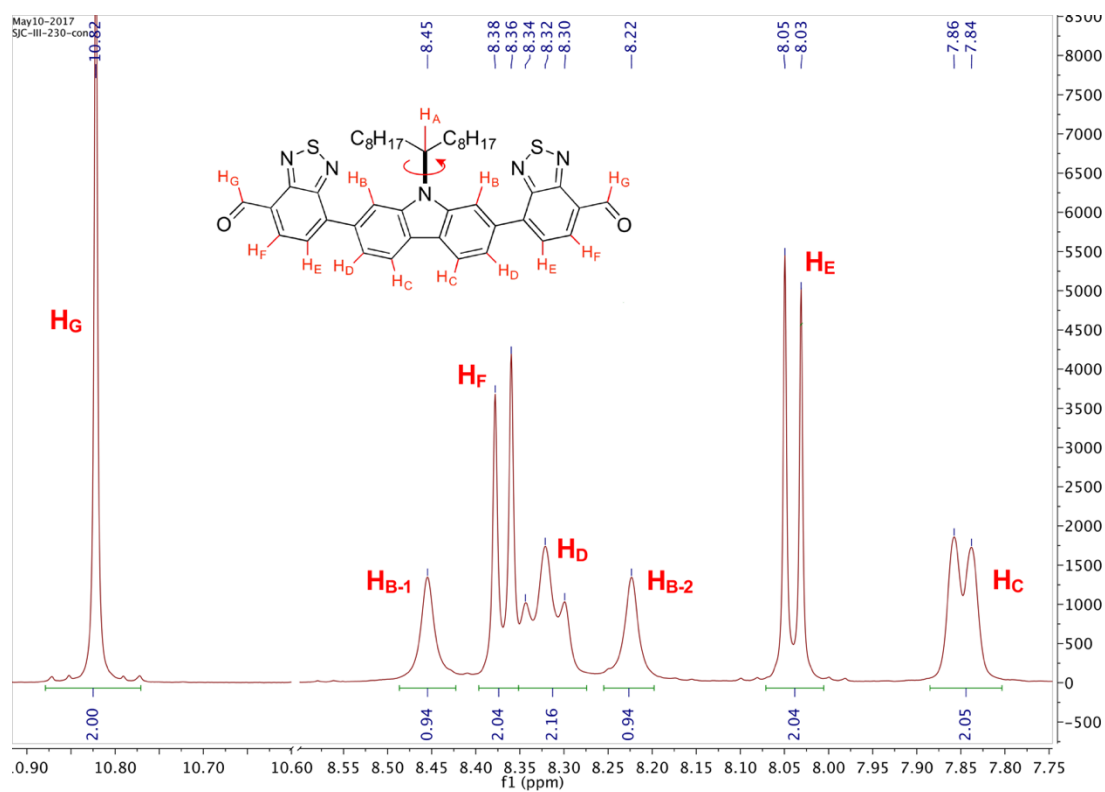


Figure 5.105 – Annotated aromatic region of 5.1 1H NMR

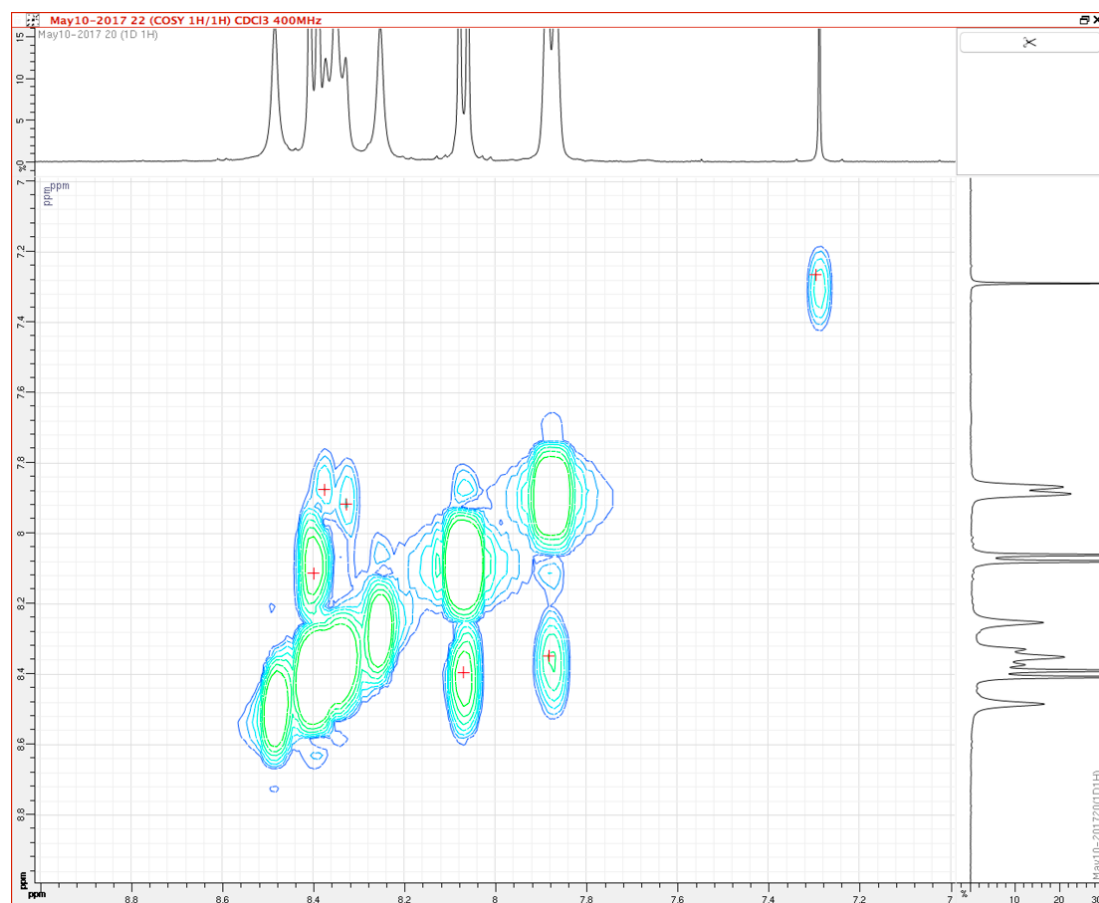


Figure 5.106 – 1H COSY spectrum of 5.1

It is well known in the literature that rotational barriers around a bond can cause line broadening and splitting of peaks due to lack of environmental equivalence,¹⁶⁴ with the NMR spectra observed being characteristic of this type of behaviour. To determine whether this was a bond-rotation effect as opposed to a purity issue, a homonuclear correlation spectroscopy (COSY) NMR sequence was performed to identify which protons were directly coupled to each other and therefore adjacent to one-another through bonds (Figure 5.106), giving insight into the peak assignment. Although it was initially speculated that the rotational barrier was around the carbazole–benzothiadiazole (**Cbz-BT**) bond, this was disproven by the COSY sequence, which showed that the two doublets at 8.04 ppm and 8.35 ppm represented adjacent protons. As both signals had defined splitting patterns, this meant that the rotational barrier could not be between the **Cbz-BT** units, and that the signals 8.04 and 8.35 ppm could be attributed solely to the **BT** unit (H_E and H_F). There is some literature precedent for rotational torsion occurring for asymmetric alkyl chains around the N-R bond of carbazoles, as illustrated by the arrow in Figure 5.105.^{165,166} The rotational torsion around this bond leads to a distortion in symmetry when proton H_A is stuck in a position pointing towards either of the H_B protons. This results in H_B being subjected to two magnetic environments, and hence two peaks with equal integrations (H_{B-1} and H_{B-2}) are visible in the spectrum.

The remaining unlabelled peaks at 7.85 ppm and 8.32 ppm must be H_C and H_D , as confirmed by their direct correlation in the COSY sequence, and with the peak at 8.32 ppm showing secondary coupling effects, the poorly resolved doublet (most likely due to the proximity to the rotational barrier) at 7.85 ppm must therefore be due to H_C .

The H_D peak at 8.32 ppm is split into a doublet due to coupling to H_C , then split further by smaller long-range J-coupling through the aromatic system to H_B . Due to the two magnetic

environments of H_B , these peaks are split again and broadened, giving the triplet-like peak observed as H_D .

Proton H_A also experiences magnetic inequivalence due to the rotational anisotropy around the N-R bond resulting in a complex multiplet at (4.77 pm) as observed in Figure 5.107

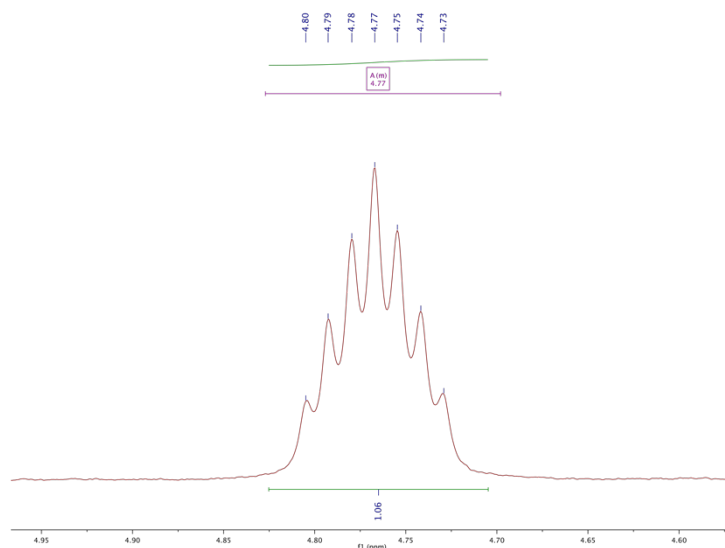


Figure 5.107 – 1H NMR of 5.1 showing complex multiplet splitting for proton H_A

Having determined that the product **5.1** was pure and the curious NMR was caused by a rotational equilibrium effect, the product could be used for the next synthetic step – a Knoevenagel condensation^{167,168} with rhodanine and indandione derivatives. The Knoevenagel condensation is an equilibrium reaction in which an enolate is formed through reaction of an aldehyde with a mild base, which then undergoes nucleophilic addition to a carbonyl group followed by dehydration to form the conjugated enone, as seen in structures **5.2 (CBR)** and **5.3 (CBI)**. The use of a mild base is required so that the aldehyde does not undergo disproportionation, and therefore strong electron withdrawing groups are required on the enolate-forming moiety to enable enolation to occur.

The formation of both **CBR** and **CBI** in refluxing *t*-BuOH using piperidine as a mild base proceeded as expected. The removal of the solvent via rotary evaporation followed by dilution in a minimum volume of chlorobenzene before precipitation into methanol and

filtration yielded both products in moderate purity. Purification of the two compounds was carried out either via recrystallization in toluene/hexane or using a recycling GPC (eluent: chlorobenzene) to remove any mono-adduct within the material, which could be detected in ^1H NMR by the presence of an aldehyde peak at 10.82 ppm. Although these purification procedures reduced the yield, extensive purification of both small molecules was required to provide the high level of purity needed for use in OPV devices. During the work-up procedures for both NFAs, all solvents were washed with K_2CO_3 then filtered to remove any mild acidity within them that could promote the reversal of the Knoevenagel reaction.

The multiple attempts to form the barbituric acid derivative **5.4** resulted in decomposition. Although NMR analysis was used to try to figure out the decomposition mechanism, the complete lack of any discernible peaks in either the starting material or the product meant little information was available. The synthesis of barbituric acid derivatives of other calamitic NFA molecules was also attempted by other group members without success, and therefore the target was abandoned.

5.3 Physical properties

5.3.1 Optimised geometry modelling

To determine the minimum energy conformations of **CBR** and **CBI**, molecular modelling using the $\omega\text{B97X-D/6-31G}^*$ functional/basis set was performed. The symmetric indandione end groups of **CBI** result in it having a higher level of symmetry than **CBR**, and therefore running the initial optimisations on **CBI** reduced the possible number of permutations to 8 (Figure 5.108), compared with 32 for **CBR**.

The 8 permutations began with the central carbazole being positioned such that the alkyl chains pointed upwards and then orientating the indandione units and **BT** units either up (U) or down (D) in relation to the alkyl chains of the central carbazole unit.

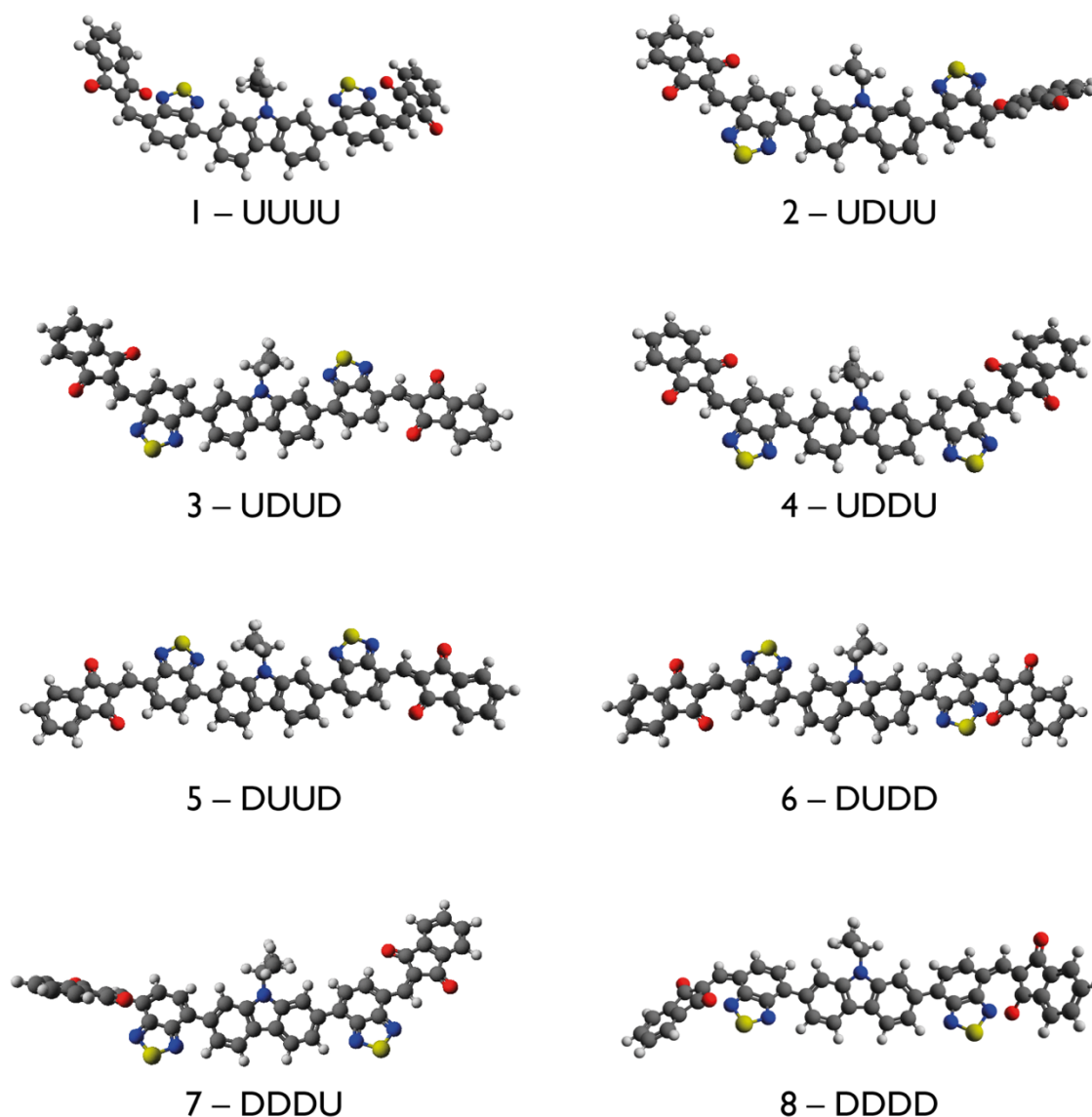
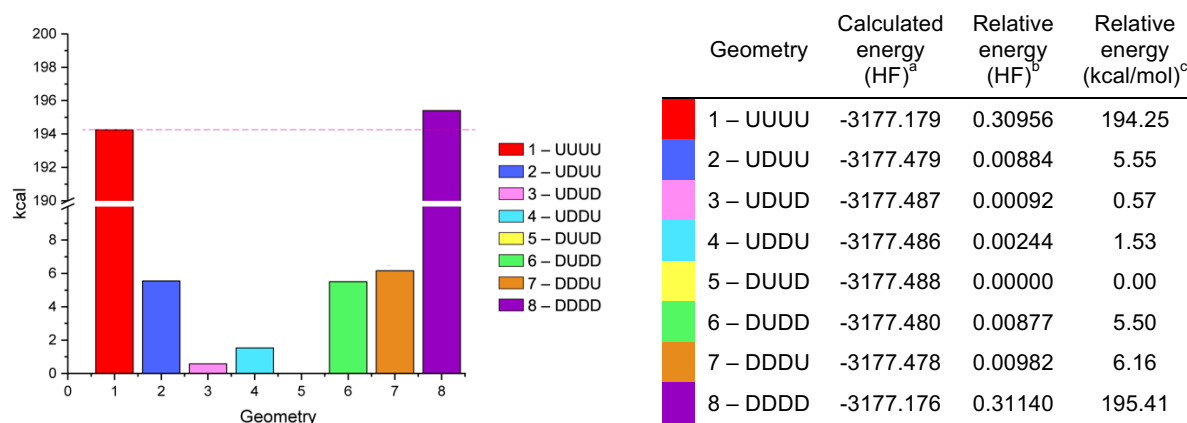


Figure 5.108 – The eight possible permutations of CBI. The first letter corresponds to the direction of the far left indandione, the second letter the left BT unit, then the right BT unit, and finally the right indandione

Each geometry was then optimised to a stationary point on the energy surface before a frequency calculation was run to check for imaginary frequencies (which would indicate that the optimisation is at a saddle point as opposed to a local minimum), of which there were none. Geometry 5 (Figure 5.108) was the global energy minimum, to which all the other geometries energies were normalised against to give the visualisation below (Figure 5.109).



a) Calculated energy, HF = hartrees; b) Relative energy compared to geometry 5; c) Relative energy converted to kcal

Figure 5.109 and Table 5.12 – Calculated Gaussian energies of optimised conformations of CBI relative to the lowest energy conformer (5 – DUUD)

Geometry 3 is the most similar in energy to geometry 5, with the relative energy being the only other geometry to be within $k_B T$ (0.59 kcal/mol at 297 K). Both geometries 1 and 8, where all units were pointing either up or down, are highly unstable – clearly seen by their twisted natures and large relative energies compared with the other conformers. Although much lower in energy than geometries 1 and 8, geometries 2, 4, 6 and 7 are still much greater than $k_B T$, making them unstable compared to geometry 5. It should be noted however that the energy required to change between conformers is unknown, and therefore once the molecule is fixed in a certain geometry, it may be difficult to move between them.

Comparing the conformers, the orientation of the **BT** units compared with the central carbazole appears to make little difference to the relative energy (e.g., conformers 4 and 5). Stabilisation appears to result from the indandione end group pointing away from the sulphur of the **BT** group, resulting in planarisation and improved conjugation between these two units. In contrast, there is a large energy cost when the **BT** unit and indandione unit point in the same direction, which causes twisting between these two units, breaking the conjugation and raising the energy of the molecule.

Knowing that **CBI** is at its lowest energy when the end groups point in the opposite direction to the **BT** sulphur, this arrangement (DUUD) could then be applied to the two different arrangements of the **CBR** molecule with the sulphur of the rhodanine pointing either up (**CBR-A**) or down (**CBR-B**) in relation to the **BT** unit (Figure 5.110).

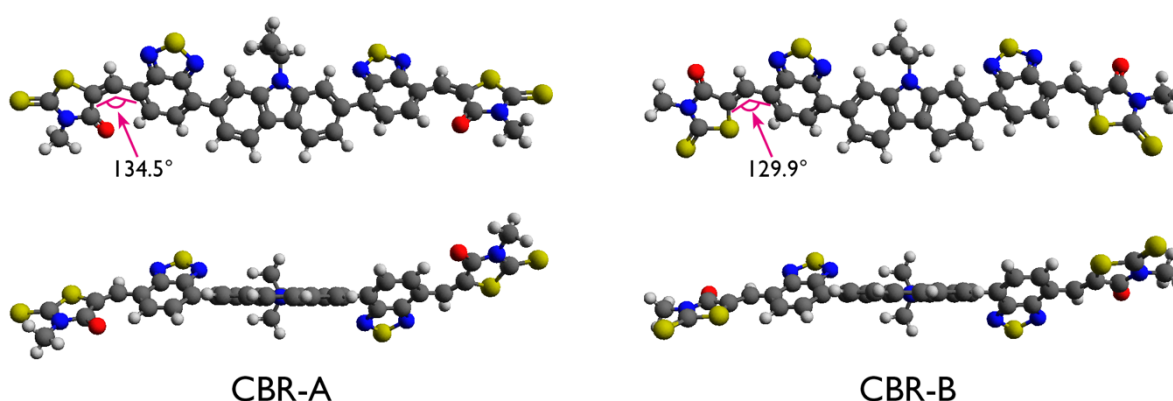


Figure 5.110 – Conformations of CBR based on the DUUD geometry of CBI

CBR-B is the lower in energy of the two conformers by 6.3 kcal / mol. Although the interaction between the **BT** and rhodanine groups is a planarising one, the steric strain between the C=O of the rhodanine and the **BT** proton causes the labelled angle to be 4.6 ° wider in **CBR-A** (Figure 5.110). This strained dihedral between the BT and rhodanine units is therefore the likely cause of the increase in energy for **CBR-A** and why **CBR-B** is the lowest energy conformer of the two.

With the two lowest energy geometries of **CBR** and **CBI** having been calculated, DFT-HF calculations could be performed to tune the ω value for each molecule so as to generate accurate MO visualisations (Figure 5.111). The ω B97XD functional was used with the expanded 6-311G** basis set which improves the accuracy of the obtained numerical outputs by the addition of two more functions for each valence atom orbital.

