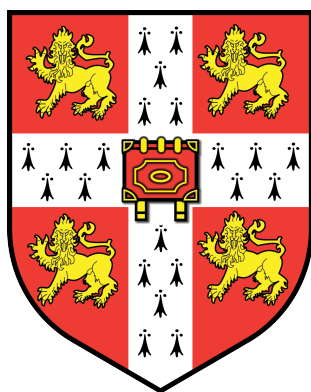


Effect of Moiety Choice on Structural and Electrical Properties in Organic Semiconductors



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St. Edmund's College

July 2019

This dissertation is submitted for the degree of Doctor of Philosophy

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text.

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Effect of Moiety Choice on Structural and Electrical Properties in Organic Semiconductors

John Joseph Moriarty

This dissertation details work conducted in the Optoelectronics Group at the University of Cambridge. It includes detailed characterisation of two groups of novel polymer semiconductors, one based on fluorinated variants of polyalkylthiophenes and the other on a series of copolymers based on a fused poly-dithieno-thiophene-benzene core. In both cases the goal is to employ highly fused moieties in order to promote a high degree of planarity within the conjugated backbone. Also discussed is the refinement of the zone casting technique in order to produce pristine films from these materials and a novel use of absorption spectroscopy data to produce estimates of polymer conjugation length.

Characterisation was conducted along the same lines for both material groups, beginning with measurements of field-effect charge carrier mobility in order to evaluate the materials' relative electrical performance, followed by a variety of characterisation techniques of their photophysical properties in order to understand the reasons for differences observed in the first set of measurements. This experimental work was supported by quantum chemical modelling.

Results suggest that, while backbone planarity is an important determinant of charge carrier mobility in polymer organic semiconductors, it can be a detriment if it causes the material's microstructure to change in such a way that hinders intermolecular charge transport: effectively sacrificing long-range charge carrier mobility for short-range charge carrier mobility. Suggestions for further development of the techniques used and for future work based on the results are included in the conclusion.

To my parents, the finest people I have had the privilege to know.

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I owe an enormous debt of gratitude to many people, without whom this thesis would not exist.

Firstly, I am incredibly grateful to my supervisor, Professor Henning Sirringhaus, for taking me on as a PhD student and for all his support and patience throughout my work.

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Chapter 1

Introduction

Organic semiconductors have been the subject of intense research over the past two decades, as the promise of low-cost, efficient devices drives work from both experimental and theoretical perspectives, often in conjunction with each other. As the understanding of charge transport in this large and diverse group of materials improves, new strategies to enhance performance are developed and tested, with the successful approaches informing further theoretical work.

In the 2000s, organic semiconductors reached a milestone: for the first time surpassing the mobility of amorphous silicon (a-Si), first in small molecular materials then in polymers^[1,2], demonstrating their potential as an alternative to their inorganic counterparts.

More recently, various organic semiconductors have begun to appear in a number of consumer products in more recent years, in particular as the active elements in organic light-emitting diode (OLED) displays^[3,4].

The history of organic semiconductors generally, as well as the theoretical basis describing charge transport in such materials is a rich topic and is covered in more detail in chapter 2, beginning with a brief history of polymers generally, then of conducting semiconductors before moving

on to the principles governing charge transport and how the understanding of them has developed over time.

In addition to the development of novel materials that are naturally predisposed to form highly ordered structures, thin film fabrication techniques have also been the subject of considerable research. While spin coating remains a ubiquitous technique, it offers little control over film formation rate. In chapter 3, the development of a zone casting procedure is discussed in detail which permitted the production of films in a much more controlled environment. Also detailed in this chapter are the various fabrication and characterisation techniques employed in this project.

A consistent theme in material optimisation in recent years has been an effort to reduce structural disorder, with particular reference to the conjugated backbone in polymeric materials. A large body of work exists demonstrating the superior charge transport properties of low-disorder materials, e.g. regioregular poly(3-hexylthiophene) (P3HT), poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) and indacene-dithiophene-co-benzothiadiazole (IDTBT), which all suggest a strong correlation between the degree of disorder in the polymer chains in a material and its charge carrier mobility. More specifically, each of these materials included a variety of features intended to force their conjugated backbones into a planar arrangement; that is, to reduce torsional backbone disorder.

The first objective of this project was to test the efficacy of a new approach to achieving similar results. The examples mentioned above exploited either side-chain arrangement or the inclusion of large, planar moieties to enforce backbone planarity. Instead, the approach described in chapter 4 involved substituting one of the hydrogen atoms attached to the thiophene rings in poly-3-alkylthiophene (P3AT) materials with a fluorine atom. It was anticipated that this would produce a hydrogen bond-like attraction between this substituted fluorine and the sulfur atom on the

adjacent thiophene ring. In addition to measuring charge carrier mobility by fabricating field-effect transistors with the materials, a variety of other methods were used to examine their physical and energetic structure including atomic force microscopy, linear absorption spectroscopy, Raman spectroscopy, photothermal deflection spectroscopy and x-ray diffraction. This broad spectrum of techniques provides a powerful set of tools to understand the charge transport dynamics of each material.