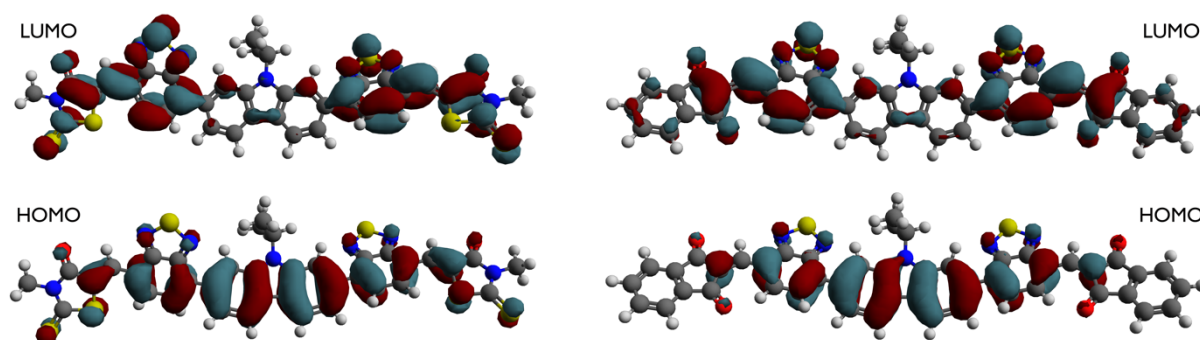


Figure 5.111 – HOMOs (bottom) and LUMOs (top) of CBR (left) and CBI (right) as calculated using DFT-HF with the ω B97XD/6-311G method and basis**

The HOMOs are fairly delocalised across the molecule in both **CBR** and **CBI**, whereas the LUMOs are localised on the flanking electron-poor moieties. This is more pronounced in **CBR**, where the LUMO extends across the **BT** and rhodanines, whereas in **CBI** the LUMO is localised more on the **BT** and carbonyl groups and does not extend out to the peripheral benzenes. That said, the sterically exposed LUMO on the outer peripheries of both **CBR** and **CBI** should be beneficial for charge transfer in BHJ-OPV devices. The further extended LUMO on **CBR** should aid performance even more through enhanced steric registry between the NFA and the polymer acceptor.

5.3.2 Optical and electronic properties

The absorption properties of **CBR** and **CBI** were studied via UV-Vis spectrometry in dilute chlorobenzene solutions and as thin films spun onto glass substrates from chlorobenzene solutions (5 mg/mL) (Figure 5.112). The λ_{max} of **CBR** in solution is observed as a wide band with a peak at 503 nm and two smaller absorption bands at 376 nm and 331 nm. In the thin film state, λ_{max} shifts by 22 nm to 525 nm, with this being due to solid-state packing effects. As the small molecules stack close together in the solid state, conjugation increases due to greater planarisation across the molecules, red-shifting the wavelength. There could also potentially be a degree of J-aggregation occurring which is where the dipoles of the molecules line up in a head-to-tail fashion in the solid state, reducing the energy of the

system and causing a bathochromic shift.¹⁶ The characteristic sharp peaks that arise from J-aggregation would be covered by the broad nature of the ICT-band and therefore cannot be explicitly dis-entangled from the solid-state packing effects.

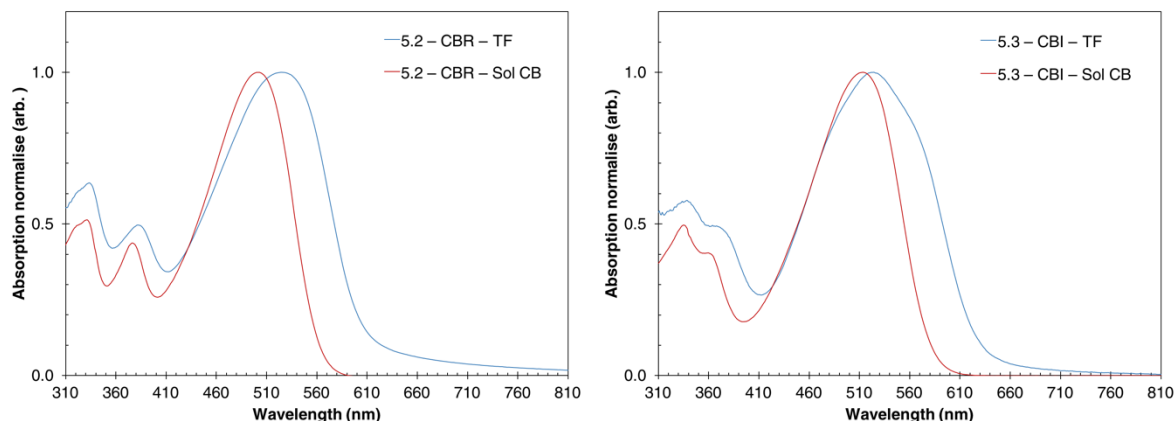


Figure 5.112 – UV-Vis spectra of CBR (5.2 – left) and CBI (5.3 – right) in CB solutions (red) and as thin films (blue)

CBI has a similar spectrum, although the solution $\lambda_{\max}$ is found at 514 nm (with two shoulders at 335 and 360 nm), and the bathochromic shift on movement to a thin-film is smaller, with $\lambda_{\max}$ being found at 524 nm. The shape of the **CBI** absorption spectrum gives the appearance of a shoulder at around 580 nm on moving from solution to thin-film, whereas no shoulder is observed for the thin-film **CBR** spectrum, with uniform bathochromic broadening being seen instead.

As with **FBR**¹¹⁹ (Figure 5.103), both **CBI** and **CBR** both have absorption profiles that extend across the visible range (compared with PC[60]BM, $\lambda_{\max} \approx 300$ nm),¹¹⁹ enhancing the potential Channel-II absorption when they are used as acceptors in BHJ-OPV devices by extending the overlap of the donor-acceptor blend with the AM1.5 spectrum¹⁶⁹ and ultimately increasing device current density.

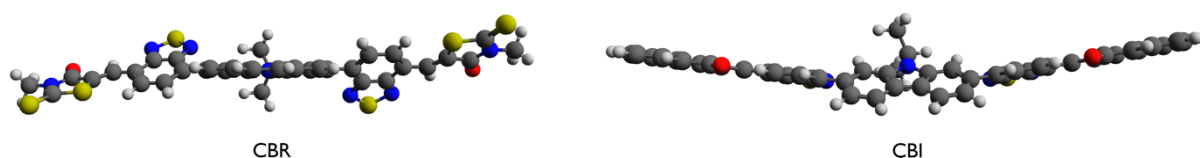


Figure 5.113 – Side-view of CBR and CBI

The optical band gap was estimated from the onsets of absorption in the thin-film UV-vis spectra, giving E_{opt} (**CBR** at 604 nm) = 2.05 eV and E_{opt} (**CBI** at 628 nm) = 1.98 eV. Overall, the larger aggregation shoulder observed in the **CBI** UV-vis could be due to the reduced twisting along the molecule backbone (Figure 5.113), supported by the low calculated dihedral angle between the **BT** and flanking unit, which was 1° for **CBI** compared to 11° for **CBR**. This decreased dihedral could allow closer π - π interactions between molecules, resulting in a stronger dipole interaction and increasing the stabilisation afforded by the planarisation/J-aggregation, thereby reducing the band gap compared with **CBR**.

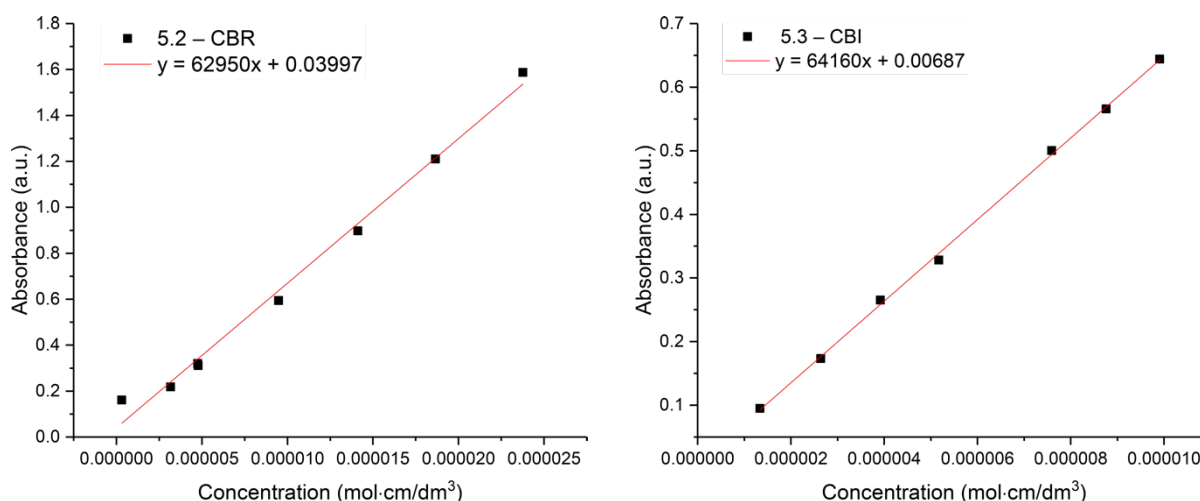


Figure 5.114 – Plots showing linear fits used to calculate the molar extinction coefficients for 5.1 – CBI at 503 nm (left) and 5.2 – CBR at 514 nm (right)

Molar extinction coefficients were calculated from a series of dilute solutions of **CBR** and **CBI** in chlorobenzene, giving values of $63,500 \text{ M}^{-1}\text{cm}^{-1}$ and $64,000 \text{ M}^{-1}\text{cm}^{-1}$, respectively (Figure 5.114). This is double the value of **FBR** ($34,600 \text{ M}^{-1}\text{cm}^{-1}$) and an order of magnitude larger than that of PC[60]BM ($4,900 \text{ M}^{-1}\text{cm}^{-1}$). The extinction coefficient is directly related to

the oscillator strength,^{14,170} and was likely improved by the large spatial HOMO/LUMO overlaps seen in both acceptors. This substantial improvement could be used as a design criterion for other similar NFAs to improve the extinction coefficients, allowing improved current generation in devices.

NFA	$\lambda_{\max}^{\text{sol}}$ (nm) ^a	$\lambda_{\max}^{\text{TF}}$ (nm) ^a	E_{opt} (eV) ^b	ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ^c	$E_{\text{HOMO-CV}}$ (eV) ^d	$E_{\text{LUMO-CV}}$ (eV) ^e
CBR	503	525	2.05	63.5	-5.39	-3.41
CBI	514	524	1.98	64.1	-5.57	-3.64
FBR^f	488	509	2.14	34.6	-5.70	-3.57

a) Extracted from UV-vis spectra; b) Estimated from optical absorption edge in thin films; c) Maximum molar extinction coefficient; d) Calculated by addition of E_{opt} to LUMO; e) Extracted from onset of oxidation in CV performed in 0.1 M n-Bu₄PF₆; f) Values taken from Holliday et al.¹¹⁹

Table 5.13 – Optoelectronic properties of NFAs

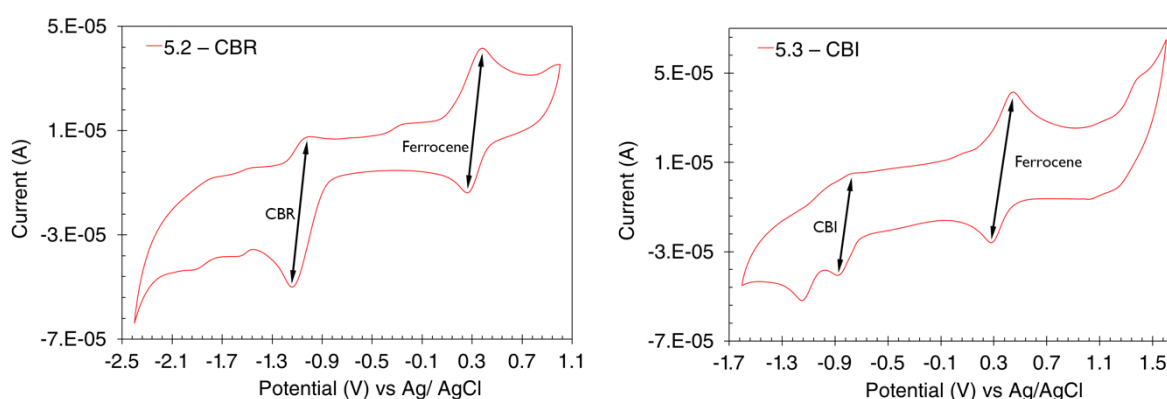


Figure 5.115 – Cyclic voltammograms of CBR and CBI in DCM solution (0.3 mM) with tetrabutylammonium hexafluorophosphate electrolyte (0.3 M) at 0.8 Vs⁻¹¹²²

Cyclic voltammetry was performed to probe the electrochemical properties of the NFAs. This was initially performed on spin-coated ITO films, however delamination of the films meant that neither oxidation nor reduction values could be obtained, and therefore CV was performed in dichloromethane solution (at an analyte concentration of 0.3 mM) using ferrocene in the solution as an internal standard (peaks at $\sim +0.3$ V vs Ag/AgCl using a 0.3 M tetrabutylammonium hexafluorophosphate electrolyte). Within the dichloromethane solvent

window, **CBR** shows a clear reduction peak followed by two smaller reduction events at higher (negative) potentials, whereas **CBI** shows two clear reduction peaks of similar magnitudes. Multiple reduction peaks are an indication that there are accessible low-lying excited states on the excited anion, which can increase the rate of charge-transfer and increase the current density.¹⁷¹

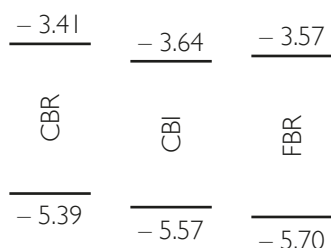


Figure 5.116 – CBR, CBI, and FBR energy levels in eV

Both **CBR** and **CBI** showed decreased band gaps compared **FBR** due to the more electron-rich carbazole core unit causing slightly more ‘push-pull’ orbital hybridisation across the cores of the molecules. For **CBR**, this raised the HOMO level by over 0.3 eV (–5.39 eV) and the LUMO by 0.16 eV (–3.41 eV). The HOMO of **CBI** (–5.57 eV) also rose in comparison to that of **FBR**, but only by 0.13 eV. This is because the indandione end groups in **CBI** are more electron poor than the rhodanines in **CBR**, meaning there was less electron density in the **CBI** system, yet greater orbital mixing, causing an overall lowering of the LUMO (–3.64 eV) and the lowest narrowest band gap of the three NFAs.

5.3.3 TGA and DSC

Thermogravimetric analysis (TGA) was performed (25 to 700 °C, 10 °C/min) to assess the thermal stabilities of **CBR** and **CBI**. Decomposition of the materials (defined by 5% mass loss) occurred at 393 °C and 363 °C, respectively (Figure 5.117).

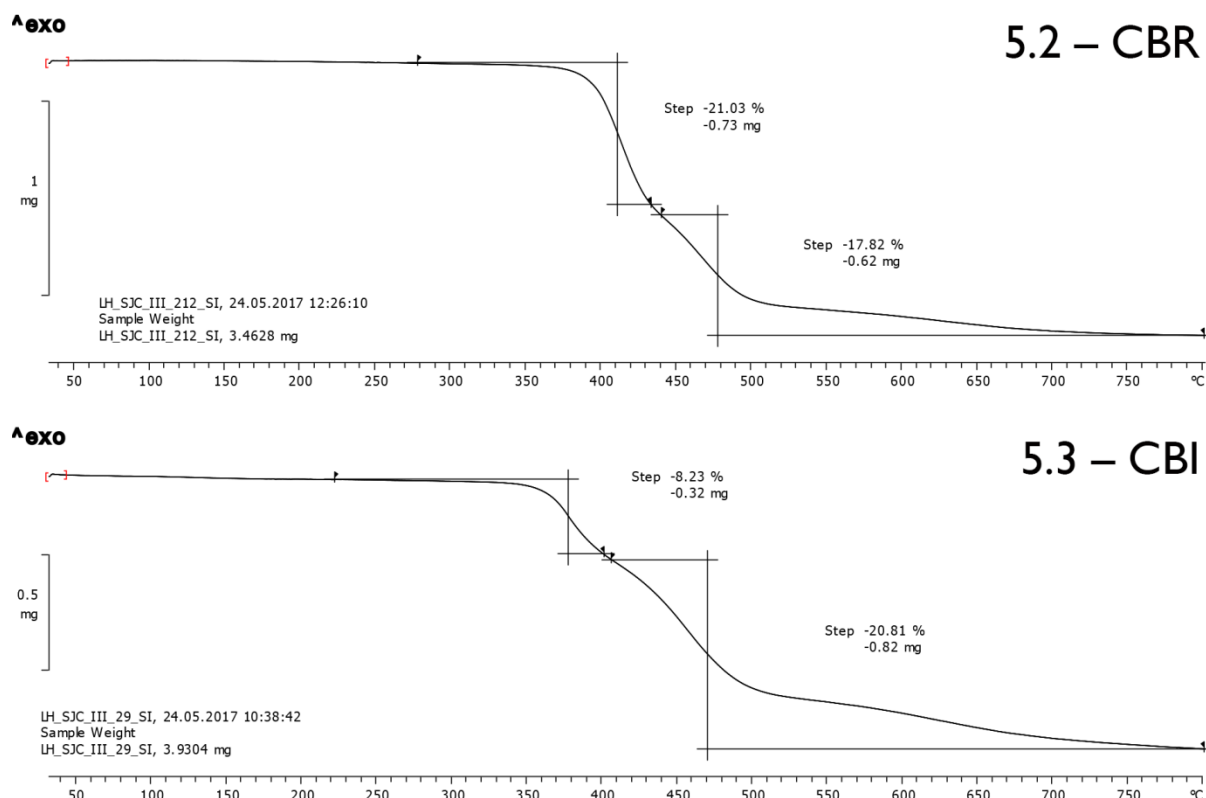


Figure 5.117 – TGA of small molecules CBR and CBI under nitrogen atmosphere

Thermal stability is an important factor as device annealing can have drastic effects on performance, with devices often enduring annealing temperatures as high as 250 °C for sustained time periods.

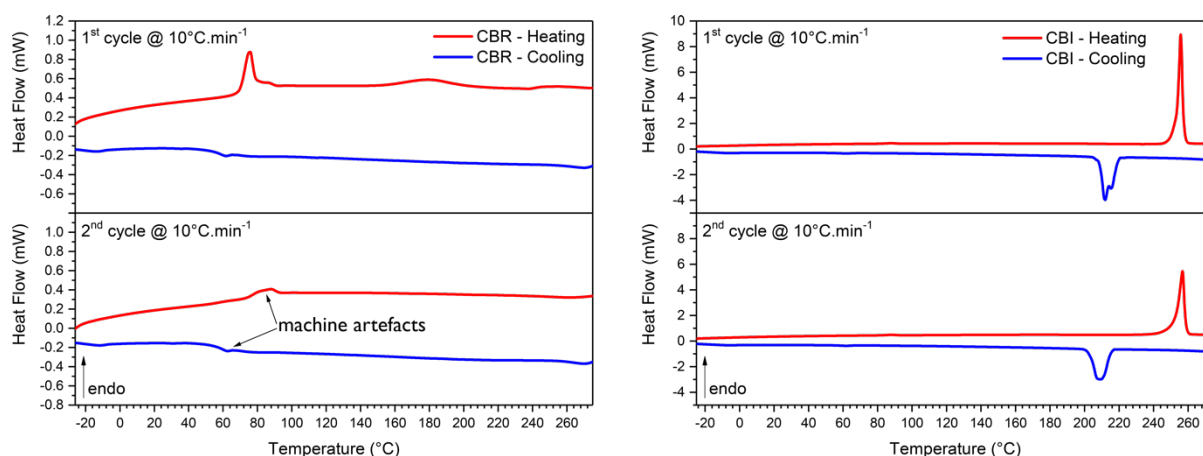


Figure 5.118 – DSC traces (under N₂) of CBR (left) and CBI (right) under heating and cooling cycles between –25 °C and 275 °C (10 °C / min). 1st cycle (top), 2nd cycle (bottom)

The thermal properties were further probed using DSC between $-25\text{ }^{\circ}\text{C}$ and $275\text{ }^{\circ}\text{C}$, with the 1st cycles being shown on the top graphs and the second cycles on the bottom of Figure 5.16.

The DSC for **CBR** shows a melt at $76\text{ }^{\circ}\text{C}$ ($\sim 6\text{ J/g}$) on the first heating cycle only, although this value is incredibly close to an artefact that is observed around $80\text{ }^{\circ}\text{C}$ on the DSC machine and therefore cannot be completely disentangled from this aberration. In the subsequent cycles, only the artefact appears and therefore it can be taken that **CBR** (much like **FBR**) is kinetically trapped in an amorphous state after the first melt. This lack of molecular order is corroborated by the non-planar / twisted nature of the molecule observed in the molecular modelling (Figure 5.110), which would potentially disrupt the packing and stop large crystallite domains from forming.

On the other hand, **CBI** has an exceptionally planar configuration (Figure 5.110) with little backbone twisting, promoting molecular order. This is evidenced by the very large melt seen at $256\text{ }^{\circ}\text{C}$ (73 J/g) on the first heating cycle, which is then repeated in subsequent cycles. The exothermic event in the first cooling cycle exhibits a slight shoulder at $215\text{ }^{\circ}\text{C}$, with the main event occurring at $212\text{ }^{\circ}\text{C}$ (56 J/g), suggesting polymorph formation on cooling. This could be evidence that there are in fact multiple geometries present in the **CBI** sample as discussed in Section 5.3.1. In subsequent cycles, this crystallisation peak is seen at slightly lower temperatures ($209\text{ }^{\circ}\text{C}$) as a broader peak with little resolution.

NFA	Cycle	Temp ($^{\circ}\text{C}$)	Integral ($\text{mW}\cdot^{\circ}\text{C}$)	Enthalpy (J/g) ^a
CBR	Heating 1	76	2.737	6.2 ^b
CBI	Heating 1	256	29.003	73.1
CBI	Cooling 1	212 / 215	-22.259	-56.1
CBI	Heating 2	257	24.960	62.9
CBI	Cooling 2	209	-20.442	-51.5

a) Positive = endothermic, negative = exothermic; b) Artefact energy removed

Table 5.14 – Exo- and endothermic events for CBR and CBI as determined by DSC

5.3.4 XRD

The molecular packing of the polymers was further investigated using X-ray diffraction (XRD) by drop casting thick films of **CBR** and **CBI** onto silicon (100) substrates from chlorobenzene solutions (10 mg / mL). The resulting XRD patterns are shown in Figure 5.119.

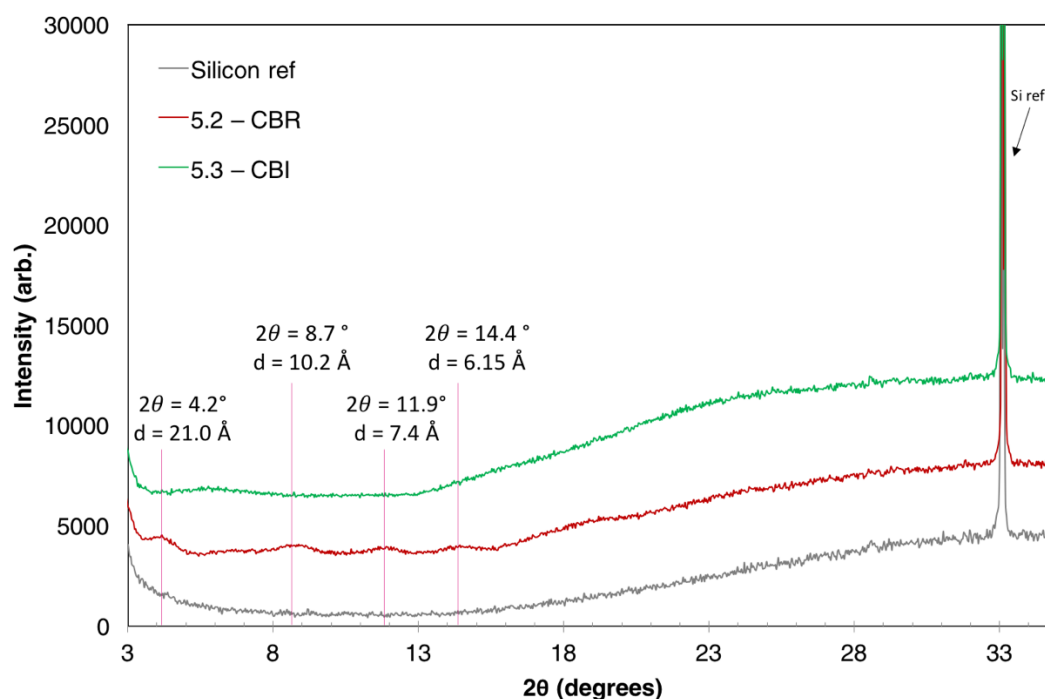


Figure 5.119 – XRD spectra of CBR and CBI – films drop casted from chlorobenzene solutions onto Si (100) wafers. Films were measured as cast

The XRD spectra are primarily amorphous in nature, with no indication of any π - π -stacking in the region $2\theta = 23$ - 33° , although some small peaks can be observed in the lamellar packing region ($2\theta = 3$ - 15°) for **CBR**. It is possible that the low melt seen in the DSC (76°C) for **CBR** is related to the break-up of this weak lamellar packing between the molecules, which could form during the slow process of drop-casting from chlorobenzene but not during the rapid cooling that takes place during DSC.

The XRD data for **CBI** is contrary to expectations, as the high enthalpy events in the DSC suggest a strong π - π -stacking between units. This might be expected to result in a signal in

the XRD, whereas an almost completely featureless XRD pattern is seen. Out-of-plane XRD (q_z) has some limitations as a technique, in that in-plane reflections cannot be seen due to the lack of 2D detection in the q_{xy} plane. This can only be observed with techniques such as GIWAXS (using a synchrotron source),¹⁷² and therefore a lack of XRD data does not definitively prove there is no long-range order within the molecule, just that it is undetectable using this particular technique.

Although long-range order is beneficial for charge-transport, a high degree of crystallinity can actually be detrimental in BHJ devices. There is a trade-off between crystallinity (which can aid charge transport) and formation of large domains, as these can hinder the development of the bi-continuous donor/acceptor network required for highly efficient devices if they are too crystalline. For example, perylene diimides are known to form large polycrystalline domains that induce self-charge-trapping, reducing current density and ultimately PCE.¹⁷³ Therefore, the determination of morphological success is best reserved until after the analysis of BHJ devices.

5.4 OPV results

The two materials underwent initial testing as acceptor materials in BHJ-OPV devices.

Unfortunately, the strong aggregation of **CBI** lead to solubility issues at a concentration of 24 mg/mL when used in a 1:1 ratio with P3HT in chlorobenzene. The materials did not fully solubilise even on heating, and when trying to remove the larger aggregates the suspension immediately blocked a 0.45 μm PTFE filter. Attempted spin coating of films resulted in inhomogeneous micro-scale aggregates forming, and therefore more extensive device optimisation will be needed before this material can be fully tested.

CBR did not have the same solubility issues, and was fabricated into inverted architecture solar cell devices (glass/ITO/ZnO/**P3HT:CBR**/MoO₃/Ag) using a 1:1 ratio of **P3HT:CBR**

spin-coated from chlorobenzene solution (16 mg/mL) without the use of additives. The processing conditions used were exactly the same as those used by Holliday et al., allowing for direct comparison of **CBR** with **FBR**.¹¹⁹ The current-density (J-V) curve and data for the best performing OPV device can be seen in Figure 5.120 and Table 5.15, where the area of the active device was 0.045 cm² and measurements were performed in a solar simulator using the AM1.5 spectrum at an intensity of 100 mWcm⁻².

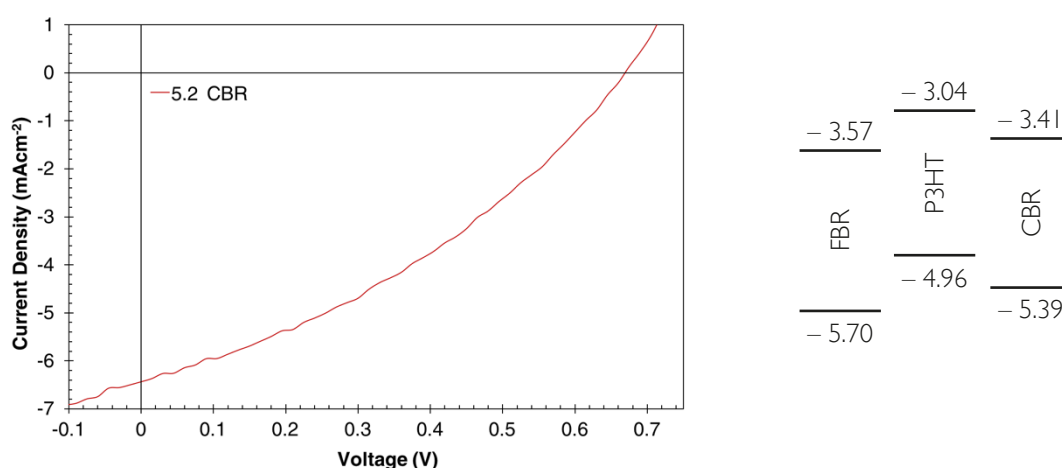


Figure 5.120 – J-V characteristics of OPV device fabricated using P3HT:CBR (left), and the HOMO and LUMO values (eV) of FBR¹¹⁹, P3HT,¹⁷⁴ and CBR (right)

At 1.5% , the PCE is lower than obtained with both **FBR** and **PCBM**, but this value is promising considering this result is a single set of non-optimised devices, and the first ever with this material. It took many years for the processing conditions for **PCBM** to be optimized to allow a PCE of 3.5% to be achieved, while Holliday et al. optimised the annealing time and temperature, the active layer thickness, the solvent ratios, and the additives used before achieving a PCE of 4.1%.

Device	J_{SC} (mAcm ⁻²)	V_{OC} (V)	Fill Factor	PCE (%)
P3HT:CBR	6.43	0.67	0.35	1.5
P3HT:FBR ^a	7.95	0.82	0.63	4.1
P3HT:PCBM ^a	9.07	0.59	0.66	3.5

a) Values taken from Holliday et al.¹¹⁹

Table 5.15 – J-V data for OPV devices of P3HT:CBR and P3HT:FBR

The V_{OC} for **CBR** is higher than obtained using **PCBM**, although much lower than seen for **FBR**. This was contrary to our expectations considering the LUMO of **CBR** is higher than that of **FBR** (Figure 5.120 – right). The low fill factor is indicative of non-ideal behaviour in the device, which is likely to be distorting the V_{OC} to a lower value than can be achieved. Factors such as morphology, vertical phase separation, poor charge extraction, or problems with contacts can all contribute to reduce the J_{SC} , fill factor, and in turn V_{OC} . Fortunately, optimisation of fabrication conditions can have a huge effect on all of these parameters, and after improving the processing conditions we would expect to see a jump in all of these values, particularly the fill factor and V_{OC} . On-going optimisations are currently being performed, and with such high extinction coefficients and well matched energy levels similar to **FBR**, the optimised PCE is expected to be much more promising.

5.5 Chapter conclusions

This chapter has discussed the design, synthesis, analysis, and initial device performance of two new OPV acceptors, **CBR** and **CBI**. These new acceptors were based on the successful **FBR** acceptor, modifying the fluorene core and flanking groups with the aim of increasing the overlap with the AM1.5 spectrum to increase J_{SC} whilst simultaneously tuning the HOMO and LUMO levels to optimise V_{OC} .

The synthesis of the new materials was somewhat facile, with an interesting NMR study being performed that found the rotational behaviour of the central alkyl chain to be causing obscure splitting effects in the ^1H NMR aromatic region.

Modelling was performed to find the lowest energy geometry of both **CBR** and **CBI**, showing that **CBR** has a delocalised LUMO similar to **FBR**, whereas **CBI** was much flatter, with the LUMO being less extended over the terminal benzene groups. The delocalised orbitals nonetheless resulted in high extinction coefficients for both, being almost double that of **FBR**.

The flat geometry of the **CBI** molecule could be observed in the strong endo- and exotherms observed in the DSC, suggesting a highly crystalline molecule compared to the lack of DSC features observed for **CBR**. This tendency for **CBI** to aggregate was observed when trying to fabricate the initial OPV devices and resulted in inhomogeneous films, proving the interplay between beneficial π - π -packing arrangements and processability is an important design principle.

Further optimisation with different solvent systems and concentrations should allow functioning devices to be made in the future, although the tendency of **CBI** to aggregate and form crystalline domains could be detrimental to the formation of an optimal morphology, ultimately affecting the PCE. Side chain engineering could greatly improve device performance, for example moving the branching point or adding an additional branch could disrupt the aggregation whilst still maintaining the beneficial properties observed for **CBI**.

CBR showed good initial performance in an OPV device with P3HT, giving a reputable J_{SC} of 6.4 mAcm^{-2} , although the fill factor was low at 0.35, and the V_{OC} was lower than expected. Further optimisation of **P3HT:CBR** devices should lead to equal if not higher PCEs than

those seen for **FBR**, having already achieved good J_{SC} and a promisingly high extinction coefficient.

In conclusion, this project has not only extended the **XBR** family of acceptors by two, but has also outlined important design criteria for controlling LUMO delocalisation, improving extinction coefficients, and increasing planarity. This has allowed an interesting investigation between the packing properties of an acceptor and the processing conditions to bring greater insight into non-fullerene acceptor derivatives.

Chapter 6

Concluding remarks and future work

Although this thesis has covered a variety of topics, this body of work all fits under the umbrella of synthesis, characterisation and device analysis of conjugated materials for plastic electronics. Chapters 2-4 focused on novel polymers for use as charge transport materials in OFETs and donor polymers in OPVs, whereas Chapter 5 looked into small molecule non-fullerene acceptors for use in OPV.

More specifically, Chapter 2 reported on the successful synthesis of a series of novel thiazole based polymers (**TzBTz**) using a new annulation method to ring close between two thiazole units, improving on the current literature standards. Polymer solubility issues required investigations into various alkyl chains including 2-ethyl-hexyl based branched chains which had problems with E2- and β -elimination. A problem that was solved by moving the alkyl chain branching point away from the reacting bromide. An initial investigation into using Sonogashira chemistry to couple TMS-acetylene and alkyl-bromides was started, but abandoned to move the project direction onwards. Were the project to continue, the development of this chemistry could yield an interesting technique to synthesising asymmetric alkyl-alkynes without the use of toxic reagents like HMPA. Although the project compared the differences between the linear and branched chains on the **TBT** unit, it would be pertinent to add the branched chains onto the **TzBTz** unit and cross co-polymerise with the linear and branched **TBT** units to give a four-polymer series for comparison. Although this project has had some interesting outcomes, overall thiazole chemistry is extremely challenging and has yet provided sufficient evidence to be worth the extended effort required for its use in conjugated materials.

Chapter 3 discussed the suite of characterisation techniques used to understand the properties of polymers **2.45** and **2.46** synthesised in chapter 2. A ‘conformational lock’ between the thiazole and thiophene units resulted in an exceptionally rigid planar polymer backbone which ultimately effected all of the properties, from the high thermal stability to the defined

UV-Vis and high molar extinction coefficients. Unfortunately, this rigidity and uniform structure did not appear to result in good charge transport properties with OFET and OPV results both being poor. Further optimisation of devices could provide higher performances and a better understanding of the polymer system. For example, the use of PFBT in OFET devices could help charge injection into the low polymer HOMO (-5.6 eV), and making devices of differing channel lengths would help to see if this injection was a performance hindering issue. In OPV devices, the use of better matched acceptor moieties, where there is a greater LUMO-LUMO offset between the donor polymer and acceptor, should improve performance drastically and allow the differences in the side-chains to become more prominent. Device optimisation plays a huge role in material performance and by making a greater number of devices using different conditions, a better understanding of the polymer properties could be achieved.

Chapter 4 reported on a new **DPP** based system with flanking **DTP** units – the first time it has been reported. An elegant synthesis saw reverse etherification used to remove *O*-alkylated side chain impurities to yield a pure monomer which exhibited a pseudo ‘hydrogen-bond’ resulting in a highly planar conformation. Successful Stille polymerisation gave a high molecular weight material (**pDTP-DPP-TT**) with a low band gap and exceptional extinction coefficients – promising for OPV devices. Unfortunately, the Suzuki polymerisation was a lot less successful (**pDTP-DPP-BT**), meaning direct comparison of the two polymers was difficult. Further optimisation of these Suzuki conditions could afford higher molecular weight materials, although this may be material intensive. Alternatively, Stille chemistry could be used exclusively with varying tin co-monomers, although electron poor tin co-monomers could cause polymerisation problems due to slow transmetallation. Another route would be to stannylate the **DTP-DPP** unit allowing a larger range of polymers to be made via Stille polymerisation with brominated co-monomers. A further project expansion would be to

polymerise the **DTP-DPP** unit with both electron rich and poor monomers which lack the rotational linearity of **TT** and **BT** – assessing whether the ‘kink’ in the polymer chain drastically effects the polymer properties. Device fabrication in both OPV and OFET devices of synthesised polymers would be paramount in assessing material performance, with fabrication guidance coming from the vast array of **DPP** based literature.

Chapter 5 looked to modify the successful **FBR** acceptor by changing the bridging atom of the central unit from a carbon to a nitrogen (fluorene to carbazole). From this, two new carbazole based acceptors with differing flanking groups were synthesised and characterised. This project could be expanded synthetically in two ways – firstly, the central carbazole could be switched out to a dithienopyrrole unit – increasing the electron rich nature of the central unit to lower the band gap of the small molecule through increased push-pull hybridisation. Secondly, differing flanking groups could be explored such as methyl- and phenyl-rhodanines as well as both the mono- and di-cyano derivatives of the indandione. In terms of device optimisation, further studies with different additives and processing conditions should enable higher performance in the **CBR** acceptor and workable devices for the **CBI** acceptor. Specifically for **CBI**, a stronger solvent such as di- or tri-chlorobenzene could be used as well as additives to help break up aggregation and allow homogenous films to be formed.

Overall this body of work has documented multiple synthetically challenging and novel monomer/small molecule units that although lacking performance in initial device testing, will further enhance the knowledge surrounding plastic electronic materials. Not only this, but on making these complex materials, synthetic pathways have been discovered and improved on which have contributed to the ever-growing toolbox of reactions available to all synthetic chemists.

Chapter 7

Experimental

7.1 General

All chemicals were purchased from commercial suppliers (Sigma Aldrich, TCI, VWR, Alfa Aesar, and Fluorochem) and used without further purification unless otherwise stated. All anhydrous reaction solvents (THF, DMF, DMSO, and toluene) were purchased from Alfa Aesar over molecular sieves and used as received. Anhydrous THF contained BHT inhibitor. All work-up solvents were GPR grade or higher and were purchased from VWR. 3,3'-dibromo-2,2'-bithiophene and bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde were purchased from Wawei Chemical Corporation. 9-(9-Heptadecanyl)-9*H*-carbazole-2,7-diboronic acid bis(pinacol) ester was purchased from Solarmer. Copper/palladium catalysts and ligands were purchased from STREM Chemicals Inc. All glassware was dried overnight in an oven at 120 °C, and anhydrous reactions were carried out under an argon atmosphere using standard Schlenk techniques. A vacuum/argon purge cycle was performed three times after addition of solid materials into the reaction vessel and prior to solvent addition. All substrates (glass, Si(100), ITO) were cleaned by sonication for 10 min each in: detergent, DI-H₂O, acetone, and IPA before being stored in IPA.

Column chromatography was carried out on silica gel (Merck Kieselgel 60) or Biotage Zip columns (80 and 120 g) using a Biotage Isolera One flash purification system. Thin layer chromatography was performed on Merck TLC F254 silica gel 60 plates, and developed under KMnO₄ dip followed by heat (for alkenes/alkynes) or visualised under 254/366 nm UV light. Microwave reactions were performed on a Biotage Initiator+. Purification of tin monomers and NFAs (**2.16**, **2.40**, **2.44**, and **5.3**) was performed on a custom-built Shimadzu recycling GPC system using an Agilent PLgel 10µm MIXED-D column.

¹H (400 MHz), ¹³C (100 MHz), HSQC, HMBC, and COSY NMR spectroscopies were performed on Bruker AV-400 or AV-500 spectrometers at 298 K unless otherwise specified. The majority of products were analysed in CDCl₃ solvent except for products **4.4** (DMSO-

d₆), **4.6** (CDCl₃ and pyridine-d₅), and **4.7** (C₆D₅Cl). Chemical shifts were measured in ppm and coupling constants in Hz, with the residual solvent peaks being used as internal standards. Mass spectrometry was primarily performed on a Micromass MALDI-TOF micro MX machine calibrated using a C60 standard, otherwise where specified an Agilent GCMS-MS with quadrupole detector was used (GC-7890A with MS-5975C).

Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent Technologies 1200 series GPC in chlorobenzene at 80 °C, using two PL mixed B columns in series and calibrated against narrow polydispersity polystyrene standards.

UV-vis spectroscopy was performed using a Shimadzu UV-1800 UV-Vis spectrophotometer in chlorobenzene solution or on glass thin-films spun from 10 mg/mL chlorobenzene solutions. Cyclic voltammetry was performed using a Metrohm Autolab PGStat101 potentiostat/galvanostat. under a nitrogen atmosphere. The experimental set-up for solution measurements used an Ag/Ag⁺ reference electrode, a platinum wire counter electrode, and an FTO working electrode. For film measurements, the working electrode was an ITO-coated glass substrate on which the materials were spin coated from 10 mg/mL chlorobenzene solutions. The electrolyte used was a degassed, anhydrous solution of tetrabutylammonium hexafluorophosphate (0.1 M or 0.3 M), and the system was calibrated after each run using ferrocene as an internal reference. The HOMO/LUMO levels are calculated from the onset of the first oxidation potential in CV via the following equations where 4.8 eV is the energy level of ferrocene below the vacuum level: $E_{\text{HOMO}} = [-e(E_{\text{onset, ox}} - 0.49 + 4.8)] \text{ eV}$, $E_{\text{LUMO}} = [-e(E_{\text{onset, red}} - 0.49 + 4.8)] \text{ eV}$.

Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 1 TGA at a scan rate of 10 °C/min from 25–700 °C. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q20 under a nitrogen atmosphere at a scan rate of 10 °C/min.

X-ray diffraction was performed on films spun from 10 mg/mL chlorobenzene solutions on Si(100) using a PANalytical X'Pert Pro MPD (Tension 40 kV, current 40 mA) between 2.5–35° with a step size of 0.033° and time per-step of 100 s.

7.2 Device fabrication

BHJ-OPV devices were fabricated in a similar manner to previous literature conditions, and were fabricated at Imperial College London by Andrew Wadsworth.³⁷

Bulk heterojunction solar cells were fabricated with an inverted architecture (glass/ITO/ZnO/polymer:acceptor/MoO₃/Ag). Glass substrates were used with pre-patterned indium tin oxide (ITO). These were cleaned by sonication in detergent, deionized water, acetone, and isopropanol, followed by oxygen plasma treatment. ZnO layers were deposited by spin coating a zinc acetate dihydrate precursor solution (2 mL 2-methoxyethanol in 60 mL monoethanolamine) followed by annealing at 150 °C for 10–15 min, giving layers of 30 nm.

P3HT:PC[60]BM (1:1 ratio by mass) active layers were spin coated at 1500 rpm from a 40 mg/mL solution in *o*-dichlorobenzene, followed by annealing in an inert atmosphere at 130 °C for 20 min, resulting in active layer thicknesses of 148 nm.

P3HT:**CBR** (1:1 ratio by mass) active layers were spin coated at 2000 rpm from a 16 mg/mL solution in chlorobenzene, followed by annealing in an inert atmosphere at 110 °C for 12 min, resulting in active layer thicknesses of 85 nm.

2.45:O-IDFBR (1:1 ratio by mass) active layers were spin coated at 2000 rpm from a 24 mg/mL solution in chlorobenzene, followed by annealing in an inert atmosphere at 120 °C for 10 min, resulting in active layer thicknesses of 70 nm.

2.46:O-IDFBR (1:1 ratio by mass) active layers were spin coated at 2000 rpm from a 24 mg/mL solution in chlorobenzene, followed by annealing in an inert atmosphere at 120 °C for 10 min, resulting in active layer thicknesses of 70 nm.

MoO₃ (10 nm) and Ag (100 nm) layers were deposited by evaporation through a shadow mask yielding active areas of 0.045 cm² in each device. (J–V) characteristics were measured using a Xenon lamp at AM1.5 solar illumination (Oriel Instruments) calibrated to a silicon reference cell with a Keithley 2400 source meter, correcting for spectral mismatch. Incident photon conversion efficiency was measured using a 100 W tungsten halogen lamp (Bentham IL1 with Bentham 605 stabilized current power supply) coupled to a monochromator with a computer controlled stepper motor. The photon flux of light incident on the samples was calibrated using a UV-enhanced silicon photodiode. A 590 nm long-pass glass filter was inserted into the beam at illumination wavelengths longer than 580 nm to remove light from second-order diffraction. Measurement duration for a given wavelength was sufficient to ensure the current had stabilized.

OFET devices were fabricated in a similar manner to previous literature conditions and were fabricated by Mark Nikolka at the Cavendish Laboratory, Cambridge University.¹²⁶

Bottom-contact top-gate OFETs were fabricated on glass substrates with photolithography patterned Ti/Au (10 nm/30 nm) electrodes. Here, patterning was done using a double layer lift-off process in *N*-methyl-2-pyrrolidone (NMP). The polymers **2.45** and **2.46** were dissolved in 1,2-dichlorobenzene (DCB) at a concentration of 5 mg/ml and deposited by spin coating, followed by a 1 h anneal at 100 °C unless otherwise stated. A 500 nm layer of CYTOP (Asahi Glass) or PMMA (GoodFellow) was deposited by spin coating as a dielectric layer. Subsequently, a 20 nm thick gold electrode was deposited by evaporation through a

shadow mask at a base pressure of <10–6 mbar. Electrical characteristics were measured in an Agilent 4155B Semiconductor Parameter Analyser, where all charge carrier mobility values were extracted from the square root of the saturation transfer curve. To guarantee reproducibility, all fabrication steps were performed in an N₂ glove box.

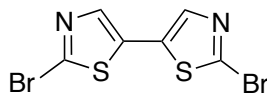
7.3 Molecular modelling

All calculations were run using Gaussian g09 revision c-01.¹⁷⁵ Geometries were optimized with the ω B97XD functional and 6-31G* basis set unless explicitly stated otherwise. An in-house tuning procedure was used to approximate Koopman's theorem^{114,116} for both the neutral and radical anion (gap tuning) by varying the range separation parameter, ω . Vertical ionisation potentials and electron affinities were calculated as the difference in energy of the neutral and relevant charged species, with solvent interactions approximated with the polarizable continuum model (PCM).