The second major strand of research conducted for this thesis involves another group of materials: a homopolymer and five alternating copolymers using its monomer as one of their copolymers. The homopolymer, poly-(dithienothiophenebenzene) (PDTTB), is a large fused moiety with similarities to indacene and fluorene. The chosen comonomers varied broadly in size and structure, from the relatively small and simple thiophene to the much larger diketopyrrolopyrrole-dithiophene (DPPDT), but all shared the planar character of the monomer. Characterisation of the PDTTB series employed similar methods to that of the fluorinated P3AT (F-P3AT) materials, with FET measurements of charge carrier mobility and a range of spectroscopic techniques providing structural information. The results of these experiments, and the implications for charge transport in these materials and organic semiconductors generally, are discussed in chapter 5.

Finally, concluding remarks and notes on possible future research can be found in chapter 6.

Chapter 2

Background and Theory

As a preliminary, we must first address the subject of semiconductors generally in addition to outlining the development of organic semiconductors, with specific reference to the contrast between these and conventional semiconductors. This chapter will then move on to discuss charge transport theory as it applies to organic semiconductors before moving on to consider how their physical structure affects the electronic properties of these materials and how spectroscopic techniques can provide insight into their electrical and physical properties.

2.1 Semiconductors

Existing between the high conductivity metals and the low conductivity insulators, semiconductors have been studied for over a century, but became the subject of intense research after the invention of the transistor in the 1940s and the onset of the Information Age as semiconductor fabrication expanded to become a global industry.

A key property of any semiconductor is its conductivity; its capacity to carry an electrical current. The units of conductivity are siemens per me-

tre (Sm^{-1}) and it is represented by the symbol σ or κ . The siemens is the inverse of the ohm, the unit of electrical resistance. Indeed, conductivity is occasionally expressed in $\Omega^{-1}\text{m}^{-1}$, the inverse units of electrical resistivity.

In a fairly general form, electrical conductivity can be expressed in terms of charge carrier concentration and mobility:

$$\sigma = en\mu \quad (2.1)$$

where e is the electronic charge, n is the charge carrier concentration and μ is the charge carrier mobility. It follows that in order to increase a material's conductivity, either more free charge carriers must be introduced into the material or the mobility of the existing charge carriers must be increased.

Charge carrier concentration can be increased via doping: introducing other materials into the semiconductor that either contribute extra electrons to the material, or capture electrons to form holes. In both cases, charge carrier concentration and conductivity increase.

However, each dopant atom introduced into the semiconductor lattice acts as a defect which can potentially scatter electrons, thereby reducing mobility. This is equally true for any impurities in the semiconductor remaining after the fabrication process: each impurity or dopant is a potential scattering centre for charge carriers and can also act as trap sites, reducing the concentration of free charge carriers in the material.

For example, crystalline silicon has an intrinsic conductivity on the order of 10^{-4} Sm^{-1} , which can be increased by multiple orders of magnitude via doping^[5]. This corresponds to charge carrier mobilities on the order of $1,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Amorphous silicon (a-Si), which is widely used in the fabrication of photovoltaic (PV) cells and thin film transistors (TFTs) has

a charge carrier mobility of approximately $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[6] and is frequently used as a benchmark for the performance of organic semiconductors.

2.2 Organic Semiconductors

Organic semiconductors have been the subject of an enormous amount of study due to their potential applications in a variety of fields. Of greatest relevance to this work is their use as the active layer in TFTs^[7–9], but other applications include photovoltaic cells^[10–12], light-emitting diodes^[13,14] and even spin valves^[15,16]. There are two factors commonly cited that make this class of materials well-suited to such applications: their processing requirements and the costs of their production.

While conventional semiconductors such as silicon or germanium are processed at temperatures in excess of 1,000 °C^[17], organic materials can be processed at room temperature with good solvents or, in the case of materials with particularly low solubility, a few hundred degrees centigrade. Processing at these lower temperatures not only reduces the energy requirements, but also permits the use of flexible substrates such as polyethylene, which enables the production of devices that would be difficult or impossible to realise using rigid substrates.

The capacity for solution processing in combination with the use of flexible substrates opens up the possibility of using large-area printing methods similar to the roll-to-roll gravure printing used in the newspaper industry as a method of producing electronic devices more quickly and more cheaply than currently possible using inorganic materials. Coupled with the reduced need for energy mentioned previously, this offers the prospect of much cheaper devices than inorganic materials would allow.

It bears mentioning that inorganic semiconductors have been used to produce a variety of electronic devices on flexible substrates^[18–20]. In many respects, this approaches the challenge of producing flexible electronics from a different direction than organic semiconductors. Charge carrier mobilities tend to be far higher than in organic semiconductors,

while fabrication on flexible substrates and resilience to mechanical stress pose far greater challenges^[21]. Thus, while device performance tends to be higher in inorganic materials, the ability to process organic semiconductors from solution allows them to circumvent the mechanical issues that inorganics encounter in the arena of flexible electronics.

The capability to produce wide-area, low-cost devices *via* printing from solution or various casting approaches has found particular use in organic light-emitting diodes (OLEDs), which unlike conventional LEDs can be used directly as the emissive elements in displays as they can be fabricated into individual pixels, are currently used in a variety of consumer electronics, such as televisions, laptop computers and mobile phones^[22].