The torsional strain graph in Figure 3.68 was calculated by locking the S-S dihedral at a fixed angle and then running a geometry optimisation to calculate the energy in this fixed position. The geometry optimisation was run using b3lyp-d3/6-31G* where the d3 is a dispersion correction energy term – a computationally cheap way to improve accuracy of the b3lyp functional without having to perform a tuning procedure for each geometry.

[illegible]

2,2'-Dibromo-5,5'-bithiazole (2.1)

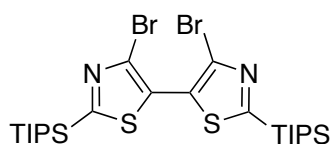


169

the aqueous layer. The toluene was dried over MgSO_4 , filtered, and the solvent removed under pressure. The crude solid was recrystallised from acetone to yield **2.1** as a yellow crystalline solid (19 g, 76%).

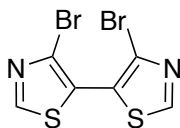
^1H NMR (400 MHz, CDCl_3) δ 7.61 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.71, 136.40, 130.89. GCMS: m/z Calc. for $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2\text{S}_2$ (M^+): 325.8, 323.8, 327.8. Found: 325.9, 327.9, 323.9.

4,4'-Dibromo-2,2'-bis(triisopropylsilyl)-5,5'-bithiazole (2.2 X=TIPS)



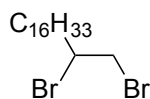
A solution of **2.1** (16 g, 49 mmol) in THF (500 mL) was cooled to $-78\text{ }^\circ\text{C}$ under an argon atmosphere. A solution of LDA (54 mL, 108 mmol, 2.0 M in THF) was added dropwise over 30 min before being left to stir for a further 30 min at $-78\text{ }^\circ\text{C}$. Tri(isopropyl)silylchloride (24 mL, 113 mmol) was subsequently added dropwise at this temperature, and the mixture was left to stir and warm up overnight. The reaction was quenched with water (300 mL) and extracted with DCM ($3 \times 200\text{ mL}$). The organics were dried over MgSO_4 , filtered, and the solvent removed under pressure. The crude mixture was plugged through a short pad of silica in chloroform before the solvent was removed *in vacuo*. The dark orange solid was recrystallised from acetone to yield **2.2 (X=TIPS)** as a yellow crystalline solid (24.7 g, 79%).

^1H NMR (400 MHz, CDCl_3) δ 1.47 (hept., $J = 7.3\text{ Hz}$, 6H), 1.16 (d, $J = 7.5\text{ Hz}$, 36H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.47, 130.33, 124.97, 18.45, 11.56. GCMS: m/z Calc. for $\text{C}_{42}\text{H}_{76}\text{N}_2\text{S}_2\text{Si}_2$ (M^+): 638.1, 636.1, 640.1. Found: 638.2, 636.2, 640.2.

4,4'-Dibromo-2,2'-bis(triisopropylsilyl)-5,5'-bithiazole (2.2 X=H)

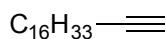
The procedure was the same as for **2.2 X=TIPS**, with the exception of quenching with excess water at 0 °C as opposed tri(isopropyl)silylchloride (2.6 g, 82%).

^1H NMR (400 MHz, CDCl_3) δ 8.86 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 129.3, 122.5. MS (EI+) m/z calc. for $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2\text{S}_2$ (M^+): 325.8. Found: 325.6.

1,2-Dibromooctadecane (2.3)

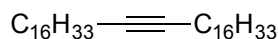
1-Octadecene (48 g, 190 mmol) was dissolved in DCM (500 mL) in the dark and under an argon atmosphere. The solution was cooled to 0 °C before bromine (9.8 mL, 192 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 30 min before being quenched with a conc. sodium sulfite solution (100 mL) and being left to stir vigorously for 5 min. The organic layer was washed with water, brine, dried over MgSO_4 , filtered under gravity, and the solvent removed *in vacuo* to give **2.3** as a clear, viscous oil (78 g, 100%).

^1H NMR (400 MHz, CDCl_3) δ 4.21 – 4.12 (m, 1H), 3.85 (dd, 1H, $J = 10.2, 4.4$ Hz), 3.63 (t, 1H $J = 10.0$ Hz), 2.18 – 2.07 (m, 1H), 1.84 – 1.72 (m, 1H), 1.66 – 1.18 (m, 28H), 0.87 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 53.19, 36.41, 36.17, 32.10, 29.87, 29.83, 29.79, 29.70, 29.55, 28.99, 26.91, 22.86, 14.28. HRMS: EI+ m/z calc. for $\text{C}_{18}\text{H}_{36}\text{Br}_2$ (M^+) 409.11. Found: 409.11.

1-Octadecyne (2.4)

1,2-Dibromooctadecane (30 g, 73 mmol) was dissolved in THF (250 mL) under argon before the solution was cooled to -78 °C and LDA (127 mL, 254 mmol, 2.0 M in THF) was added dropwise. The solution was warmed to room temperature and heated for 3 h at 40 °C before being left to stir overnight at room temperature. The reaction was quenched with water (300 mL) before hexane (300 mL) was subsequently added. The aqueous layer was extracted with hexane (3 x 75 mL) and the organic layers combined and washed with brine (500 mL). The organics were then dried over MgSO₄, filtered under gravity, and the solvent was removed *in vacuo* to give a brown oil which was purified by column chromatography (hexane:DCM, 3:1) to give **2.4** as a viscous clear oil (18 g, 99%).

¹H NMR (400 MHz, CDCl₃) δ 2.18 (td, 2H, *J* = 7.2, 2.7 Hz), 1.94 (t, 1H, *J* = 2.6 Hz), 1.57 – 1.20 (m, 28H), 0.88 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 144.25, 139.21, 128.40, 127.93, 125.70, 114.22, 84.64, 68.16, 34.03, 32.16, 29.94, 29.90, 29.86, 29.76, 29.61, 29.40, 29.36, 29.18, 29.07, 28.99, 28.73, 22.90, 18.58, 15.74, 14.25. HRMS: EI+ *m/z* calc. for C₁₈H₃₄ (M⁺) 250.266. Found: 250.266.

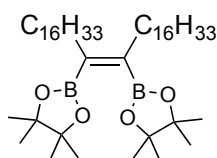
Tetratriacont-17-yne (2.5)

1-octadecyne (8.3 g, 33 mmol) was dissolved in THF (100 mL) under argon, then HMPA (5.75 mL, 33 mmol) was added and the solution was cooled to -78 °C. *n*-BuLi (16 mL, 40 mmol) was added slowly via syringe before the solution was warmed to room temperature and 1-bromohexadecane (10.3 mL, 33.5 mmol) was added. The solution was heated to 65 °C for 2.5 h before being cooled to room temperature. The THF was washed with HCl (2 M, 75 mL) and brine (100 mL). The remaining THF was concentrated under vacuum and EtOAc

(250 mL) was added, and the resulting suspension was left in the fridge overnight. The white precipitate was filtered off under vacuum and washed with water (2×20 mL), cold hexane (2×20 mL) and methanol (2×20 mL) to give **2.5** as a white solid (6.5 g, 41%).

^1H NMR (400 MHz, CDCl_3) δ 2.13 (t, 4H, $J = 7.0$ Hz), 1.51 – 1.18 (m, 56H), 0.87 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 80.40, 32.10, 29.87, 29.82, 29.74, 29.53, 29.45, 29.35, 29.04, 22.86, 18.93, 14.27. HRMS: EI+ m/z calc. for $\text{C}_{34}\text{H}_{66}$ (M^+) 474.517. Found: 474.516.

(Z)-2,2'-(Tetratriacont-17-ene-17,18-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)
(2.6)

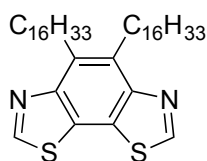


Tetratriacont-17-yne (2.48 g, 5.22 mmol), bis(pinacolato)diboron (1.48 g, 5.8 mmol) and $\text{Pt}(\text{PPh}_3)_4$ (210 mg, 0.17 mmol) were placed in a microwave vial under an argon atmosphere. Previously degassed DMF (30 mL) was added and the solution degassed for a further 10 min. The solution was then heated at 80 °C overnight before being quenched with water (80 mL). Diethyl ether (50 mL) was added and the aqueous layer was extracted further with diethyl ether (3×30 mL). The organic layers were combined, dried over MgSO_4 , filtered under gravity, and the solvent was removed *in vacuo* to give a white waxy solid. This was further purified via column chromatography (EtOAc:hexane, 1:39) to give **2.6** as a white solid (1.8 g, 47%).

^1H NMR (400 MHz, CDCl_3) δ 2.16 (m, 4H), 1.35 – 1.20 (m, 80H), 0.88 (t, 6H, $J = 6.8$ Hz).

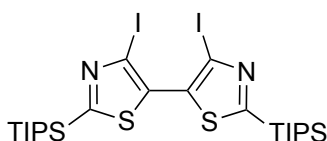
^{13}C NMR (100 MHz, CDCl_3) δ 83.23, 31.96, 31.58, 30.84, 30.02-29.36, 24.89, 22.70, 14.10.

HRMS: EI+ m/z calc. for $\text{C}_{46}\text{H}_{90}\text{B}_2\text{O}_4$ (M^+) 729.7103. Found: 729.710.

General procedure for Suzuki ring closures to form 4,5-dihexadecylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole) (2.7**)**

A microwave vial was charged with 4,4'-dibromo-5,5'-bithiazole (**2.2** **X=H**, 100 mg, 0.307 mmol), **2.6** (235 mg, 0.322 mmol), K₂CO₃ (255 mg, 1.84 mmol) and Pd(dppf)Cl₂ (12.5 mg, 0.05 mmol). The vial was purged with argon before previously degassed THF (6 mL) and water (0.3 mL, 50 equiv.) were added and the solution was heated at 60 °C for 72 h. Diethyl ether (30 mL) and water (50 mL) were added and the aqueous layer was further extracted with diethyl ether (3 × 20 mL). The organic layers were combined, washed with brine (75 mL), dried over MgSO₄, filtered under gravity, and the solvent was removed *in vacuo*. The crude product was further purified via column chromatography (DCM:hexane, 3:2) to yield **2.7** as a highly viscous oil (10 mg, 5.1%).

¹H NMR: (400 MHz, CDCl₃) δ 8.99 (s, 2H), 3.33 (m, 4H), 1.78 – 1.64 (m, 4H), 1.55 – 1.43 (m, 4H), 1.40 – 1.15 (m, 56H), 0.85 (t, 6H, *J* = 6.8 Hz). ¹³C NMR: (100 MHz, CDCl₃) δ 151.93, 151.27, 134.27, 124.08, 32.09, 31.65, 30.32, 29.88, 29.83, 29.78, 29.64, 29.53, 24.07, 22.85, 14.28. GCMS: *m/z* Calc. for C₄₀H₆₈N₂S₂ (M⁺): 640.5, 641.5, 642.5. Found: 640.6, 641.6, 642.6.

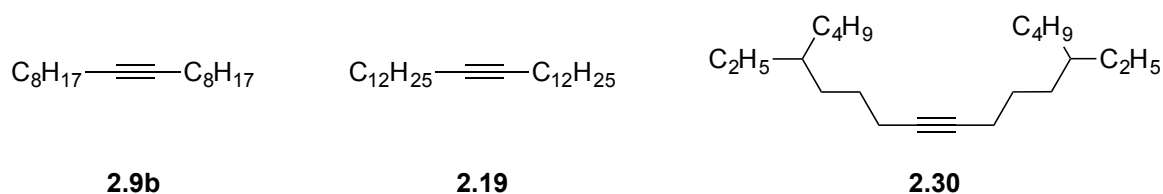
4,4'-Diiodo-2,2'-bis(triisopropylsilyl)-5,5'-bi-thiazole (2.8**)**

A solution of **2.2** **X=TIPS** (15 g, 23.5 mmol) in THF (300 mL) was cooled to -78 °C under an argon atmosphere. A solution of *n*-BuLi (19.7 mL, 49.3 mmol, 2.5 M in THF) was added

dropwise, wherein an orange precipitate was observed. The solution was raised above the dry ice bath and stirred for 30 min before being stirred for a further hour back in the ice bath at -78 °C. In a separate flask, iodine (13.1 g, 51.7 mmol) was dissolved in THF (150 mL), and this solution was then added dropwise into the stirring solution of **2.2** via cannula. The solution was then left to slowly warm up to room temperature before being stirred overnight. The reaction was quenched with a minimum of sodium sulfite solution and the THF was concentrated under vacuum before being diluted with chloroform (300 mL) and washed with water (300 mL). The aqueous layer was extracted with chloroform (2 × 100 mL) before the organics were combined, dried over MgSO₄, filtered, and the solvent was removed under pressure to yield a yellow oil. The oil was dissolved in a minimum volume of chloroform and precipitated into stirring cold methanol (500 mL) before being filtered and dried. Compound **2.8** was isolated as a cream powder (13.7 g, 80%).

¹H NMR (400 MHz, CDCl₃) δ 1.46 (hept., *J* = 7.4 Hz, 6H), 1.17 (d, *J* = 7.4 Hz, 36H). ¹³C NMR (100 MHz, CDCl₃) δ 175.81, 130.72, 105.06, 18.61, 11.75. GCMS: *m/z* Calc. for C₂₄H₄₂I₂N₂S₂Si₂ (M⁺): 732.1, 733.1, 734.1. Found: 732.2, 733.2, 734.2.

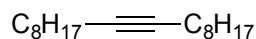
Generic synthesis procedure for coupling of a terminal alkyne and bromo-alkane to form a di-alkylalkyne (2.9b, 2.19, 2.30)



The terminal alkyne (1.0 equiv.) was dissolved in THF (4 mL / mmol) under argon, whereupon HMPA (1.2 equiv.) was added and the solution was cooled to -78 °C. *n*-BuLi (1.2 equiv.) was added slowly via syringe before the solution was warmed to room temperature and 1-bromoalkane (1.05 equiv.) was added. The solution was heated to 65 °C for 2.5 h

before being cooled down and the THF removed *in vacuo* to give a slushy oil. The oil was diluted with hexane and plugged through silica to remove the HMPA. The organics were removed *in vacuo* to give the desired di-alkyl alkyne product.

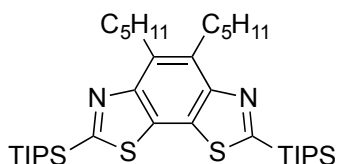
Octadec-9-yne (**2.9b**)



As per the generic synthesis above to yield **2.9b** as a colourless oil (11.5 g, 71%).

^1H NMR (400 MHz, CDCl_3) δ 2.14 (t, $J = 7.0$ Hz, 4H), 1.53 – 1.40 (m, 4H), 1.41 – 1.19 (m, 20H), 0.88 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 80.25, 80.22, 32.06, 29.44, 29.38, 29.35, 29.06, 22.85, 18.92, 14.20. GCMS: m/z Calc. for $\text{C}_{18}\text{H}_{34}$ (M^+): 250.3, 251.3, 252.3. Found: 250.3, 251.3, 252.3.

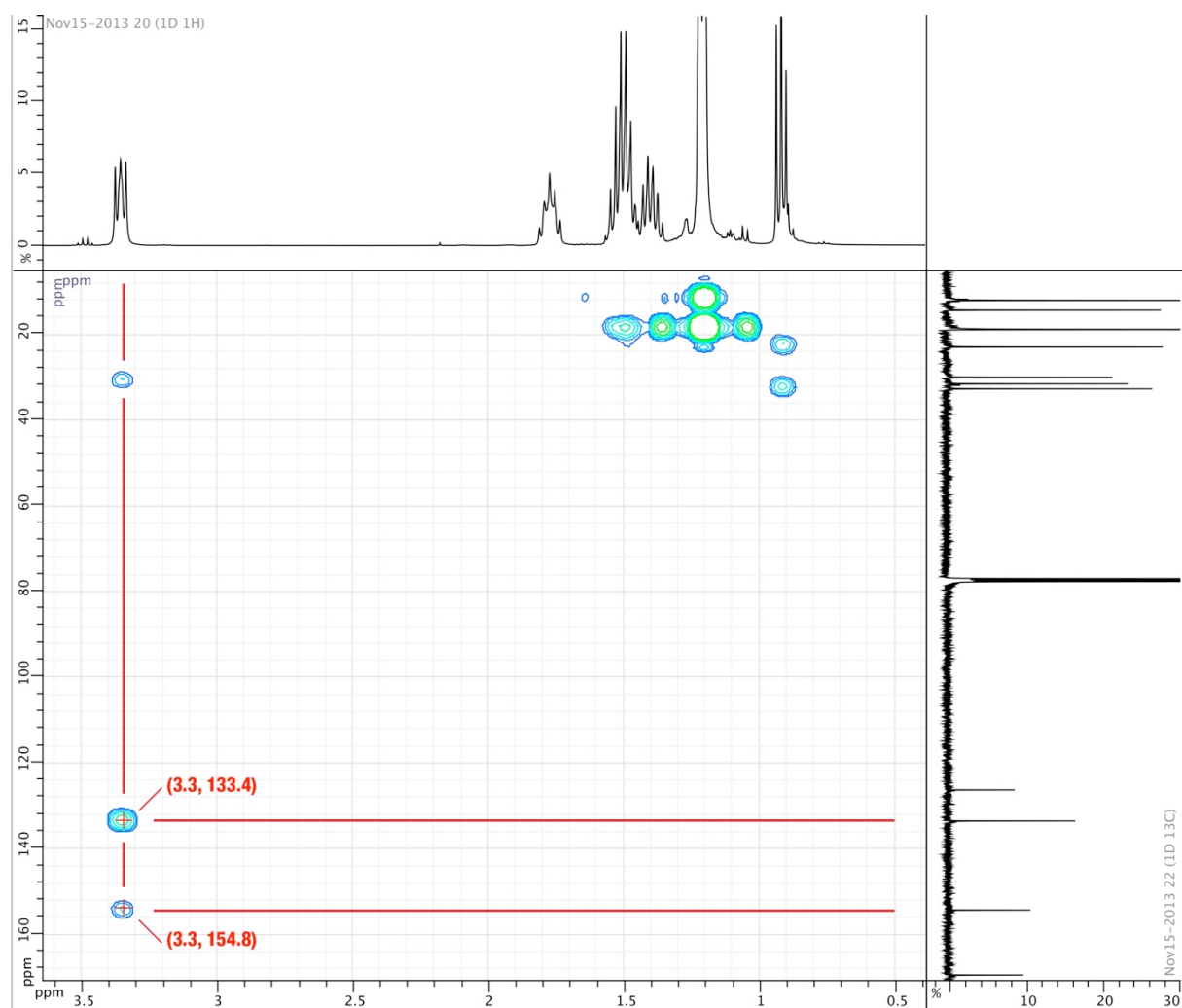
General procedure for the alkyne ring closure of **2.8** with **2.9** to give 4,5-dipentyl-2,7-bis(triisopropylsilyl)benzo[1,2-*d*:4,3-*d'*]bis(thiazole) (**2.10a**)



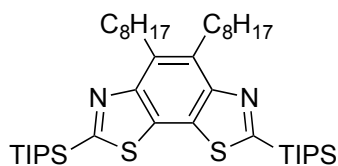
2.8 (0.70 g, 0.96 mmol) and **2.9a** (0.32 g, 1.91 mmol) were sealed in a microwave vial and put under an argon atmosphere before being dissolved in previously degassed DMF (5 mL). The solution was degassed for a further 30 min before the microwave cap was removed for the addition of $\text{Pd}(\text{OAc})_2$ (21 mg, 0.01 mmol) and *N,N*-dicyclohexylmethylamine (0.37 g, 1.91 mmol) and resealed. The solution was degassed for a further 10 min before being heated at 130 °C for 4 h. The crude reaction mixture was diluted in hexane (30 mL) before being passed through a short pad of silica in hexane, whereupon the solvent was removed under pressure to leave a dark oil. The oil was then purified via column chromatography using hexane as an eluent to give **2.10a** as a light yellow oil (0.13 g, 21%).

^1H NMR (400 MHz, CDCl_3) δ 3.37 (m, 4H), 1.78 (m, 4H), 1.52 (dt, $J = 14.7, 7.4$ Hz, 36H), 1.45 – 1.33 (m, 14H), 1.22 (d, $J = 7.5$ Hz, 36H), 0.92 (t, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.13, 153.97, 133.19, 125.97, 32.41, 31.26, 29.73, 22.65, 18.57, 14.09, 11.77. GCMS: m/z Calc. for $\text{C}_{36}\text{H}_{64}\text{N}_2\text{S}_2\text{Si}_2$ (M^+): 644.4, 645.4, 646.4. Found: 644.6, 645.5, 646.5.

HMBC for **2.10a**:



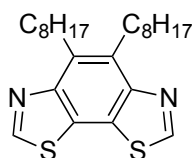
General procedure for the alkyne ring closure of **2.8 to give 4,5-dioctyl-2,7-bis(triisopropylsilyl)benzo[1,2-d:4,3-d']bis(thiazole) (**2.10b**)**



The synthesis was carried out as reaction **2.10a** above using **2.8** (2.93 g, 4 mmol) and **2.9b** (2.03 g, 8 mmol). The crude oil was then purified via column chromatography using hexane as an eluent to give **2.10b** as a light-yellow oil (1.35 g, 46%) which was used directly in the next step.

^1H NMR (400 MHz, CDCl_3) δ 3.34 (m, 4H), 1.75 (m, 4H), 1.55 – 1.24 (m, 26H), 1.20 (d, J = 7.4 Hz, 36H), 0.86 (t, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.12, 153.96, 133.20, 125.96, 31.99, 31.59, 30.23, 29.77, 29.60, 29.34, 22.70, 18.57, 14.14, 11.76.

TIPS deprotection of **2.10b to form 4,5-dioctylbenzo[1,2-d:4,3-d']bis(thiazole) (**2.11**)**

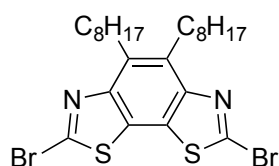


A solution of **2.10b** (1.35 g, 1.85 mmol) was dissolved in THF (25 mL) under an argon atmosphere before being cooled to 0 °C. A solution of tetrabutylammonium fluoride (7.4 mL, 7.4 mmol, 1.0 M in THF) was added dropwise and the reaction was monitored via TLC (hexane) until completion – typically 2 h. The reaction was quenched with water (20 mL) before being extracted with chloroform (3 × 25 mL). The organic fractions were dried over MgSO_4 , filtered, and the solvent was removed under pressure. The crude reaction mixture was purified by column chromatography (3:7 DCM:Hex) to yield **2.11** as a white solid (0.59 g, 76%).

^1H NMR (400 MHz, CDCl_3) δ 8.99 (s, 2H), 3.30 (m, 4H), 1.73 (pent., $J = 7.7$ Hz, 4H), 1.57 – 1.45 (m, 4H), 1.42 – 1.21 (m, 16H), 0.88 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.13, 153.97, 133.21, 125.97, 31.99, 31.60, 30.24, 29.77, 29.60, 29.35, 22.71, 18.57, 14.15, 11.77. GCMS: m/z Calc. for $\text{C}_{24}\text{H}_{36}\text{N}_2\text{S}_2$ (M^+): 416.2, 417.2, 418.2. Found: 416.3, 417.3, 418.3.

Bromination of **2.11** to form 2,7-dibromo-4,5-dioctylbenzo[1,2-d:4,3-d']bis(thiazole)

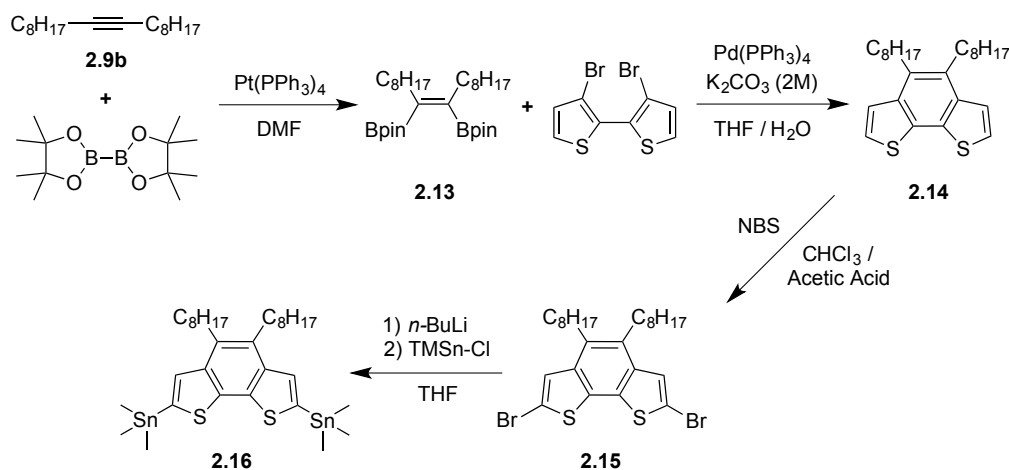
(**2.12 TzBTzC8**)



Compound **2.11** (551 mg, 1.32 mmol) was dissolved in THF (10 mL) under an argon atmosphere and cooled to -78 °C. A solution of *n*-BuLi (1.74 mL, 2.78 mmol, 1.6 M in THF) was added dropwise, whereupon a change from colourless to yellow was observed. After stirring for 45 min, a solution of 1,2-dibromo-1,1,2,2-tetrachloroethane (1.00 g, 3.07 mmol) in THF (4 mL) was added dropwise, and the solution turned dark orange in colour. The vessel was removed from the ice bath and left to warm to room temperature. The reaction was quenched with saturated sodium sulfite solution (3 mL) before being extracted with DCM (3×5 mL). The organic fractions were dried over MgSO_4 , filtered, and the solvent removed under pressure. The crude reaction mixture was purified by column chromatography (1:9 DCM:Hex) to yield **2.12** as a white solid (674 mg, 89%).

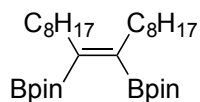
^1H NMR (400 MHz, CDCl_3) δ 3.17 (m, 4H), 1.66 (pent., $J = 7.6$ Hz, 4H), 1.46 (pent., $J = 6.8$ Hz, 4H), 1.40 – 1.21 (m, 16H), 0.89 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.82, 135.48, 134.35, 126.19, 32.08, 31.39, 30.07, 29.60, 29.44, 22.85, 14.28. GCMS: m/z Calc. for $\text{C}_{24}\text{H}_{34}\text{Br}_2\text{N}_2\text{S}_2$ (M^+): 574.1, 576.1, 572.1. Found: 574.3 576.2 572.3.

7.4.2 TBTC8 co-monomer synthesis



Scheme 7.2 – Synthesis of the TBTC8 monomer

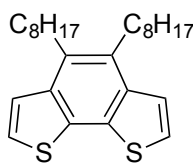
(*Z*)-2,2'-(Octadec-9-ene-9,10-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2.13**)



As per generic synthesis of **2.6** using **2.9b** as starting material to yield **2.13** a white solid (3.62 g, 97%).

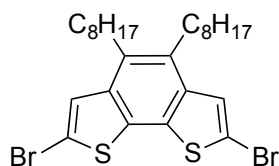
^1H NMR (400 MHz, CDCl_3) δ 2.16 (m, 4H), 1.45 – 1.09 (m, 48H), 0.87 (t, $J = 6.7$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 83.38, 32.07, 31.00, 30.19, 29.91, 29.64, 29.38, 25.06, 22.85, 14.25.

4,5-dioctylbenzo[2,1-*b*:3,4-*b'*]dithiophene (BDT) (2.14)

As per the generic ring closure procedure for **2.7** using 3,3'-dibromo-2,2'-bithiophene, **2.13**, and a Pd(OAc)₂/SPhos catalyst/ligand system. The crude mixture was purified by column chromatography (1:4 DCM:Hex) to yield **2.14** as a yellow oil (600 mg, 16%).

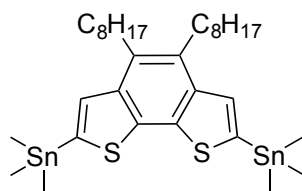
¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 5.4 Hz, 2H), 7.37 (d, *J* = 5.4 Hz, 2H), 3.02 (m, 4H), 1.66 (pent., *J* = 8.0, 7.5 Hz, 4H), 1.49 (pent., *J* = 6.9 Hz, 4H), 1.42 – 1.21 (m, 16H), 0.89 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 137.63, 131.76, 123.74, 123.59, 32.07, 31.72, 30.62, 30.36, 29.68, 29.48, 22.84, 14.27. GCMS: *m/z* Calc. for C₂₆H₃₈S₂ (M⁺): 414.2, 415.2, 416.2. Found: 414.3, 415.3, 416.3.

Bromination to form 4,5-dioctylbenzo[2,1-*b*:3,4-*b'*]dithiophene (2.15)

A solution of **2.14** (472 mg, 1.14 mmol) was dissolved in CHCl₃ (10 mL) and acetic acid (4 mL) before NBS (464 mg, 2.3 mmol) was added portion wise over the period of 2 h. The reaction was monitored to completion via TLC before being quenched with sat. Na₂SO₃ (2 mL) followed by dilution with additional CHCl₃ (50 mL) and water (50 mL). The aqueous layer was extracted with CHCl₃ (3 × 30 mL) before the organic fractions were combined, dried over MgSO₄, filtered, and the solvent was removed under pressure. The crude mixture was purified by column chromatography (hexane) to give **2.15** as a white solid (489 mg, 75%).

^1H NMR (400 MHz, CDCl_3) δ 7.40 (s, 2H), 2.89 (m, 4H), 1.57 (m, 4H), 1.45 (m, 4H), 1.39 – 1.25 (m, 16H), 0.89 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.32, 133.95, 131.53, 126.32, 112.55, 31.91, 31.44, 30.38, 30.11, 29.47, 29.30, 22.67, 14.11. GCMS: m/z Calc. for $\text{C}_{26}\text{H}_{36}\text{Br}_2\text{S}_2$ (M^+): 572.1, 574.1, 570.1. Found: 572.2, 574.2, 570.2.

Stannylation to form (4,5-dioctylbenzo[2,1-*b*:3,4-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane) (2.16 – TBTC8)

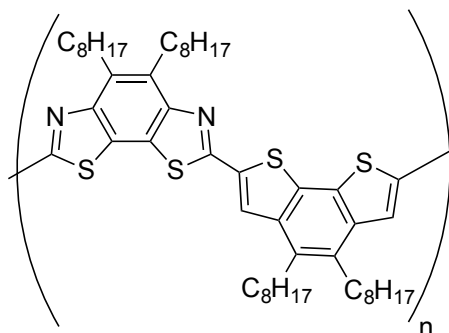


A solution of **2.15** (308mg, 0.54 mmol) in THF (8 mL) under an argon atmosphere was cooled to $-78\text{ }^\circ\text{C}$. A solution of *n*-BuLi (0.74 mL, 1.18 mmol, 1.6 M in THF) was added dropwise and the solution left to stir at $-78\text{ }^\circ\text{C}$ for 1 h, whereupon a yellow suspension had formed. A solution of trimethyltin chloride (1.3 mL, 1.29 mmol, 1.0 M in THF) was added in one portion and the solution was left to stir for a further hour. The solution was warmed to room temperature, whereupon the solution had turned colourless once more. The solution was diluted with diethyl ether (50 mL) and water (50 mL). The aqueous layer was extracted with diethyl ether ($3 \times 25\text{ mL}$) and the organic fractions were combined, dried over MgSO_4 , filtered, and the solvent was removed under pressure. The crude mixture was purified via preparative GPC in hexane in two batches. The fractions were combined to yield the purified monomer **11** as a light yellow oil (98.3 mg, 25%).

^1H NMR (400 MHz, Acetone) δ 7.68 (s, 2H), 3.11 (m, 4H), 1.69 (m, 4H), 1.52 (m, 4H), 1.47 – 1.23 (m, 16H), 0.88 (t, 6H), 0.45 (s, 18H).

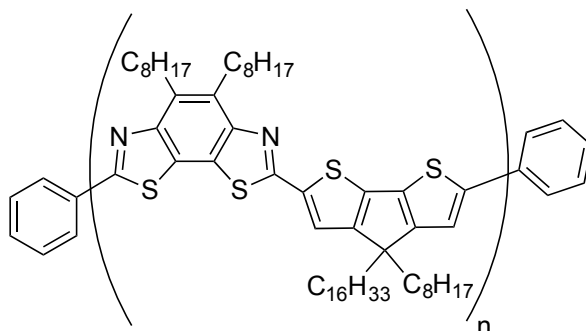
7.4.3 Polymerisation of (pTzBTzC8)-*alt*-(co-monomer)

Polymerisation of **2.12** and **2.16** to form poly(4,5-dioctylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole)-*alt*-4,5-dioctylbenzo[2,1-*b*:3,4-*b'*]dithiophene) (TzBTzC8-TBTC8)



A microwave vial was charged with **2.12** – **TzBTzC8** (76.3 mg, 0.133 mmol) and **2.16** – **TBTC8** (98.3 mg, 0.133 mmol) before being evacuated and filled with argon. Previously de-gassed *o*-xylene (2 mL) was added and the solution was de-gassed for a further 10 min. Pd(PPh₃)₄ (3.3 mg, 2.86 μmol) was added in one portion before a further 10 min of degassing. The vial was then heated in a microwave for 2 min at 100 °C, 2 min at 120 °C, 5 min at 140 °C, 5 min at 160 °C, and 30 min at 180 °C. The solution was precipitated in methanol (200 mL) and conc. HCl (2 mL) before being filtered into a glass fibre thimble and Soxhlet extracted. The orange material was insoluble in a range of hot solvents: hexane, chloroform, chlorobenzene, dichlorobenzene, and trichlorobenzene.

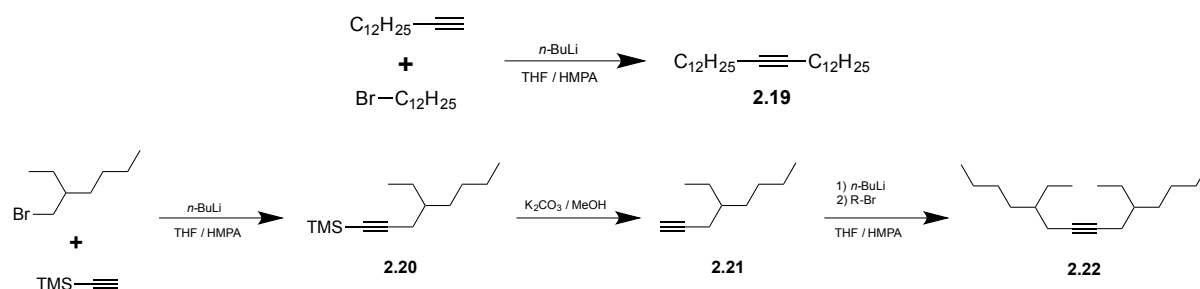
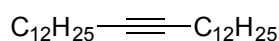
Polymerisation of 2.12 and CPDT to form poly(4,5-dioctylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole)-*alt*-4,4-dihexadecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene) (TzBTzC8-CPDTC16)



A microwave vial was charged with **2.12** (50.85 mg, 88.5 μmol) and **CPDTC16** (74.65 mg, 88.5 μmol) before being evacuated and filled with argon. Previously de-gassed *o*-xylene (2 mL) was added and the solution was de-gassed for a further 10 min. $\text{Pd}(\text{PPh}_3)_4$ (2.01 mg, 1.77 μmol) was added in one portion before a further 10 min of degassing. The vial was heated in a microwave for 2 min at 100 $^\circ\text{C}$, 2 min at 120 $^\circ\text{C}$, 5 min at 140 $^\circ\text{C}$, 5 min at 160 $^\circ\text{C}$, and 30 min at 180 $^\circ\text{C}$. Trimethyl(phenyl)tin (0.05 mL, 0.28 mmol) was added before heating the solution in the microwave for 1 min at 100 $^\circ\text{C}$, 1 min at 120 $^\circ\text{C}$, 1 min at 140 $^\circ\text{C}$, 1 min at 160 $^\circ\text{C}$, and 3 min at 180 $^\circ\text{C}$. After the addition of 1-bromobenzene (0.1 mL, 0.95 mmol), the solution was again heated in the microwave for 1 min at 100 $^\circ\text{C}$, 1 min at 120 $^\circ\text{C}$, 1 min at 140 $^\circ\text{C}$, 1 min at 160 $^\circ\text{C}$, and 3 min at 180 $^\circ\text{C}$. The solution was precipitated in methanol (200 mL) and conc. HCl (2 mL) before being filtered into a glass-fibre thimble and Soxhlet extracted in acetone (6 h), hexane (6 h), and chloroform (6 h). The majority of the polymer was soluble in the hexane fraction, which was washed with an aqueous solution of sodium diethyldithiocarbamate to remove residual palladium. The hexane was removed *in vacuo* before the polymer was dissolved in a minimum of CB, precipitated in methanol, and collected by filtration.

GPC. $M_n = 7.6 \text{ kg/mol}$, $M_w = 15 \text{ kg/mol}$, $\bar{D} = 2.4$

7.4.4 C12 and Cbranch (ext. branched) alkyl chains

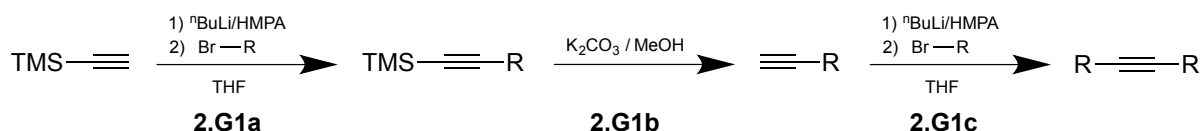
Scheme 7.3 – Synthesis of alkyl alkynes **2.19** and **2.22**Hexacos-13-yne (**2.19**)

As per generic synthesis for **2.9b** with further purification by recrystallization in pentane to yield **2.19** as white crystals (11.3 g, 70%).

^1H NMR (400 MHz, CDCl_3) δ 2.13 (t, $J = 7.0$ Hz, 4H), 1.47 (pent., $J = 7.0$, 4H), 1.42 – 1.33 (m, 4H), 1.33 – 1.20 (m, 32H), 0.87 (t, $J = 6.9$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 80.41, 32.09, 29.85, 29.81, 29.74, 29.52, 29.34, 29.03, 22.85, 18.93, 14.27. GCMS: m/z Calc. for $\text{C}_{26}\text{H}_{50}$ (M^+): 362.4, 363.4, 364.4. Found: 362.4, 363.4, 364.4.

Generic synthetic procedures for the di-alkyl alkyne synthesis from TMS-acetylene

(2.G1)



Scheme 7.4 – Generic synthetic pathway for alkyl alkynes

2.G1a: TMS-acetylene (2.0 equiv.) was dissolved in THF (4 mL / mmol) under argon, wherein HMPA (1.2 equiv.) was added and the solution was cooled to -78°C . $n\text{-BuLi}$ (1.2 equiv.) was added dropwise before the solution was warmed to room temperature and 1-bromoalkane (1.0 equiv.) was added. The solution was heated to 65°C for 2.5 h before

being cooled down and the THF removed *in vacuo* to give a slushy oil. The oil was diluted with hexane and plugged through silica to remove the HMPA. The organics were removed *in vacuo* to give the desired **TMS-protected-mono-alkyl-alkyne** product.

2.G1b: K₂CO₃ (2.5 equiv.) was suspended in methanol (5 mL / mmol) before the **TMS-protected-mono-alkyl-alkyne** was added dropwise and left to stir for 2 h. The mixture was diluted with hexane (10 mL/mmol) and water (10 mL/mmol) before the aqueous layer was extracted with further hexane (×3). The combined organic layers were washed with brine before being dried over MgSO₄, filtered, and the solvent removed *in vacuo* to give the desired **terminal-alkyl-alkyne**.

2.G1c: The **terminal-alkyl-alkyne** product (1.0 equiv.) was dissolved in THF (4 mL/mmol) under argon, wherein HMPA (1.2 equiv.) was added and the solution cooled to -78 °C. *n*-BuLi (1.1 equiv.) was added dropwise before the solution was warmed to room temperature and 1-bromoalkane (0.95 equiv.) was added. The solution was heated to 65 °C for 2.5 h before being cooled down and the THF removed *in vacuo* to give a slushy oil. The oil was diluted with hexane and plugged through silica to remove the HMPA. The organics were removed *in vacuo* to give the desired **di-alkyl-alkyne** product.

(4-Ethyloct-1-yn-1-yl)trimethylsilane (2.20)

Procedure followed as per **2.G1a** (69 mg, 14%).

¹H NMR (400 MHz, CDCl₃) δ 2.19 (d, *J* = 5.7 Hz, 2H), 1.47 – 1.22 (m, 9H), 0.93 – 0.82 (m, 6H), 0.14 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 139.98, 136.61, 136.40, 123.12, 112.72, 106.70, 85.33, 38.75, 32.79, 30.46, 29.07, 26.17, 23.93, 23.07, 14.22, 11.25 GCMS: *m/z* Calc. for C₁₃H₂₆Si (M⁺): 210.2. Found: 210.2.

4-Ethyloct-1-yne (2.21)

Procedure followed as per **2.G1b**, being careful during rotary evaporation to limit any product being removed under vacuum (37 mg, 84%).

^1H NMR (400 MHz, CDCl_3) δ 2.22 – 2.16 (m, 2H), 1.51 – 1.22 (m, 10H), 0.93 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 83.33, 68.81, 38.45, 32.64, 29.01, 25.87, 22.93, 22.22, 14.07, 11.05. GCMS: m/z Calc. for $\text{C}_{10}\text{H}_{17}^+$ (M $^+$): 138.1. Found: 138.0.

5,10-Diethyltetradec-7-yne (2.22)

Same as **2.G1c**. Final product could not be isolated.

General procedure for the Sonogashira coupling of deactivated alkyl bromides and terminal alkyl-acetylenes (2.G2)¹⁰¹

A microwave vial was charged with [Allyl] PdCl_2 (0.025 equiv.), 1,3-di-*tert*-butylimidazolium chloride (0.05 equiv.), CuI (0.075 equiv.), and CsCO_3 (1.4 equiv.) before being evacuated and purged with argon ($\times 3$). Separately and previously de-gassed $\text{Et}_2\text{O}:\text{DMF}$ (2:1, 2 mL/mmol) were added before the reaction mixture was further purged with argon. Terminal alkyne (1.3 equiv.) and alkyl bromide (1 equiv.) were added before the mixture was heated at 45 °C for 16 h. The reaction was cooled before the solvent was removed *in vacuo* and the whole mixture was diluted in hexane before being passed through a pad of silica. The hexane was removed *in vacuo* to yield the desired coupled alkyne.

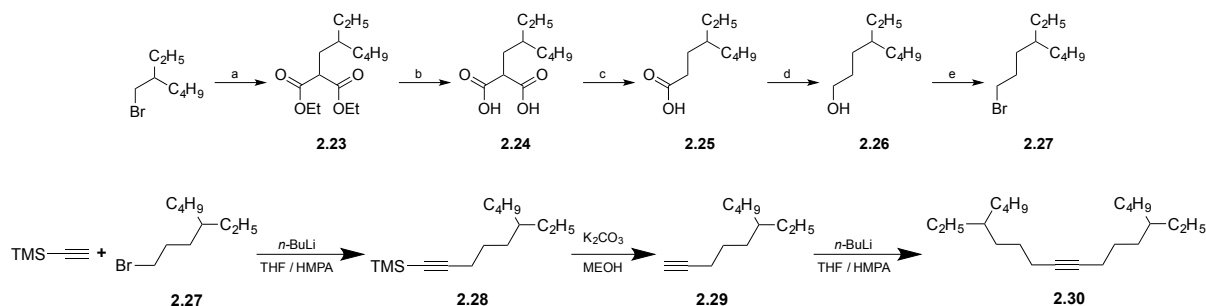
Hexadec-7-yne (Table 2.3 – rxn 3c)

Repeat of literature conditions.¹⁰¹

^1H NMR (400 MHz, CDCl_3) δ 2.17 – 2.10 (m, 4H), 1.52 – 1.42 (m, 4H), 1.42 – 1.33 (m, 4H), 1.33 – 1.19 (m, 12H), 0.93 – 0.81 (m, 6H).

7.4.5 Extended branching point synthesis¹⁰⁵

The following synthesis was based on literature conditions with some modifications.



Scheme 7.5 – Synthesis of extended branching point alkyl-alkyne

Diethyl 2-(2-ethylhexyl)malonate (2.23)

As per literature conditions.¹⁷⁶ Sodium (5.95 g, 259 mmol), diethyl malonate (41.5 g, 259 mmol) and ethanol (1000 mL) were stirred for an hour at room temperature under argon. 3-(Bromomethyl)heptane (50 g, 259 mmol) was added before the whole reaction was refluxed at 90 °C overnight. The solution was reduced in volume *in vacuo* before being diluted with diethyl ether (1000 mL) and water (1000 mL). The aqueous layer was extracted further with diethyl ether (3 × 150 mL) and the organic fractions were combined, dried over MgSO₄, filtered, and the solvent removed under pressure. The crude oil was then purified by vacuum distillation to yield **2.23** (42 g, 68%) as an oil.

¹H NMR (400 MHz, CDCl₃) δ 4.20 (q, *J* = 7.3 Hz, 4H), 3.40 (t, *J* = 7.9 Hz, 1H), 1.83 (m, 2H), 1.39-1.14 (m, 15H), 0.87 (m, 6H).

2-(2-Ethylhexyl)malonic acid (2.24)

Diethyl 2-(2-ethylhexyl)malonate (40 g, 184 mmol) was suspended in ethanol (1000 mL) before a solution of KOH (52 g, 920 mmol) in water (300 mL) was slowly added and the whole reaction was refluxed at 90 °C for 4 h. The ethanol was removed under rotary evaporation before the suspension was acidified with HCl (conc.). Diethyl ether (300 mL)

was added before the aqueous layer was washed further with diethyl ether (3×150 mL) and the organic fractions were combined, dried over MgSO_4 , filtered, and the solvent was removed under pressure to give **2.24** (37 g, 94%) as a light-yellow solid. The crude reaction mixture was used directly for the next step.