However, the charge carrier mobilities measured to date in organic semiconductors are far lower than those of their more conventional inorganic counterparts. Even the highest mobilities measured to date are on the order of $1\text{-}10\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ^[6,23,24], two orders of magnitude lower than in polycrystalline silicon. However, as noted by Choi *et al.*, there are a variety of issues surrounding mobility extraction that can lead to the reporting of erroneously high mobility values^[25], so care must be taken when assessing reports of high mobility in novel materials. A significant milestone in organic semiconductor development occurred near the beginning of the millenium, when charge carrier mobility exceeded that of amorphous silicon (a-Si) for the first time^[26,27].

Another issue relevant to the practical applications of organic semiconductor devices is their environmental stability. Some are prone to oxidation in air^[28–30], which introduces extra trapping sites into the material, significantly degrading their overall performance and usable lifetime. A similar problem exists in a wider range of organic semiconductors due to the use of reactive cathode materials to aid charge injection^[31]. To address this, many such devices are fully encapsulated in order to avoid oxidation or other contamination, although some work has focussed specifically on

synthesising materials with greater ambient stability^[32–34]. One approach to achieving this is to synthesise materials with deeper HOMOs, which increases their oxidative stability^[35].

In summary, the differences between conventional, inorganic semiconductors and their organic counterparts dictate their potential applications. While conventional semiconductors excel in areas where high charge carrier mobility and fast operation are necessary, such as data processing, organic semiconductors with charge carrier mobilities on par with a-Si can find use where their lower production costs and solution processability permit the fabrication of large area devices on flexible substrates, a process that remains in its infancy for conventional semiconductors^[26,36,37].

Conjugated Polymers

In broad terms, organic semiconductors can be divided into two groups: small molecules and conjugated polymers. Small molecule organic semiconductors, such as the phthalocyanine complexes studied as early as the 1960s^[38,39] or the far more recent pentacene and its derivatives^[40–43], while exhibiting comparable or sometimes superior electrical performance to conjugated polymers, are beyond the scope of this thesis and will be discussed only as required for context.

Since their discovery in the first half of the 20th century, polymers have been the subject of extensive research. Taking their name from the Ancient Greek words *polus* (meaning “many”) and *meros* (“parts”) due to their structure comprised of a single repeating unit linked together many times over, polymers were first given their modern definition by Herman Staudinger in 1920 when he advanced the concept of macromolecules.^[44] This led to him being awarded the Nobel prize in Chemistry for “discoveries in the field of macromolecular chemistry” in 1953.

Until much more recently however, polymers were thought to exclusively be insulating molecules. The earliest references to conducting organic materials as more than a theoretical possibility appear in the literature in the 1960s, with reports of conductive polypyrroles by Bolto *et al.*^[45]. Reports of functional devices followed later, perhaps the earliest example being a threshold switch using melanin as the semiconducting material in 1974^[46]. The first organic FET employed polythiophene as the semiconducting material and was produced in 1987 by Koezuka *et al.*^[47]. Also of note is the work of Shirakawa *et al.* on the conductive properties of polyacetylene^[48]. This work earned Shirakawa, alongside Heeger and MacDiarmid, the Nobel Prize in Chemistry in 2000 for “the discovery and development of conductive polymers”.

As the name implies, conjugated polymers are a class of materials which share the distinguishing feature of a conjugated backbone: a chain of carbon atoms linked together by alternating single and double bonds, the simplest example being polyacetylene*, shown in Fig. 2.1. Their semiconducting properties arise from this molecular structure.

Within the backbones there are two types of covalent bond: σ -bonds and π -bonds. The σ -bonds are the stronger of the two, and arise from direct overlap between the electronic orbitals of two atoms. In the case of

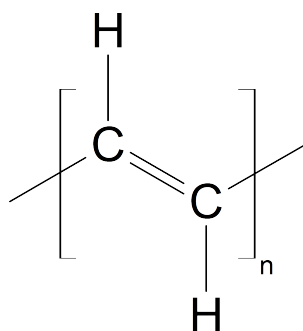


Figure 2.1: Structure of polyacetylene.

*IUPAC name polyethyne

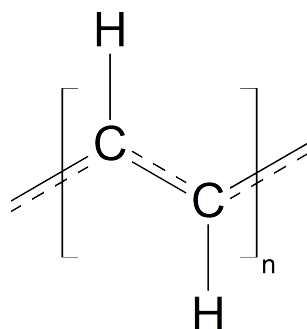


Figure 2.2: Structure of polyacetylene with dotted “half-bonds” to illustrate the delocalised electron cloud.

polyacetylene, three out of four of each carbon atom’s valence electrons exist in such bonds; one with the associated hydrogen atom and two with the neighbouring carbon atoms. In terms of electronic orbitals, these states are hybrids of the $2s$ and $2p$ orbitals (specifically, the $2p_x$ and $2p_y$ orbitals) known as sp^2 orbitals. In order to minimise the free energy in the system, these bonds arrange themselves as far apart as possible i.e. in the plane of the p_x/p_y orbitals at 120° to each other^[49].

The remaining electron (the second in the double bond) exists in a π -bond, which is formed by the overlap of the $2p_z$ orbitals of each carbon atom, which exist out-of-plane with the other hybrid orbitals, again, to minimise the system’s free energy. Due to the lower binding energy of π -bonds, the electrons in these states are less strongly localised and can travel along the conjugated backbone^[50].

Conceptually, it can be tempting, even useful, to think of the conjugated backbone as a series of “three-half” bonds as illustrated in Fig. 2.2, despite the fact that this does not reflect physical reality. If this were a truly accurate model, each carbon atom in the backbone would be equidistant from both its neighbours, which would produce a metallic band character without the bandgap characteristic of semiconducting materials, including organic semiconductors.

This incongruity was resolved by Peierls,^[51] who determined that a polyacetylene chain with perfectly evenly distributed carbon atoms is inherently unstable.

To elaborate, Peierls considered the effects of displacing every n th carbon atom in the polyacetylene chain on the energetic landscape. Rather than the smooth energetic landscape corresponding to metallic characteristics of the undistorted chain, a periodic distortion introduces $n - 1$ gaps into the energy band, evenly distributed in k -space at intervals of π/na , with the states on either side of the gaps shifted equally up or down in energy.

If the energy bands are entirely filled, there is no difference in total energy between the distorted and undistorted chains. However, since the electronic energy bands in conjugated polymers are only partially filled, there is always a value of n such that the states shifted upwards in energy are empty while the states shifted downwards are filled, leading to an overall reduction in energy.

The size of the gap in the energetic band is inversely related to the value of n , meaning that the reduction in total energy produced by periodic distortion is maximised when $n = 2$. As a result, perfectly uniform polyacetylene chains are inherently unstable due to the partially filled electron band, leading to the distortion of the chain into a series of pairs of atomic sites as the equilibrium state.

The effects of this distortion on the energetic landscape are illustrated in Fig. 2.3. In the hypothetical case of a pristine, evenly distributed chain, the energy is described by the dotted line. Without any distortion in the conjugated chain, there is no gap in the energetic band, implying that charge transport occurs as in a metal. As the atoms move away from their equilibrium positions into pairs, the energy landscape shifts towards the solid line, a bandgap appears and charge transport takes on the characteristics of a semiconductor.

By contrast, more modern conceptualisations of organic semiconductors have moved from the band model of organic semiconductors as bulk materials towards treating each molecule (or in the case of conjugated polymers, each conjugated segment within a polymer chain) individually, before considering the effects of electron-electron interactions afterwards. Due to the much lower dielectric constants in organic semiconductors, these interactions are much more significant than in their inorganic counterparts due to the reduction in dielectric screening effects^[49].

While the structure of other conjugated polymers is more complex than polyacetylene, the feature common to all of them is the conjugated backbone containing delocalised π -electrons that facilitate charge transport. Various structures in addition to a chain of alternating single and double carbon-carbon bonds can compose the conjugated backbone, with benzene or thiophene rings being commonly used moieties^[52–56].

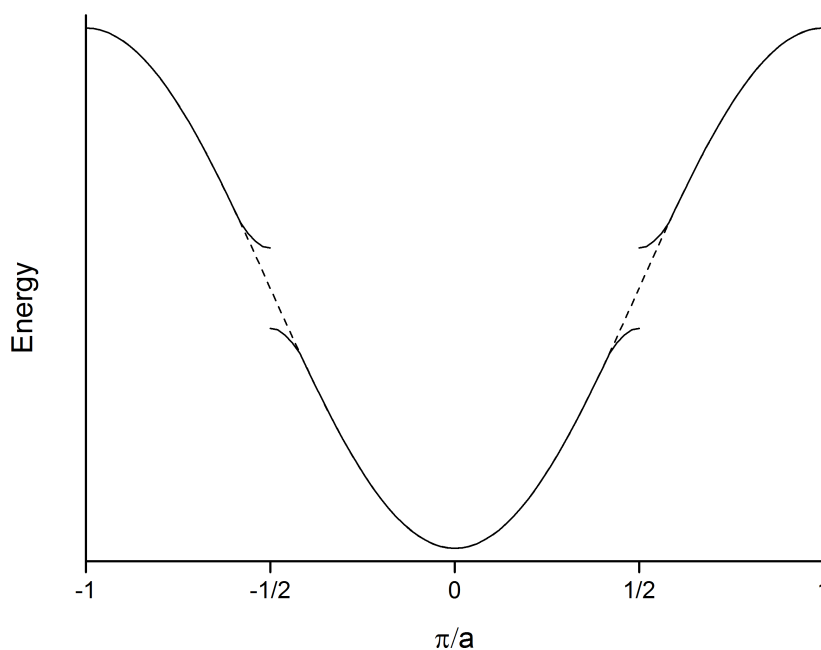


Figure 2.3: Energy curves illustrating the effect of the Peierls distortion.

2.3 Charge Transport

Having explored the basics of electronic structure, we will now examine the theoretical understanding of charge transport and how it has evolved over time as advances in available materials have necessitated revisions to the dominant theories.

For the purposes of describing charge transport, materials can be split into three categories: conductors, insulators or semiconductors. Prior to demonstrations of electrical conductivity in the 1960s,^[38,45] it was assumed that polymers were electrical insulators.

As explained in the previous section, what distinguishes conjugated polymers from the more widely known insulating polymers are the delocalised electronic orbitals running along their backbones which permit charge transport. Theoretical models of charge transport in these materials have evolved considerably over time: at first taking their lead from existing models of inorganic systems, before adapting over time as continued experimentation revealed deficiencies in earlier approaches.

We will briefly discuss the older theoretical models in order to contextualise their successors before moving on to a more comprehensive discussion of contemporary theory.