^1H NMR (400 MHz, CDCl_3) δ 8.90 (s (b), 2H), 3.53 (t, $J = 7.5$ Hz, 1H), 1.94 – 1.85 (m, 2H), 1.41 – 1.14 (m, 9H), 0.87 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.42, 49.82, 36.84, 32.69, 32.39, 28.51, 25.52, 23.13, 14.20, 10.45.

4-Ethyl octanoic acid (**2.25**)

The crude solid **2.24** (33 g, 153 mmol) was heated in air at 180°C until no more gas evolution was seen, yielding **2.25** as an oil (26 g, 99%).

^1H NMR (400 MHz, CDCl_3) δ 10.07 (s (b), 1H), 2.33 (m, 2H), 1.61 (m, 2H), 1.35 – 1.20 (m, 9H), 0.86 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 180.50, 38.33, 32.43, 31.55, 28.76, 27.98, 25.52, 23.05, 14.08, 10.69.

4-Ethyl octan-1-ol (**2.26**)

2.25 (26 g, 151 mmol) was dissolved in diethyl ether (300 mL) before being cooled to 0°C . LiAlH_4 (79 mL, 317 mmol, 4.0 M) was added dropwise via cannula before the whole solution was warmed to room temperature then heated at 45°C overnight. The crude reaction mixture was slowly poured onto ice (2 L) before diethyl ether (500 mL) was further added along with NaCl (~200 g) and conc. HCl (~30 mL) to aid separation. The aqueous layer was extracted further with diethyl ether (3×200 mL) and the organic fractions were combined, dried over MgSO_4 , filtered, and the solvent removed under pressure to give **2.26** (23 g, 98%) as an oil which was used directly in the next step.

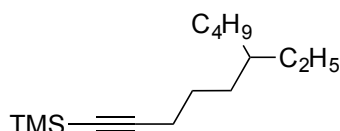
^1H NMR (400 MHz, CDCl_3) δ 3.61 (t, $J = 6.7$ Hz, 2H), 1.52 (m, 2H), 1.36 – 1.14 (m, 11H), 0.85 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 63.62, 38.81, 32.93, 30.13, 29.25, 29.06, 25.98, 23.25, 14.25, 10.94. GCMS: m/z Calc. for $\text{C}_{10}\text{H}_{21}\text{O}^-$ (M $^-$): 157.2, 158.2. Found: 157.1, 157.2.

1-Bromo-4-ethyloctane (2.27)

2.26 (18.4 g, 116 mmol) was dissolved in DCM (500 mL) before PPh_3 (33.5 g, 127 mmol) was added and the solution was cooled to 0 °C. NBS (21.7 g, 122 mmol) was added portion-wise making sure to keep the temperature below 10 °C before the reaction was left to warm to room temperature overnight. The DCM was then removed via rotary evaporation to give a beige slush, which was then diluted in hexane (150 mL) and passed through a plug of silica. The hexane was removed *in vacuo* before the crude product was purified further via column chromatography (hexane as eluent) to give **2.27** as an oil (22 g, 87%).

^1H NMR (400 MHz, CDCl_3) δ 3.40 (t, $J = 6.9$ Hz, 2H), 1.83 (m, 2H), 1.37 (d, $J = 8.4$ Hz, 2H), 1.32 – 1.20 (m, 9H), 0.97 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 38.43, 34.66, 32.89, 31.87, 30.36, 29.04, 25.94, 23.24, 14.29, 10.95. GCMS: m/z Calc. for $\text{C}_{10}\text{H}_{21}\text{Br}$ (M $^+$): 220.1, 222.1, 221.1. Found: 220.1, 222.1, 221.

(6-Ethyldec-1-yn-1-yl)trimethylsilane (2.28)

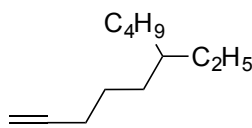


The synthesis was carried out as per the generic synthesis **2.G1a** to yield the clear oil **2.28** (3.46 g, 72%).

^1H NMR (400 MHz, CDCl_3) δ 2.19 (t, $J = 7.1$ Hz, 2H), 1.54 – 1.43 (m, 2H), 1.39 – 1.11 (m, 11H), 0.86 (m, 6H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 108.01, 84.44, 38.58, 33.00,

32.33, 29.11, 26.04, 25.96, 23.28, 20.39, 14.31, 11.00, 0.33. GCMS: m/z Calc. for $C_{15}H_{30}Si$ (M⁺): 238.2, 239.2. Found: 238.2, 239.2.

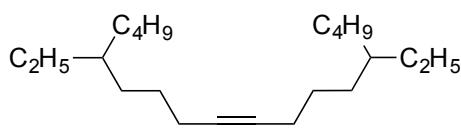
6-Ethyldec-1-yne (2.29)



The synthesis was carried out as per the generic synthesis **2.G1b** to yield the clear oil **2.29** (1.92 g, 91%).

1H NMR (400 MHz, $CDCl_3$) δ 2.19 (td, $J = 7.1, 2.7$ Hz, 2H), 1.96 (t, $J = 2.7$ Hz, 1H), 1.52 (m, 2H), 1.39 – 1.22 (m, 11H), 0.91 (t, $J = 6.8$ Hz, 3H), 0.86 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.99, 68.18, 38.63, 32.94, 32.51, 29.08, 25.98, 25.95, 23.27, 18.99, 14.30, 10.97. GCMS: m/z Calc. for $C_{12}H_{21}^+$ (M⁺): 165.2. Found: 165.0.

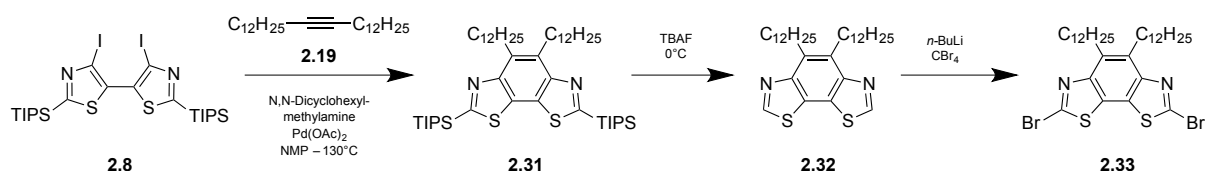
5,14-Diethyloctadec-9-yne (2.30)



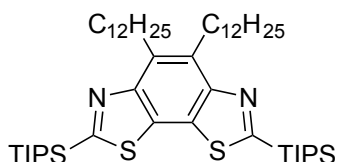
The synthesis was carried out as per the generic synthesis **2.G1c** with further purification through distillation (product at 120 °C, 5–10mbar) to yield **2.30** as a clear oil (1.61 g, 88%).

1H NMR (400 MHz, $CDCl_3$) δ 2.14 (m, 4H), 1.54 – 1.42 (m, 4H), 1.42 – 1.20 (m, 22H), 0.89 (t, $J = 6.9$ Hz, 6H), 0.84 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.46, 38.67, 33.00, 32.58, 29.12, 26.58, 26.04, 23.30, 19.35, 14.31, 11.00. GCMS: m/z Calc. for $C_{22}H_{42}$ (M⁺): 306.3, 307.3, 308.3. Found: 306.3, 307.3, 308.3.

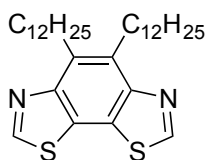
7.4.6 TzBTzC12 monomer



Scheme 7.6 – Synthesis of the TzBTzC12 monomer

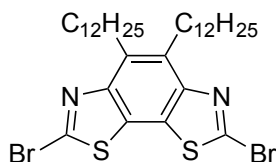
4,5-Didodecyl-2,7-bis(triisopropylsilyl)benzo[1,2-*d*:4,3-*d'*]bis(thiazole) (2.31)

The synthesis was carried out as for **2.10a** except using degassed NMP as a solvent to yield **2.31** as a yellow waxy oil which was used directly in the next step.

4,5-Didodecylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole) (2.32)

The synthesis was carried out as for **2.11** to yield **2.32** as a white solid (900 mg, 31%).

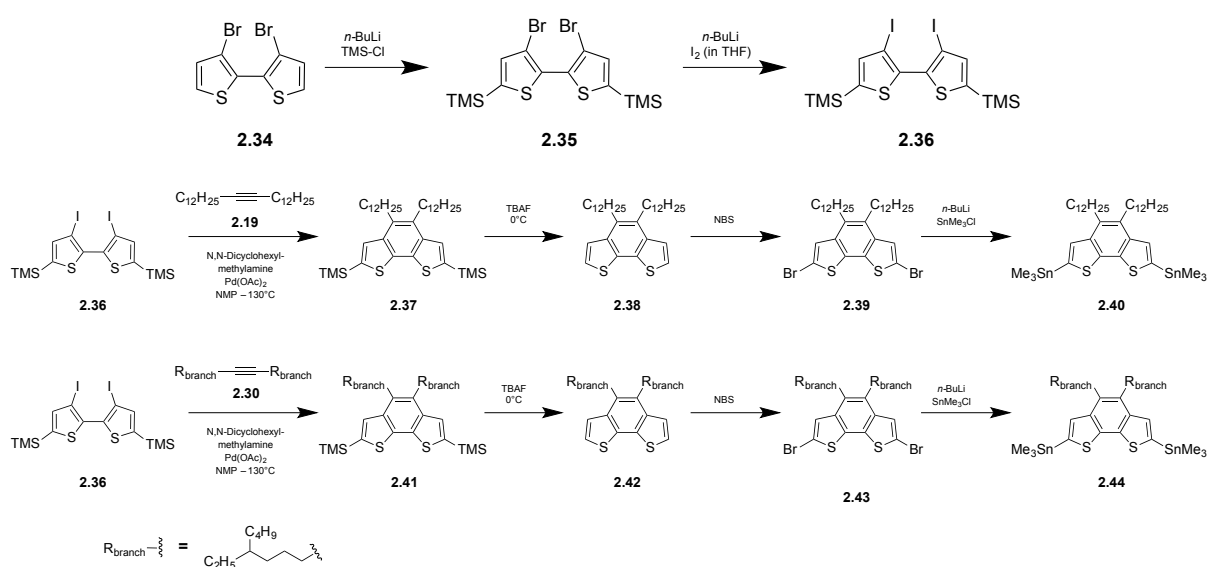
^1H NMR (400 MHz, CDCl_3) δ 8.97 (s, 2H), 3.30 (m, 4H), 1.72 (m, 4H), 1.52 (m, 4H), 1.27 (m, 32H), 0.87 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.88, 151.19, 134.21, 124.02, 32.07, 31.63, 30.30, 29.85, 29.81, 29.76, 29.51, 22.83, 14.25. GCMS: m/z Calc. for $\text{C}_{32}\text{H}_{52}\text{N}_2\text{S}_2$ (M^+): 528.4, 529.4, 530.4. Found: 528.4, 529.4, 530.4.

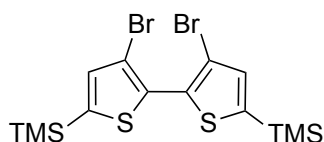
2,7-Dibromo-4,5-didodecylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole) (2.33)

2.32 (101 mg, 0.19 mmol) was dissolved in THF (20 mL) and cooled to $-78\text{ }^{\circ}\text{C}$ before *n*-BuLi (0.25 mL, 0.40 mmol, 1.6 M in hexane) was added dropwise, whereupon a yellow colour was observed. After 2 h of stirring at $-78\text{ }^{\circ}\text{C}$, CBr_4 (150 mg, 0.45 mmol) was added in small portions over 20 min before the solution was removed from the ice bath and left to warm to room temperature over 2 h. The reaction was then quenched with sat. sodium sulfite (2 mL) before being extracted with DCM (40 mL) and water (40 mL). The aqueous layer was further extracted with DCM ($3 \times 15\text{ mL}$) before the organics were combined, dried over MgSO_4 , and the solvent removed *in vacuo*. The crude mixture was purified twice by column chromatography (chloroform:hexane 1:4) to yield **2.33** as white crystals (161 mg, 50%).

^1H NMR (400 MHz, CDCl_3) δ 3.17 (m, 4H), 1.66 (m, 4H), 1.45 (m, 4H), 1.40 – 1.16 (m, 32H), 0.87 (t, $J = 6.8\text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.68, 135.32, 134.21, 31.95, 31.23, 29.91, 29.72, 29.68, 29.63, 29.50, 29.38, 29.29, 22.71, 14.14. GCMS: m/z Calc. for $\text{C}_{32}\text{H}_{50}\text{Br}_2\text{N}_2\text{S}_2$ (M^+): 686.2, 688.2, 684.2. Found: 686.3, 688.3, 684.3.

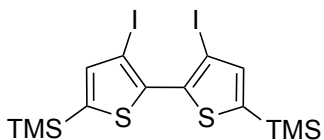
7.4.7 TBTC12 co-monomer synthesis^{81,177}



(3,3'-Dibromo-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (2.35)

A solution of 3,3'-dibromo-2,2'-bithiophene (**2.34**, 10 g, 30.9 mmol) in THF (350 mL) was cooled to -78°C before LDA (38.6 mL, 77.0 mmol, 2.0 M in THF/heptane) was added dropwise over 30 min. The solution initially formed a red precipitate before turning orange and eventually yellow. After stirring for 1.5 h at -78°C , TMS-Cl (11.75 mL, 93 mmol) was added dropwise, with a light red colour forming almost instantly upon addition. The solution was stirred for an hour at -78°C before being warmed to room temperature. The reaction was then quenched with water (20 mL) before being extracted with EtOAc (400 mL) and water (400 mL). The aqueous layer was further extracted with EtOAc (3×100 mL) before the organics were combined, dried over MgSO_4 , and the solvent was removed *in vacuo*. The crude mixture was passed through a pad of silica using toluene as an eluent, then the toluene was removed *in vacuo* and the product further purified by recrystallization twice from EtOH to yield **2.35** (11.4 g, 77%) as a pale yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 2H), 0.34 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.06, 137.16, 134.09, 113.09, -0.22. GCMS: m/z Calc. for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{S}_2\text{Si}_2$ (M^+): 467.9, 465.9, 469.9. Found: 467.9, 466.0, 469.9.

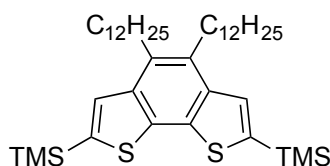
(3,3'-Diiodo-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (2.36)

A solution of **2.35** (10 g, 21.4 mmol) in THF (150 mL) was cooled to -78°C under an argon atmosphere. A solution of *n*-BuLi (18 mL, 45 mmol, 2.5 M in THF) was added dropwise

over 30 min, whereupon an orange precipitate was observed. The solution was stirred for 1 h at -78 °C. In a separate flask, iodine (11.6 g, 46 mmol) was dissolved in THF (150 mL) and then added dropwise into the stirring solution of **2.35** via cannula. The solution was then left to slowly warm up and stir overnight. The reaction was quenched with a minimum of sodium sulfite solution and the THF was concentrated under vacuum before being diluted with chloroform (300 mL) and washed with water (300 mL). The aqueous layer was extracted with chloroform (2 × 100 mL) before the organics were combined, dried over MgSO₄, filtered, and the solvent was removed under pressure to yield a yellow oil. The oil was dissolved in a minimum of chloroform and precipitated into stirring cold methanol (500 mL) before being filtered and dried. Compound **2.36** was isolated as a cream powder (9.7 g, 78%).

¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 2H), 0.34 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 145.04, 141.85, 139.89, 85.68, -0.29. GCMS: m/z Calc. for C₁₄H₂₀I₂S₂Si₂ (M⁺): 561.9, 562.9, 562.9. Found: 561.9, 562.9, 563.9.

(4,5-Didodecylbenzo[2,1-*b*:3,4-*b'*]dithiophene-2,7-diyl)bis(trimethylsilane) (2.37)

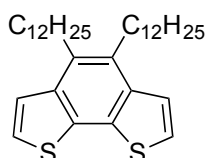


The procedure was based on the literature^{81,82} and a modified version of procedure **2.10a**:

2.36 (2.0 g, 3.6 mmol), **2.19** (1.7 g, 4.62 mmol), and Pd(OAc)₂ (40 mg, 0.18 mmol) were sealed in a microwave vial and evacuated with argon before being dissolved in previously degassed NMP (15 mL). *N,N*-dicyclohexylmethylamine (1.7 g, 8.5 mmol) on molecular sieves was added and the solution was degassed for a further 10 min. The vial was then heated in a microwave for 2 min at 100 °C, 2 min at 120 °C, 2 min at 140 °C, 2 min at 160 °C, and 50 min at 180 °C before being poured into HCl (150 mL). Diethyl ether

(200 mL) was added before the aqueous layer was washed further with diethyl ether (2 × 75 mL) before the organics were combined, dried over MgSO₄, filtered and the solvent was removed under pressure to yield a light-yellow oil. The crude oil was then purified via column chromatography (hexane) to yield **2.37** as a light oil. Due to the product running at a similar R_f value to the excess alkyl chain, the product was directly used in the next step.

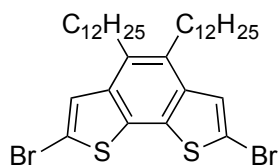
4,5-Didodecylbenzo[2,1-*b*:3,4-*b'*]dithiophene (**2.38**)



The procedure was carried out as per **2.11** to yield **2.38** (890 mg, 47% over two steps).

¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 5.4 Hz, 2H), 7.37 (d, *J* = 5.4 Hz, 2H), 3.01 (m, 4H), 1.64 (m, 4H), 1.48 (pent., *J* = 6.7 Hz, 4H), 1.42 – 1.17 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 137.63, 131.76, 123.74, 123.58, 32.09, 31.72, 30.62, 30.35, 29.86, 29.81, 29.73, 29.52, 29.34, 29.03, 22.85, 18.93, 14.27. GCMS: *m/z* Calc. for C₃₄H₅₄S₂ (M⁺): 526.4, 527.4, 528.4. Found: 526.4, 527.4, 528.4.

2,7-Dibromo-4,5-didodecylbenzo[2,1-*b*:3,4-*b'*]dithiophene (**2.39**)

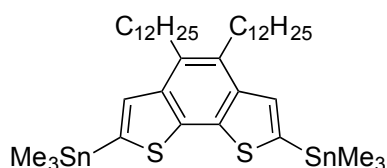


2.38 (810 mg, 1.54 mmol) was dissolved in chloroform (12 mL) and acetic acid (4 mL) before being covered in foil. NBS (685 mg, 3.84 mmol) was added portion wise over 10 min and the reaction was left to stir overnight. The reaction was quenched with sat. Na₂SO₃ (4 mL) before the aqueous layer was extracted with chloroform (2 × 10 mL), the organics were combined, washed with brine, dried over MgSO₄, filtered, and the solvent was removed

under pressure. The crude product was purified by column chromatography (hexane) to yield **2.39** (720 mg, 68%) as a white crystalline solid.

^1H NMR (400 MHz, CDCl_3) δ 7.40 (s, 2H), 2.89 (m, 4H), 1.59 (pent., $J = 7.8$ Hz, 4H), 1.46 (pent., $J = 7.0$ Hz, 4H), 1.40 – 1.18 (m, 32H), 0.88 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.30, 131.51, 131.40, 126.31, 112.55, 31.95, 31.44, 30.39, 30.11, 29.71, 29.67, 29.52, 29.38, 22.72, 14.14. GCMS: m/z Calc. for $\text{C}_{34}\text{H}_{52}\text{Br}_2\text{S}_2$ (M^+): 684.2, 686.2, 682.2. Found: 684.3, 686.3, 682.3.

(4,5-Didodecylbenzo[2,1-*b*:3,4-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane) (2.40)



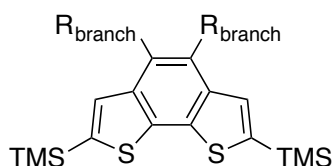
2.39 (303mg, 0.44 mmol) was dissolved in THF (70 mL) before being cooled to -78 °C. *n*-BuLi (0.61 mL, 0.97 mmol, 1.6 M in THF) was added dropwise and the solution was left to stir for 2 h. SnMe_3Cl (1.1 mL, 1.1 mmol, 1.0 M in hexanes) was added dropwise over 5 min before the solution was removed from the ice bath and left to warm to room temperature over an hour. The crude material was quenched with water (100 mL) before being diluted in hexane. The aqueous layer was washed further with hexane (2×50 mL) before the organics were combined, washed with brine, dried over MgSO_4 , filtered, and the solvent was removed under pressure. The crude material was purified via recycling GPC to yield **2.40** (110 mg, 29%) as a clear highly viscous oil.

^1H NMR (400 MHz, CDCl_3) δ 7.48 (s, 2H), 3.03 (m, 4H), 1.66 (pent., $J = 7.7$ Hz, 4H), 1.49 (pent., $J = 6.7$ Hz, 4H), 1.28 (d, $J = 8.8$ Hz, 32H), 0.87 (t, $J = 6.6$ Hz, 6H), 0.44 (s, 18H).

^{13}C NMR (100 MHz, CDCl_3) δ 138.34, 136.90, 131.35, 130.80, 31.94, 31.47, 30.38, 30.12, 29.74, 29.69, 29.54, 29.38, 22.71, 14.13, -8.21. MALDI-TOF MS: m/z Calc. for $\text{C}_{40}\text{H}_{69}\text{S}_2\text{Sn}_2^+$ (M^+): 851.3, 853.3, 849.3. Found: 851.0, 853.0, 850.0.

7.4.8 TBTCbranch co-monomer synthesis

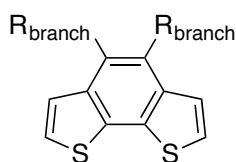
(4,5-Bis(4-ethyloctyl)benzo[2,1-*b*:3,4-*b'*]dithiophene-2,7-diyl)bis(trimethylsilane) (**2.41**)



The procedure was carried out as for **2.37** except using the alkyl chain **2.30** in place of **2.19**.

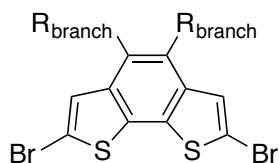
This yielded **2.41** as a light-yellow oil that was used directly in the next step.

4,5-Bis(4-ethyloctyl)benzo[2,1-*b*:3,4-*b'*]dithiophene (**2.42**)



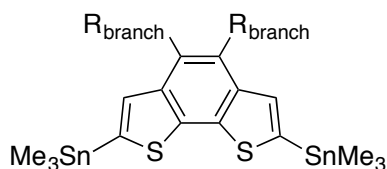
The procedure was carried out as per **2.11** to yield **2.42** (488 mg, 64% over two steps) as a clear oil.