Su-Schrieffer-Heeger Model

Initially, theories of charge transport in organic semiconductors took their lead from the dominant theories used to deal with their inorganic counterparts. Developed in 1979, the Su-Schrieffer-Heeger (SSH) model was reasonably successful at describing the behaviour of charge carriers in early organic semiconductors.^[57]

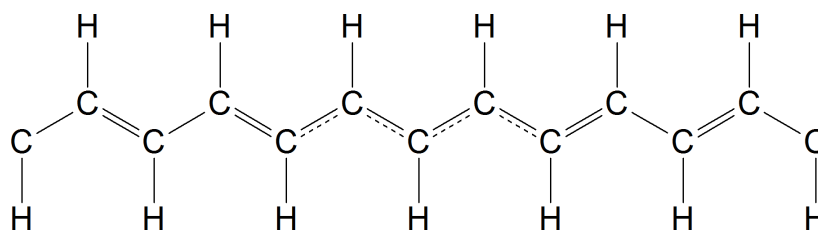


Figure 2.4: Transition between two regions in polyacetylene with dotted bonds representing the soliton.

The model was developed considering solitons in polyacetylene. The solitons in this context are travelling electron wave-packets which in physical terms are regions in the polyacetylene chain where the pattern of alternating double and single bonds inverts, as illustrated in Fig. 2.4. Rather than a sharp transition where a single or double bond is immediately followed by another like it, the π -electrons within the boundary region are delocalised across it.

However, some of the central assumptions of the SSH model do not hold in organic semiconductors. Specifically, when electrons are excited into the conduction band to form excitons, the SSH model assumes that the exciton quickly separates, leaving the electron and hole independent. In energetic terms, the exciton binding energy is assumed to be relatively weak, while electron-phonon coupling (which separates the exciton) is assumed to be relatively strong^[58].

However, a number of different measurements and theoretical analyses have produced values for the exciton binding energy of approximately 0.5 eV^[59–62] at room temperature. Given that electron-phonon coupling is expected to overcome this under the SSH model, and that the associated phonon energies would be comparable to $k_B T$, these values are almost 20 times larger than the SSH model would assume.

Likewise, the same assumption would suggest rapid conversion between singlet and triplet states in organic semiconductors since thermal fluc-

tuations would be similar to the exchange energy due to weak electron interactions. This would imply that phosphorescence should not occur at room temperature, since triplet states would convert back to singlets before being able to decay *via* phosphorescence^[58]. However, a variety of studies have observed phosphorescence in organic semiconductors^[63,64] and the exchange energy between singlet and triplet states has been established to be approximately 0.7 eV, again far greater than $k_B T$ ^[65,66].

In addition to these issues, the SSH model does not account for disorder which, as will be discussed below, is critically important in modern charge transport models. Despite being the subject of considerable debate in the past, modern consensus has abandoned the SSH model and favours theories describing charge transport as a series of interactions between much smaller chromophores, whether individual monomer units within the polymer or larger conjugated segments of them, and accounting for the effects of disorder.

Due to the strength of the electron-phonon interactions resulting from the relatively low dielectric constants in organic semiconductors, charge carriers exist as polarons; quasiparticles consisting of electrons and their associated distortions in the molecular lattice resulting from Coulombic interactions with the surrounding material and coupling to the local phonons. This reflects the notion of a travelling soliton in the SSH model, but polarons are often far more delocalised than solitons were once thought to be.

Thus, the vast majority of theoretical models used to describe charge transport in organic semiconductors are polaronic in nature and are the subject of the next section.

Polaronic Models

In describing charge carrier behaviour in organic semiconductors, we begin with the Hamiltonian of the electrons themselves:

$$\hat{\mathbf{H}}_e = \sum_j \epsilon |j\rangle \langle j| + \tau |j\rangle \langle j+1| \quad (2.2)$$

where ϵ is the state energy, τ is the electron transfer integral and j is the site index. The electrons have an effective mass which is inversely related to mobility and given by the expression $m^* = \hbar^2 / (2|\tau|a^2)$, where a is the distance between neighbouring sites.

In order to refine the model, the nuclear vibrations are then considered. For simplicity, these are treated as a single vibrational mode associated with each molecule with a frequency ω , leading to the nuclear Hamiltonian:

$$\hat{\mathbf{H}}_n = \sum_j \frac{\hbar\omega}{2} (q_j^2 + p_j^2) \quad (2.3)$$

where q_j and p_j are the displacement and momentum of the oscillator at site j multiplied by $\sqrt{m\omega/\hbar}$ and $1/\sqrt{m\omega\hbar}$ respectively to render them dimensionless. When this nuclear Hamiltonian is combined with the electronic Hamiltonian, the two terms are independent but since the equilibrium state changes when electrons are added or removed, a third term describing the local electron-phonon coupling must be included.

$$\hat{\mathbf{H}}_{e-ph} = g\hbar\omega \sum_j q_j |j\rangle \langle j| \quad (2.4)$$

where g is the electron-phonon coupling constant, which reflects the change in equilibrium position of the nuclear oscillator on site j when

an electron is present: shifting from 0 to $-g$. This in turn reduces the potential energy associated with the equilibrium state by $g^2\hbar\omega/2$.

This interaction between electrons and phonons is treated as a single quasiparticle: the previously mentioned polaron. Since it is expected that the lattice distortion resulting from the electron motion will be roughly evenly distributed throughout the lattice, such polaronic wavefunctions are generally assumed to be band-like and form the basis of so-called polaron band theories.

For a system in which the charge carriers have a polaronic character, the total Hamiltonian is simply the sum of the electronic, nuclear vibrational and two electron-phonon coupling terms. In such cases it is possible to replace the electronic Hamiltonian with a polaronic quasiparticle Hamiltonian via a basis set transformation^[67]:

$$\hat{\mathbf{H}}_{po} = \sum_j \epsilon' |j\rangle \langle j| + \tau' |j\rangle \langle j+1| \quad (2.5)$$

where the j states in the equation now represent polarons and therefore include a portion of H_n . Likewise, ϵ' and τ' are different from their counterparts in H_e , with τ' in particular being inversely related to temperature and m^* , leading to reduced charge carrier mobility at higher temperatures, similar to the temperature dependence of mobility in conventional semiconductors.

In the high-temperature limit, as τ' tends towards 0 and m^* towards infinity, there is no interaction between adjacent sites, meaning the polaronic wavefunction is effectively localised to a single atomic site and can be described using only that site and its nearest neighbour:

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_n + g\hbar\omega q_1 |1\rangle \langle 1| + g\hbar\omega q_2 |2\rangle \langle 2| + \tau'(|1\rangle \langle 2| + |2\rangle \langle 1|) \quad (2.6)$$

where the final term represents the polaron hopping between the two sites. In this limit transport is no longer band-like and the process can be described by Marcus theory like a conventional chemical reaction, including the associated reaction rate constant, k , which in the high-temperature, diabatic limit can be approximated to:

$$k_d = \frac{\tau^2}{\hbar} \left(\frac{\pi}{k_B T \Lambda} \right)^{1/2} e^{\frac{-\Lambda}{4k_B T}} \quad (2.7)$$

where, τ is the electronic transfer integral between localised molecular orbitals, $\Lambda = 2g^2\hbar\omega$ is the reorganisation energy, k_B is the Boltzmann constant and T is temperature.

The potential energy curves for this process for three different ratios between the transfer integral and reorganisation energy are shown in Fig. 2.5. For adiabatic systems, polaron hopping can occur when thermal energy exceeds the reorganisation energy. As τ approaches $\Lambda/2$ however, the two potential minima merge in adiabatic systems, rendering the idea of a localised polaron invalid. Also, it bears mentioning that Marcus theory, while providing reasonable qualitative predictions regarding the differences in charge carrier transport between different materials, fails to produce accurate quantitative predictions, limiting its usefulness as a theoretical framework.^[68]

A key difference between this hopping model and the previously discussed polaron band model is the change in temperature dependence between the two. While the band-like model predicts an inverse relationship between temperature and charge carrier mobility resulting from increasing localisation of the polaron, the hopping model predicts that mobility and temperature are directly correlated due to the relationship between temperature and the polaron's effective mass.

The experimental evidence for many years favoured the hopping model, with the vast majority of materials investigated prior to the early 2000s

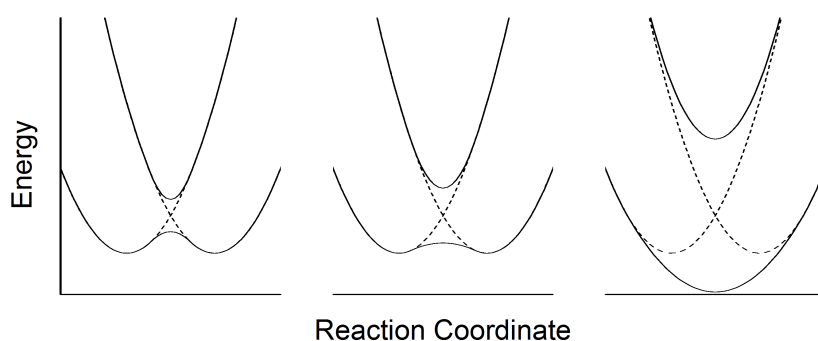


Figure 2.5: Effect of increasing transfer integral, τ , on the potential energy landscape between adjacent atomic sites. Solid and dotted lines represent adiabatic and diabatic electrons respectively.

displaying thermally activated charge transport^[8,68], leading to the fairly reasonable assumption that polaronic hopping was a generally valid model to describe charge carrier behaviour.

However, more recent work using small molecule semiconductors such as pentacene or rubrene has observed band-like transport^[69–71] in ultrapure samples of these materials in contrast to the hopping transport observed in unpurified samples. From this it was deduced that hopping transport in these materials arises from the presence of defects rather than from their intrinsic properties.

Unfortunately, concluding that charge transport is generally band-like, with the polaronic charge carrier becoming localised and reverting to hopping transport in materials with a high degree of disorder, introduces other problems. Specifically, detailed theoretical studies of small molecule semiconductors have shown that, while charge carriers in these systems may be localised, this arises as a result of disorder rather than the carrier's intrinsic nature^[68,72].

Also, given the mobilities observed in small molecule organic semiconductors ($\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), the mean free path of the delocalised polaron

would be comparable to the intermolecular spacing, which is at odds with the notion of a delocalised charge carrier undergoing only occasional scattering as it encounters defects^[68].

The tension between these two contrasting models was finally resolved via a model that accounts for the effects of thermal disorder on localised polaronic charge carriers.