^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 5.4$ Hz, 2H), 7.38 (d, $J = 5.5$ Hz, 2H), 3.00 (m, 4H), 1.63 (m, 4H), 1.46 (m, 4H), 1.37 – 1.03 (m, 22H), 0.89 (t, $J = 6.3$ Hz, 6H), 0.86 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.46, 131.60, 123.52, 123.49, 38.75, 33.87, 32.86, 31.02, 29.03, 28.81, 25.91, 23.15, 14.18, 10.89. GCMS: m/z Calc. for $\text{C}_{30}\text{H}_{46}\text{S}_2$ (M^+): 470.3, 471.3, 472.3. Found: 470.3, 471.3, 472.4.

2,7-Dibromo-4,5-bis(4-ethyloctyl)benzo[2,1-*b*:3,4-*b'*]dithiophene (2.43)

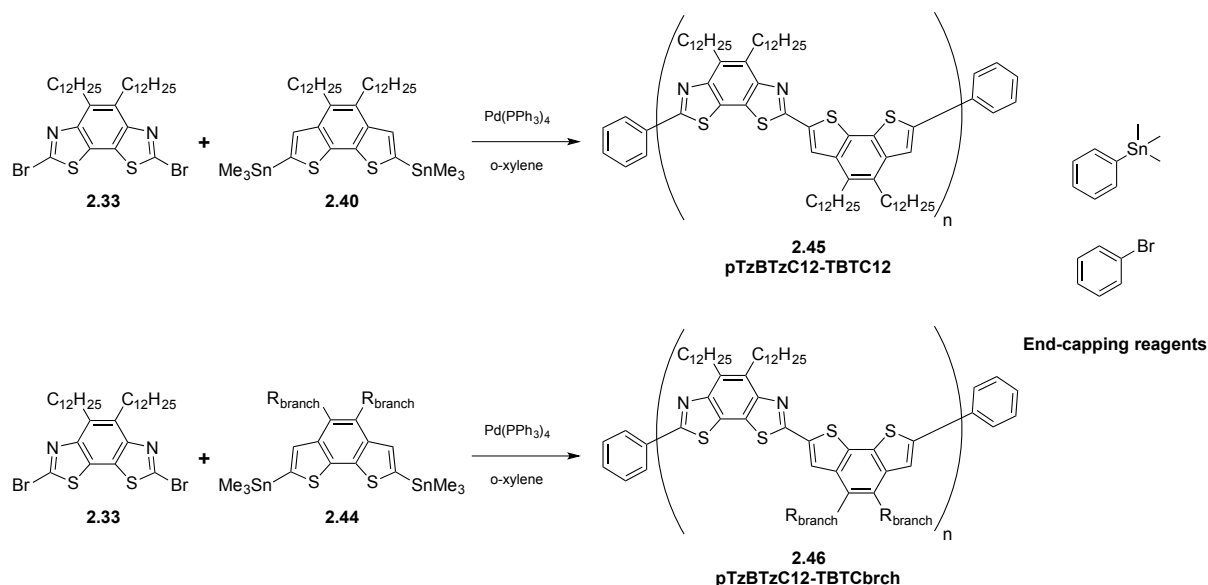
The procedure was carried out as per **2.39** to yield **2.43** (830 mg, 77%) as a clear oil.

^1H NMR (400 MHz, CDCl_3) δ 7.39 (s, 2H), 2.87 (m, 4H), 1.56 (m, 4H), 1.43 (m, 4H), 1.28 (m, 18H), 0.90 (t, $J = 7.5$ Hz, 6H), 0.86 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.29, 131.51, 131.43, 126.27, 112.60, 38.69, 33.77, 32.81, 30.90, 29.01, 28.70, 25.90, 23.16, 14.20, 10.90. GCMS: m/z Calc. for $\text{C}_{30}\text{H}_{44}\text{Br}_2\text{S}_2$ (M^+): 628.1, 630.1, 626.1. Found: 628.2, 630.2, 626.2.

(4,5-Bis(4-ethyloctyl)benzo[2,1-*b*:3,4-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane) (2.44)

The procedure was carried out as per **2.40** to yield the final monomer **2.44** (362 mg, 63%) as a highly viscous clear oil.

^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 2H), 3.02 (m, 4H), 1.64 (m, 4H), 1.48 (m, 4H), 1.30 (m, 18H), 0.91 (t, $J = 7.4$ Hz, 6H), 0.87 (t, $J = 7.0$ Hz, 6H), 0.45 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.34, 136.97, 135.67, 131.32, 130.76, 38.63, 33.77, 32.86, 30.98, 29.00, 28.69, 25.91, 23.19, 14.21, 10.91, -8.23. MALDI-TOF MS: m/z Calc. for $\text{C}_{36}\text{H}_{61}\text{S}_2\text{Sn}_2^+$ (M^+): 796.2, 798.2. Found: 796.6, 798.6.

7.4.9 Polymerisation of (pTzBTzC12)-*alt*-(co-monomer)Scheme 7.8 – Polymerisation conditions for **2.45** and **2.46**

Polymerisation of **2.33 and **2.40** to form poly(4,5-didodecylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole)-*alt*-4,5-didodecylbenzo[2,1-*b*:3,4-*b'*]dithiophene) (TzBTzC12-TBTC12)**

The oily tin monomer **2.40** was dissolved in dichloromethane and transferred to a microwave vial, then the solvent was removed *in vacuo* and the vial was left under vacuum overnight to give **2.40 – TBTC12** (54.19 mg, 63.6 μmol) in the reaction vessel. **2.33 – TzBTzC12** (43.61 mg, 63.6 μmol) and PdPPh_3 (2.9 mg, 2.5 μmol) were added before the vessel was sealed and evacuated with argon. Previously de-gassed *o*-xylene (1 mL) was added and the solution was de-gassed for a further 10 min. The vial was heated in a microwave for 2 min at 100 °C, 2 min at 120 °C, 5 min at 140 °C, 5 min at 160 °C, and 30 min at 180 °C.

Trimethyl(phenyl)tin (0.05 mL, 0.28 mmol) was added before heating the solution in the microwave for 1 min at 100 °C, 1 min at 120 °C, 1 min at 140 °C, 1 min at 160 °C, and 3 min at 180 °C. After the addition of 1-bromobenzene (0.1 mL, 0.95 mmol), the solution was again heated in the microwave for 1 min at 100 °C, 1 min at 120 °C, 1 min at 140 °C, 1 min at 160 °C, and 3 min at 180 °C. The solution was precipitated in methanol (200 mL) and conc.

HCl (2 mL) before being filtered into a fibreglass thimble and Soxhlet extracted in methanol (overnight), acetone (overnight), hexane (overnight), and chloroform (6 h). The polymer was completely soluble in chloroform, and this fraction was subsequently washed extensively with an aqueous solution of sodium diethyldithiocarbamate to remove residual palladium.

The chloroform was removed *in vacuo* and the polymer was dissolved in a minimum of chlorobenzene before being precipitated in methanol (200 mL) and filtered to give

TzBTzC12-TBTC12 (55 mg, 82%).

GPC (Chlorobenzene): $M_n = 63$ kg/mol, $M_w = 105$ kg/mol, $\bar{D} = 1.66$

Polymerisation of 2.33 and 2.44 to form poly(4,5-didodecylbenzo[1,2-*d*:4,3-*d'*]bis(thiazole)-*alt*-4,5-bis(4-ethyloctyl)benzo[2,1-*b*:3,4-*b'*]dithiophene) (TzBTzC12-TBTCbranch)

The oily tin monomer **2.44** was dissolved in diethyl ether and transferred to a microwave vial, whereupon the solvent was removed *in vacuo* before being left under vacuum overnight to give **2.44 – TBTCbranch** (71.90 mg, 90.3 μ mol) in the reaction vessel. **2.33 – TzBTzC12** (62.05 mg, 90.3 μ mol) and PdPPh₃ (3.3 mg, 2.8 μ mol) were added before the vessel was sealed and evacuated with argon. Previously de-gassed *o*-xylene (1 mL) was added and the solution was de-gassed for a further 10 min. The vial was heated in a microwave for 2 min at 100 °C, 2 min at 120 °C, 5 min at 140 °C, 5 min at 160 °C, and 30 min at 180 °C.

Trimethyl(phenyl)tin (0.05 mL, 0.28 mmol) was added before heating the solution in the microwave for 1 min at 100 °C, 1 min at 120 °C, 1 min at 140 °C, 1 min at 160 °C, and 3 min at 180 °C. After the addition of 1-bromobenzene (0.1 mL, 0.95 mmol), the solution was again heated in the microwave for 1 min at 100 °C, 1 min at 120 °C, 1 min at 140 °C, 1 min at 160 °C and 3 min at 180 °C. The solution was precipitated in methanol (200 mL) and conc. HCl (2 mL) before being filtered into a fibreglass thimble and Soxhlet extracted in methanol

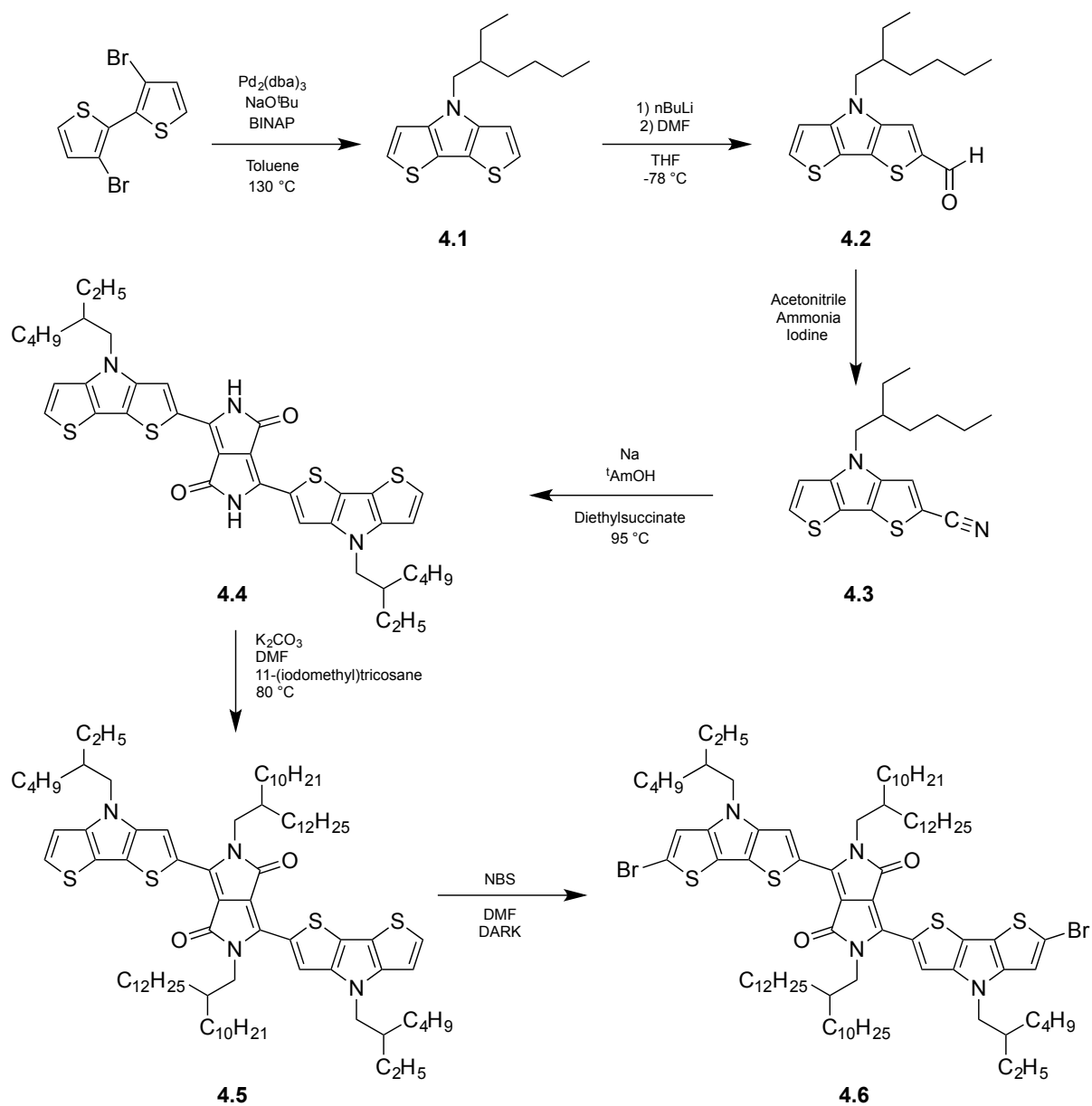
(overnight), acetone (6 h), hexane (overnight), and chloroform (6 h). The polymer was completely soluble in chloroform, and this fraction was subsequently washed extensively with an aqueous solution of sodium diethyldithiocarbamate to remove residual palladium.

The chloroform was removed *in vacuo* and the polymer was dissolved in a minimum volume of chlorobenzene before being precipitated in methanol (200 mL) and filtered to give

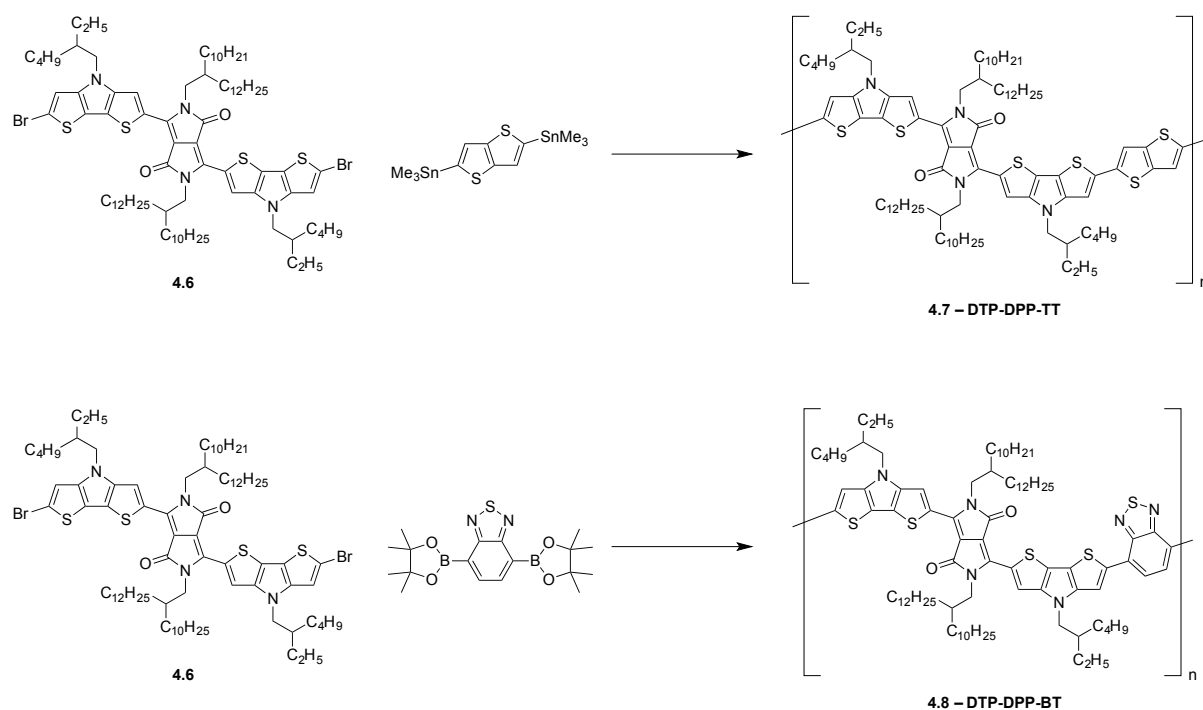
TzBTzC12-TBTCbranch (77 mg, 85%).

GPC (Chlorobenzene): $M_n = 61$ kg/mol, $M_w = 117$ kg/mol, $\bar{D} = 1.91$

7.5 Chapter 4 experimental

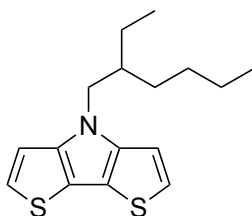


Scheme 7.9 – DTP-DPP monomer synthesis



Scheme 7.10 – DTP-DPP polymerisation

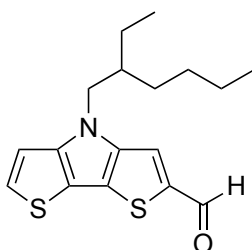
4-(2-Ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (4.1) ^{136,137}



A flask was charged with 3,3'-dibromo-2,2'-bithiophene (15 g, 46.3 mmol) and toluene (250 mL) before being degassed through bubbling with argon for 1 h. To this solution was added Pd₂(dba)₃ (1.054 g, 1.15 mmol), NaO^tBu (11.1 g, 116 mmol), and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP – 2.87 g, 4.61 mmol) before a further 1 h of degassing. 2-Ethylhexan-1-amine (8.4 mL, 51.3 mmol) was added dropwise and the solution was heated for 24 h. The solution was cooled and the toluene removed under reduced pressure to give a sticky red solid. The crude material was purified by column chromatography (EtOAc:Hex 1:4) to yield **4.1** as a red viscous oil in high yield (13.3 g, 98%).

^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, J = 5.3 Hz, 2H), 6.98 (d, J = 5.3 Hz, 2H), 4.06 (hept., J = 7.5 Hz, 2H), 1.95 (pent., J = 6.5 Hz, 1H), 1.42 – 1.21 (m, 8H), 0.90 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 122.5, 114.4, 111.0, 51.1, 40.3, 30.5, 28.5, 23.9, 22.9, 14.0, 10.6. GCMS: m/z Calc. for $\text{C}_{16}\text{H}_{21}\text{NS}_2$ (M^+): 291.1 292.1, 293.1. Found: 290.9, 291.9, 292.9.

4-(2-Ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde (**4.2**)

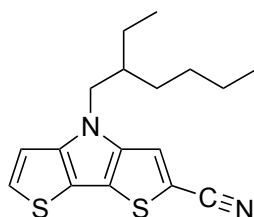


4.1 (7.9 g, 27.2 mmol) was dissolved in THF (300 mL) under an argon atmosphere before being cooled to $-78\text{ }^\circ\text{C}$. *n*-BuLi (11.5 mL, 27.1 mmol, 2.36 M in THF) was added dropwise over 1 h, and the solution was then stirred for a further hour at $-78\text{ }^\circ\text{C}$. DMF (2.6 mL, 33.7 mmol) was added dropwise and the solution was stirred for 30 min at $-78\text{ }^\circ\text{C}$ before being warmed to room temperature. The THF was concentrated under vacuum and the reaction was quenched with water (300 mL) before being extracted with DCM (300 mL). The aqueous layer was extracted with DCM ($3 \times 100\text{ mL}$) before the organics were combined, washed with brine twice, dried over MgSO_4 , filtered, and the solvent was removed under pressure. The crude material was passed through a pad of silica (EtOAc:Hex 1:4) to yield **4.2** as a viscous red oil (8.2 g, 94%).

^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 1H), 7.62 (s, 1H), 7.37 (d, J = 5.4 Hz, 1H), 7.00 (d, J = 5.4 Hz, 1H), 4.08 (m, 2H), 1.95 (pent., J = 6.3 Hz, 1H), 1.42 – 1.20 (m, 8H), 0.91 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 182.8, 149.3, 144.4, 139.9,

128.3, 124.5, 123.0, 119.3, 110.8, 51.3, 40.3, 30.4, 28.4, 23.9, 22.8, 13.8, 10.5. GCMS: m/z Calc. for $C_{17}H_{21}NOS_2$ (M^+): 319.1, 320.1, 321.1. Found: 319.1, 320.1, 321.1.

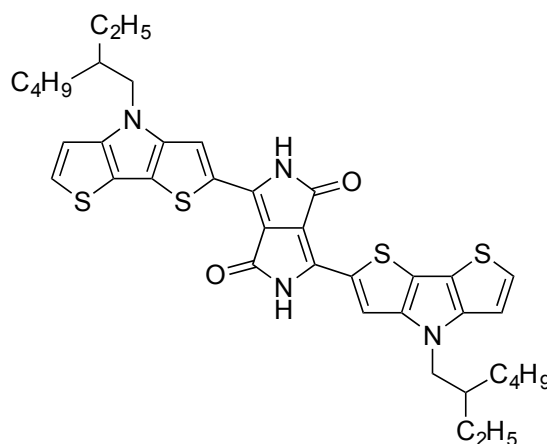
4-(2-Ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbonitrile (**4.3**)



4.2 (8.2 g, 25.6 mmol) was dissolved in acetonitrile (150 mL) and THF (30 mL) before the addition of ammonia water (60 mL), after which the solution was cooled to 0 °C. Iodine (7.2 g, 28.4 mmol) was added in small portion over 2 h, waiting for the colour to change from brown back to colourless before the addition of subsequent iodine. After completion of the iodine addition, the reaction was stirred for a further 3 h at 0 °C. The progress of the reaction was monitored to completion using GCMS before being quenched with sat. sodium sulfite (200 mL), after which DCM (300 mL) was added. The aqueous layer was extracted with DCM (3 × 100 mL) before the organics were combined, washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed under pressure. The crude material was purified via column chromatography (DCM:Hex 1:1 + 2% EtOAc) to yield **4.3** as a dark brown tacky oil (4.6 g, 57%).

1H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.33 (d, $J = 5.4$ Hz, 1H), 7.00 (d, $J = 5.4$ Hz, 1H), 4.07 (m, 2H), 1.92 (pent., $J = 6.4$ Hz, 1H), 1.40 – 1.19 (m, 8H), 0.95 – 0.81 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.99, 142.60, 127.36, 120.30, 119.93, 116.08, 114.26, 111.04, 104.16, 77.34, 77.23, 77.02, 76.71, 51.57, 40.47, 30.64, 28.65, 24.04, 22.93, 13.98, 10.65. GCMS: m/z Calc. for $C_{17}H_{20}N_2S_2$ (M^+): 316.1, 317.1, 318.1. Found: 316.1, 317.1, 318.1.

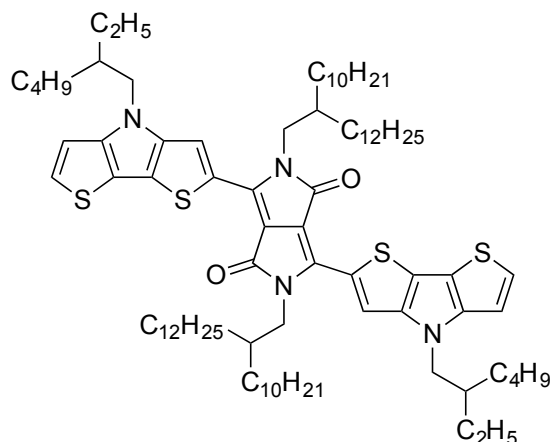
3,6-Bis(4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4.4)



Sodium metal (370 mg, 16.4 mmol) was stirred in ^tAmOH (50 mL) at 120 °C until no sodium was present. The basic solution was cooled to 85 °C before a solution of **4.3** (3.35 g, 10.6 mmol) and diethyl succinate (0.75 mL, 4.44 mmol) dissolved in ^tAmOH (15 mL) was added dropwise to the basic solution. A dark blue tinge to the reaction was seen within the first hour, and the reaction was left to stir overnight at 95 °C. The reaction was cooled to room temperature before acetic acid (10 mL) was added and the suspension was left to stir. The solvents were removed under reduced pressure before methanol (50 mL) was added and the suspension subject was to ultrasounded, filtered, and washed with more methanol (2 × 20 mL) to yield **4.4** as a dark blue solid (1.3 g, 41%).

¹H NMR (400 MHz, DMSO) δ 11.19 (s, 2H), 8.30 (s, 2H), 7.58 (d, *J* = 5.2 Hz, 2H), 7.30 (d, *J* = 5.5 Hz, 2H), 4.17 (d, *J* = 7.5 Hz, 4H), 1.98 (m, 2H), 1.41 – 1.14 (m, 16H), 0.89 (t, *J* = 7.5 Hz, 6H), 0.82 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, DMSO) δ 161.53, 148.57, 144.77, 135.98, 128.07, 127.48, 119.89, 114.06, 111.91, 108.33, 50.54, 29.99, 27.82, 23.41, 22.48, 13.80, 10.42. MALDI-TOF MS: *m/z* Calc. for C₃₈H₄₂N₄O₂S₄ (M⁺): 714.2. Found: 714.7.

2,5-Bis(2-decyltetradecyl)-3,6-bis(4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4.5)

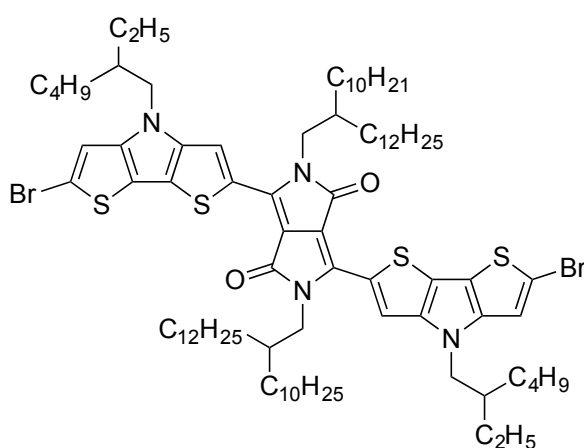


4.4 (200 mg, 0.18 mmol) and K_2CO_3 (155 mg, 1.12 mmol) were dissolved in DMF (15 mL) under an argon atmosphere before being heated at 80 °C for 2 h. 11-(Iodomethyl)tricosane (530 mg, 1.14 mmol) was added dropwise, and the reaction monitored by TLC ($R_f \sim 0.8$ in 10% EtOAc/Hex) until completion (approx. 4 h). The DMF was removed under reduced pressure and then the crude mixture was extracted with chloroform (200 mL) and water (200 mL). The aqueous layer was further extracted with chloroform (3×100 mL) before the organics were combined, washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed under pressure to leave a dark blue oil. The crude material was purified by column chromatography (hexane + 1% EtOAc) to give a mix of *N*- and *O*-alkylated products. To remove any *O*-alkylated product, the material was further dissolved in dioxane before conc. HCl (10 drops) was added and the reaction was heated at 120 °C for 2 h. The dioxane was removed under reduced pressure and the crude material was purified again by column chromatography (hexane + 1% EtOAc) to yield **4.5** as a dark blue/green oil (70 mg, 18%).

1H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 2H), 7.29 (d, $J = 5.4$ Hz, 2H), 7.00 (d, $J = 5.4$ Hz, 2H), 4.17 (m, 8H), 2.05 (dd, $J = 17.1, 10.6$ Hz, 4H), 1.46 – 1.15 (m, 100H), 0.95 (t, $J = 7.4$

Hz, 6H), 0.86 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.69, 148.28, 145.71, 140.05, 126.88, 126.49, 120.00, 118.26, 114.69, 111.13, 107.54, 51.38, 46.50, 41.34, 40.49, 37.82, 36.07, 31.93, 31.59, 31.14, 30.71, 30.13, 29.72, 29.68, 29.65, 29.38, 29.06, 28.88, 28.72, 27.67, 26.21, 26.18, 24.13, 23.02, 22.69, 22.66, 22.61, 22.57, 20.44, 19.42, 18.75, 14.31, 14.11, 14.05, 11.42, 10.73. MALDI-TOF MS: m/z Calc. for $\text{C}_{86}\text{H}_{142}\text{N}_4\text{O}_2\text{S}_4$ (M^+): 1391.0. Found: 1391.7.

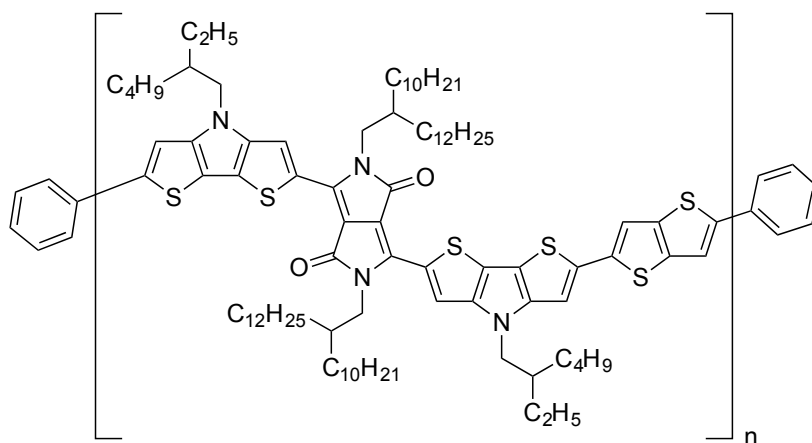
3,6-Bis(6-bromo-4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4.6)



A microwave vial was charged with **4.5** (266 mg, 192 μmol) in THF (30 mL) under an argon atmosphere and covered in foil before being cooled to 0 °C. Previously recrystallized NBS (70 mg, 393 μmol) was added in one portion before the reaction was stirred at 0 °C for 2 h in the dark. Sat. Na_2SO_3 (2 mL) was added and the solution was stirred for a further 10 min in the dark. The reaction was extracted with DCM (100 mL) and water (100 mL). The aqueous layer was further extracted with DCM (3 $\times$ 50 mL) before the organics were combined, washed with K_2CO_3 (2 M), brine, dried over MgSO_4 , filtered, and the solvent was removed under pressure. The crude reaction mixture was purified via column chromatography (DCM:Hex 1:4) to yield **4.6** as a dark blue oil (138 mg, 46%).

^1H NMR (400 MHz, CDCl_3) δ 9.17 (s, 2H), 7.04 (s, 2H), 4.12 (m, 8H), 2.01 (m, 2H), 1.45 – 1.13 (m, 100H), 0.94 (t, $J = 7.4$ Hz, 6H), 0.87 (m, 18H). ^{13}C NMR (100 MHz, Pyr) δ 161.64, 146.42, 144.67, 140.07, 127.70, 120.43, 118.93, 115.34, 114.89, 114.18, 107.79, 51.38, 40.38, 38.09, 31.97, 31.40, 30.78, 30.24, 29.88, 29.80, 29.75, 29.51, 29.48, 29.37, 28.73, 26.38, 26.31, 24.21, 23.17, 22.77, 14.14, 14.10, 10.67. MALDI-TOF MS: m/z Calc. for $\text{C}_{86}\text{H}_{140}\text{Br}_2\text{N}_4\text{O}_2\text{S}_4$ (M^+): 1546.8. Found: 1546.9.

2,5-Bis(2-decyltetradecyl)-3,6-bis(4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione-*alt*-thieno[3,2-*b*]thiophene (4.7 – pDTP-DPP-TT)



The dark blue oily monomer **4.6** was dissolved in diethyl ether and placed in a microwave vial. The solvent was removed under vacuum and the vial was left under vacuum overnight to give **4.6** (66.75 mg, 43.17 μmol). 2,5-Bis(trimethylstannyl)thieno[3,2-*b*]thiophene (20.11 mg, 43.17 μmol), $\text{Pd}_2(\text{dba})_3$ (1.10 mg, 1.2 μmol), and tri(*o*-tolyl)phosphine (1.46 mg, 4.8 μmol) were added to the vessel before it was sealed and purged with argon. Previously degassed chlorobenzene (1 mL) was added before the reaction was microwave heated for 2 mins at 100 °C, 2 min at 120 °C, 5 min at 140 °C, 5 min at 160 °C, and 30 min at 180 °C.

Trimethyl(phenyl)tin (0.05 mL, 0.28 mmol) was added before heating the solution in the microwave for 1 min at 100 °C, 1 min at 120 °C, 1 min at 140 °C, and 5 min at 160 °C. After

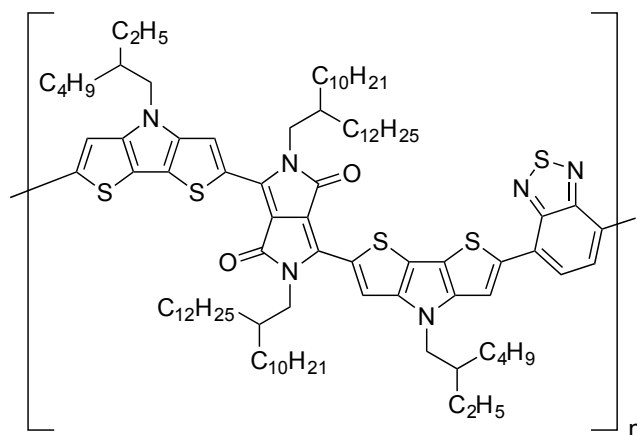
the addition of 1-bromobenzene (0.1 mL, 0.95 mmol), the solution was again heated in the microwave for 1 min at 100 °C, 1 min at 120 °C, 1 min at 140 °C, and 5 min at 160 °C. The solution was precipitated in methanol (200 mL) before filtered into a glass-fibre thimble and Soxhlet extracted in methanol (overnight), acetone (overnight), hexane (overnight), and chlorobenzene (6 h), leaving some insoluble polymer in the thimble. The chlorobenzene fraction was washed extensively with an aqueous solution of sodium diethyldithiocarbamate to remove residual palladium, followed by washing with water twice.

The chlorobenzene was removed *in vacuo* and the polymer was dissolved in a minimum of chlorobenzene before being precipitated in methanol (200 mL) and filtered, then washed with more MeOH (30 mL). **pDTP-DPP-TT (4.7)** was collected as a dark green/black shiny plastic (18 mg, 27%).

GPC (Chlorobenzene): $M_n = 170$ kg/mol, $M_w = 184$ kg/mol, $\bar{D} = 1.06$

NMR spectrum not obtained due to poor resolution at concentrations available.

2,5-Bis(2-decyltetradecyl)-3,6-bis(4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione-*alt*-benzo[*c*][1,2,5]thiadiazole (4.8 pDTP-DPP-BT)

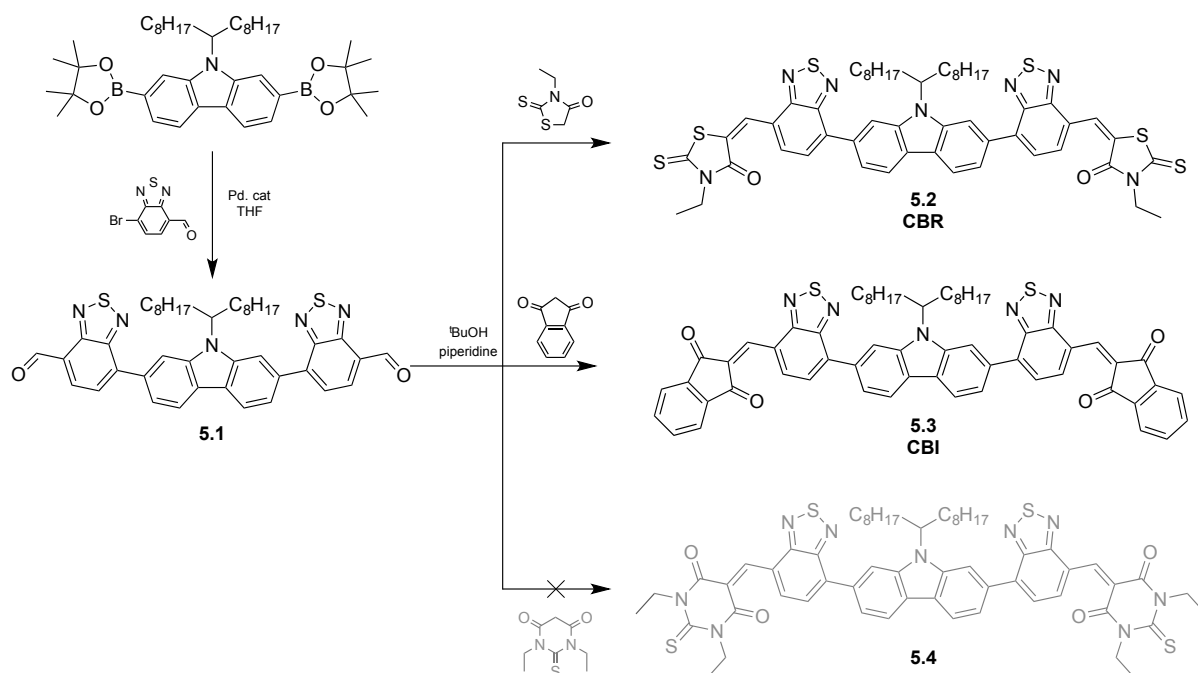


The dark blue oily monomer **4.6** was dissolved in diethyl ether in a microwave vial and the solvent was removed under vacuum, then the vial was left under vacuum overnight to give **4.6** (67.79 mg, 43.85 μmol). 4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (17.01 mg, 43.85 μmol), $\text{Pd}_2(\text{dba})_3$ (1.27 mg, 1.38 μmol), tri(*o*-tolyl)phosphine (1.70 mg, 5.88 μmol), and Aliquat 336 (1 drop) were added to the vessel before it was sealed and purged with argon. Previously degassed toluene (1 mL) and Na_2CO_3 (0.25 mL, 1.0 M) were added and the solution was degassed for a further 2 min. The vial was placed in a pre-heated oil-bath at 120 °C and left to stir for 48 h. The dark green/black solution was precipitated in methanol (200 mL) before filtered into a glass-fibre thimble and Soxhlet extracted using methanol (overnight), acetone (overnight), hexane (overnight), and chloroform (4 h). The hexane fraction was washed extensively with an aqueous solution of sodium diethyldithiocarbamate to remove residual palladium, then twice with water. The hexane was removed *in vacuo* and the polymer was dissolved in a minimum volume of chlorobenzene before being precipitated in methanol, filtered, and washed with further methanol to yield **pDTP-DPP-BT (4.8)** as a dark green/black powder (14 mg, 21%).

GPC (Chlorobenzene): $M_n = 4.3 \text{ kg/mol}$, $M_w = 7.1 \text{ kg/mol}$, $\bar{D} = 1.6$

NMR spectrum not obtained due to extremely poor resolution at concentrations available.

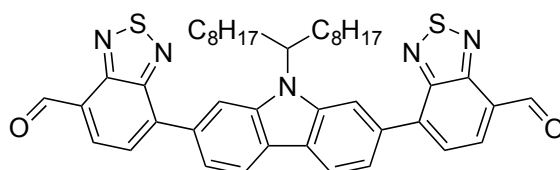
7.6 Chapter 5 experimental



Scheme 7.11 – Synthesis of carbazole-based NFAs

The synthesis follows a modified literature procedure for **FBR**.¹¹⁹

7,7'-(9-(Heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-4-carbaldehyde) (**5.1**)

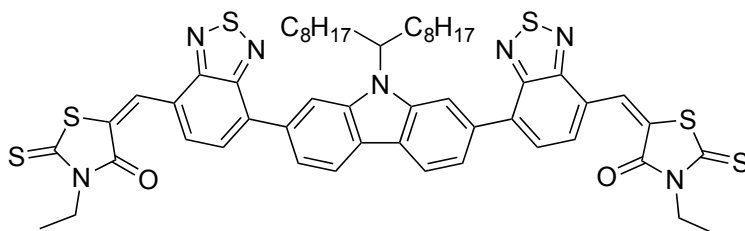


9-(9-Heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester (1.05 g, 1.60 mmol), 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde (980 mg, 4.03 mmol), Pd(OAc)₂ (14 mg, 0.06 mmol), SPhos (54 mg, 0.13 mmol), K₃PO₄ (1.3 g, 6.12 mmol), and Aliquat 336 (2 drops) were dissolved in previously degassed THF (20 mL) and degassed for a further 5 min. Previously degassed H₂O (3.4 mL, mmol) was added, and the solution was de-gassed for another 5 min before being heated at 80 °C overnight. The crude mixture was extracted with DCM (200 mL) and water (200 mL). The aqueous layer was extracted with further DCM (3 ×

75 mL) before the organics were combined, washed with brine, dried over MgSO_4 , filtered, and the solvent was removed under pressure. The crude reaction mixture was purified via column chromatography (DCM:Hex 1:1 + 2% EtOAc) to yield **5.1** as a bright orange solid (727 mg, 62%).

^1H NMR (400 MHz, CDCl_3) δ 10.83 (s, 2H), 8.50 (s, 1H), 8.38 – 8.30 (m, 2H), 8.36 (d, J = 7.3 Hz, 2H), 8.28 (s, 1H), 8.06 (d, J = 7.3 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 4.77 (m, 1H), 2.47 (m, 2H), 2.04 (m, 2H), 1.39 – 1.22 (m, 6H), 1.22 – 1.05 (m, 18H), 0.75 (t, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 189.15, 154.39, 154.05, 143.14, 141.46, 139.70, 134.49, 133.89, 132.89, 132.85, 127.34, 126.24, 124.52, 123.20, 121.21, 120.97, 120.62, 113.89, 111.08, 56.92, 34.06, 31.88, 29.54, 29.47, 29.33, 26.97, 22.70, 14.16. MALDI-TOF: Exact: 729.3 Found. 730.0.

(5E,5'E)-5,5'-(((9-(Heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methaneylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (5.2 – CBR)

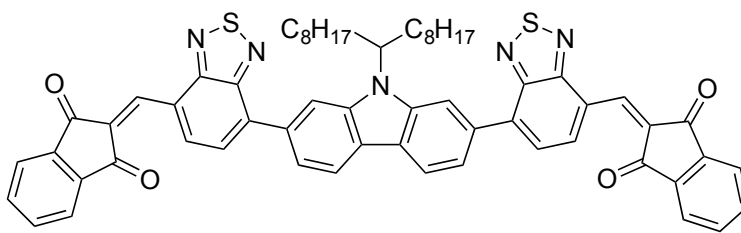


5.1 (105 mg, 0.143 mmol) and 3-ethyl-2-thioxothiazolidin-4-one (67 mg, 0.416 mmol) were dissolved in $t\text{BuOH}$ (50 mL) before piperidine (10 drops) was added and the reaction mixture was heated under reflux at 85 °C overnight (the reaction turned a dark red colour within 15 min at 85 °C). The reaction was cooled and the $t\text{BuOH}$ was removed under vacuum before the crude mixture was dissolved in a minimum of chlorobenzene and precipitated in stirring MeOH (150 mL), after which it was filtered using a fine sinter. The crude material was

precipitated twice more and then recrystallised from toluene/hexane, yielding **5.2** as a dark red solid (72 mg, 46%).

^1H NMR (400 MHz, CDCl_3) δ 8.59 (s, 2H), 8.44 (s, 1H), 8.30 (t, $J = 8.9$ Hz, 2H), 8.21 (s, 1H), 7.99 (d, $J = 7.5$ Hz, 2H), 7.85 (d, $J = 7.6$ Hz, 4H), 4.76 (m, 1H), 4.27 (q, $J = 7.1$ Hz, 4H), 2.46 (m, 2H), 2.03 (m, 2H), 1.35 (t, $J = 7.1$ Hz, 6H), 1.38 – 1.05 (m, 24H), 0.77 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 193.28, 167.65, 154.80, 153.82, 131.25, 128.04, 127.45, 125.67, 125.63, 40.10, 34.08, 31.90, 29.57, 29.49, 29.36, 27.00, 22.72, 14.18, 12.48.

2,2'-(((9-(Heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methaneylylidene))bis(1H-indene-1,3(2H)-dione) (5.3** – CBI)**

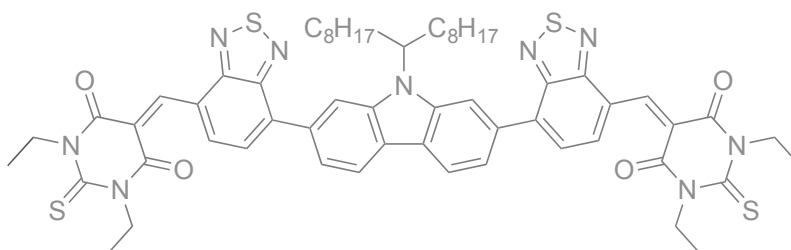


5.1 (92 mg, 0.126 mmol) and 1H-indene-1,3(2H)-dione (51 mg, 0.349 mmol) were dissolved in $^t\text{BuOH}$ (50 mL) before piperidine (15 drops) was added and the reaction mixture was heated under reflux at 85 °C overnight. The reaction was cooled and the $^t\text{BuOH}$ was removed under vacuum before the crude mixture was dissolved in a minimum volume of chlorobenzene and precipitated in stirring MeOH (150 mL), then filtered using a fine sinter. The crude material was purified via recrystallization from toluene/hexane followed by recycling GPC (chlorobenzene) and precipitation from a minimum volume of CB into stirring methanol to yield **5.3** as a dark red solid (63 mg, 51%).

^1H NMR (400 MHz, CDCl_3) δ 9.78 (d, $J = 7.7$ Hz, 2H), 9.06 (s, 2H), 8.49 (s, 1H), 8.32 (m, 3H), 8.11 (d, $J = 7.8$ Hz, 2H), 8.09 (m, 4H), 7.92 (dd, $J = 8.2, 1.3$ Hz, 2H), 7.87 (dd, $J = 5.6, 3.1$ Hz, 4H), 4.78 (m, 1H), 2.47 (m, 2H), 2.05 (m, 2H), 1.45 – 1.23 (m, 6H), 1.23 – 1.03 (m,

18H), 0.76 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.53, 135.46, 135.32, 130.47, 124.43, 123.51, 123.42, 33.97, 31.76, 29.44, 29.36, 29.21, 26.90, 22.58, 14.03.

5,5'-(((9-(Heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methaneylylidene))bis(1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione) (5.4)



5.1 (42 mg, 55.0 μmol) and 1,3-diethyl-2-thiobarbituric acid (33 mg, 164 μmol) were dissolved in $t\text{BuOH}$ (10 mL) before piperidine (5 drops) was added and the reaction mixture was heated under reflux at 85 $^{\circ}\text{C}$ overnight. Unlike **5.2** and **5.3**, the reaction turned brown instead of dark red, and after analysis of the crude mixture no product was detected by NMR.

Chapter 8

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8.1 References

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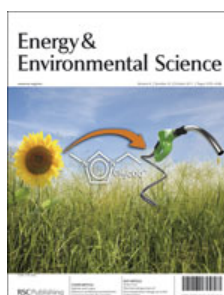


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