Dynamic Disorder

Initially, it was thought that the $\hat{H}_e$, $\hat{H}_n$ and $\hat{H}_{e-ph}$ provided a complete description of polaronic transport, but more recent work by Hannewald *et al.* revealed that in order to account for the variation in coupling between the sites j and $j + 1$ as q_j and q_{j+1} change, a fourth term representing this non-local electron-phonon coupling was required.^[73]

$$\hat{H}_{e-ph/NL} = G\hbar\omega \sum_j (q_j - q_{j+1})(|j\rangle \langle j+1| + |j+1\rangle \langle j|) \quad (2.8)$$

where G is the electron-phonon coupling constant for interactions between neighbouring sites.

From this starting point, in an attempt to resolve the inconsistent observations of both band-like and localised polaronic transport in a variety of organic semiconductors, a new model has been developed which describes charge transport using polaronic wavefunctions which while intrinsically delocalised over multiple sites, can be temporarily localised via transient phonon interactions^[74–77].

In these models, mobility can be expressed in terms of the transient localisation length, L_c , which describes the degree to which the polaronic

wavefunction is localised by electron-phonon interactions, the characteristic duration of the localisation, t_c (meaning that t_c^{-1} is the frequency of the vibration), and the temperature T :

$$\mu = \frac{eL_c^2}{2k_B T t} \quad (2.9)$$

While the transient localisation in this model behaves in a superficially similar way to earlier hopping models, it avoids the pitfalls of those models in high-mobility materials, which would necessitate unphysically high hopping rates.

Recent work by Fratini *et al.* has revealed a strong correlation between L_c and the distribution of the transfer integrals along different lattice dimensions^[77]. Specifically, they found that isotropic systems where the transfer integrals in each direction are equal, have considerably higher predicted values for L_c and that such systems are more resilient to the effects of dynamic disorder.

It remains an open question to what extent such models apply to polymer semiconductors, as charge transport in such materials is still largely considered to be a process governed by hopping transport at various length scales^[24]. However, recent observations of band-like transport in cyclopentadithiophene–benzothiadiazole (CDT-BTZ) suggest that it is, in principle at least, possible to access this regime in polymers as well as small molecules^[78,79].

2.4 Optoelectronic Processes

Considerable information about the physical and electronic properties of a material can be probed via various spectroscopic techniques. Such investigation is not limited to potential photovoltaics and light-emitting diodes, where the interaction of light with the material's electronic structure is central to their figures of merit, but can be extended to any material.

Linear Absorption Spectroscopy

A relatively straightforward method to probe a material's energetic landscape, linear absorption spectroscopy measures the transmission of light across a range of frequencies through a sample in order to determine which of those wavelengths are most strongly absorbed. On initial analysis, these spectra can provide indications of structural order based on the energy of the spectral features, with higher energy absorption bands corresponding to more localised excited states, as well as their bandwidth, which correlates with the degree of uniformity in the sample.

In combination with an understanding of the relevant selection rules, absorption spectroscopy can also be used to produce useful estimates of exciton bandwidth and conjugation length as demonstrated by Clark *et al.*^[80].

Raman Spectroscopy

In addition to the basic energetic structure probed via linear absorption spectroscopy, the vibronic structure of a material can be investigated using Raman spectroscopy. Rather than measuring the transmitted spectra,

Raman measures the frequency shift between the incident laser and the light emitted during relaxation from excited vibronic states to the ground state. By doing so, it is possible to build up a spectrum illustrating the most dominant vibronic modes.

For structures for which an extensive quantity of prior research exists, aspects of Raman spectra can be used to infer information about the material's other properties. For example, the Raman spectrum of polythiophenes tends to be dominated by a pair of very intense peaks that correspond to the stretching mode of the carbon-carbon bonds^[81]. Tsoi *et al.* have suggested that the ratio between the two is correlated with conjugation length and backbone torsion^[82], providing a useful - albeit indirect - measurement of intramolecular order.

Aside from the information the Raman spectrum provides by itself, it can also be used to gauge the validity of a structure predicted using quantum chemical simulation: if the simulated spectrum is similar to the measured spectrum that indicates that the simulated structure is reasonably accurate.

Photothermal Deflection Spectroscopy

Emerging more recently as a highly sensitive method to examine absorption coefficients in materials that are near transparent, making more straightforward transmissive measurements difficult, photothermal deflection spectroscopy (PDS) measures the deflection of a probe laser beam as a result of heating of the liquid medium above a sample via convection^[83]. It can also be used to probe energetic disorder by investigating the so-called Urbach tails in the sub-bandgap region of a material^[84,85].

In the sub-bandgap region of an absorption spectrum, the relationship between the absorption coefficient, α , frequency, and the Urbach energy, E_U , is described by the expression:

$$\alpha(h\nu, T) = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_U(T)}\right) \quad (2.10)$$

where α_0 and E_0 are constants specific to a given system that are the values of α and E where curves plotting them at different temperatures converge (the so-called Urbach bundle's convergence point)^[84-87], h is Planck's constant, ν is the frequency of the incident photons and E_U is the system's Urbach energy.

By measuring the absorption coefficient across the bandgap region it is possible to find the system's Urbach energy, which is affected by thermal, structural and compositional disorder^[85,88]. Where sufficiently pure samples are available the Urbach energy provides a useful proxy to compare the relative energetic disorder between different organic semiconductors. This is due to its derivation from the inverse of the sub-bandgap gradient of the density of states. In a hypothetical perfectly ordered sample, no states would extend into the bandgap and the Urbach energy would be 0. As disorder increases, the distribution of band-edge states will extend further and further into the bandgap, producing the so-called 'Urbach tail' from which the gradient is taken and the Urbach energy derived.

2.5 Structure-Property Relationships

Crucial to each of the properties discussed in the preceding sections is the physical structure of a material, both at the molecular and the microscopic scale. These structure-property relationships are the focus of continuing research, as the ability to purposefully design polymers with specific properties would be of considerable utility both in terms of potential applications and further research.

One of the most important properties of any such polymer is its conjugation length; the average length of a chain segment with a single delocalised π -electron cloud within a polymer chain. Charge transport within such a segment is relatively fast due to the delocalised nature of these states, so increasing the conjugation length of a polymer is an obvious approach to enhancing charge carrier mobility. Conjugation can be interrupted by both flexion and torsion of the backbone^[89–93], and a considerable amount of research has been conducted to study how they can be minimised.

One widely used approach involves the inclusion of fused aromatic segments alongside single covalent bonds in the conjugated backbone^[30,32,94–96]. The presence of these larger fused moieties effectively guarantees a planar or near-planar structure within the fused segments themselves, in addition to limiting flexion and torsion in neighbouring regions of the backbone.

Heeney *et al.* were one of the earliest groups to employ this approach in the synthesis of PBTTT^[30,97]. Rather than the thiophene monomer unit used in polythiophenes, the monomer unit in PBTTT consists of a pair of fused thiophene rings connected to a pair of unfused rings as illustrated in Fig. 2.6. The fused segment enforces planarity within the conjugated backbone, leading to a higher conjugation length than that

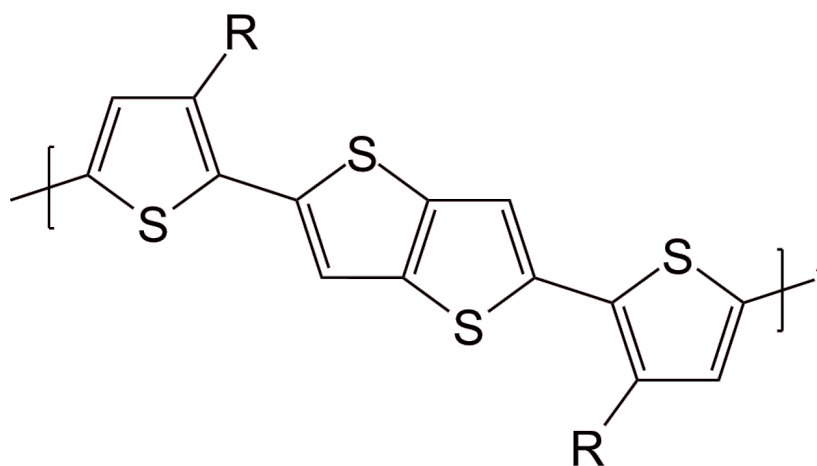


Figure 2.6: Chemical structure of PBTTT. The thienothiophene moiety enforces planarity on the conjugated backbone, while the alkyl chains improve intermolecular order.

observed in polythiophenes. In terms of charge transport, this manifests in a significant increase in charge carrier mobilities: at time of publishing a variety of unfused thiophene polymers were being experimented with and exhibiting charge carrier mobilities of $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[30,98], while the high-performing variants of PBTTT exhibited mobilities in excess of $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[30,99].

A more recent example can be seen in the use of diketopyrrolopyrrole (DPP) moieties by groups such as Kanimozhi *et al.*^[100]. Like the fused thienothiophene unit in PBTTT, the fused DPP core (see Fig. 2.7) enforces a degree of planarity on a particular section of the conjugated backbone, limiting the possible avenues for structural disorder. A secondary benefit provided by this moiety is a significant reduction in the bandgap energy of the host polymer by virtue of the electron-withdrawing nature of the DPP group, thereby combining a low-torsion backbone with the potential for a donor-acceptor structure if combined with an appropriate comonomer^[101,102].

Aside from alterations made to the conjugated backbone, modification

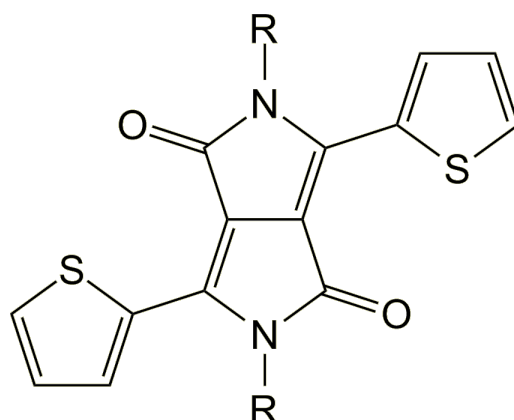


Figure 2.7: Chemical structure of DPP, another planar moiety that is also a strong electron acceptor, enabling the synthesis of donor-acceptor copolymers.

of any side chains attached to it can also have profound effects on the molecular structure^[103]. These modifications can alter the length of the side chains^[2,12,104–106], their spacing along the backbone^[2,107], introduce branches into them^[12,108] or change the branching point's proximity to the backbone^[105,109]. In addition to altering the preferred packing structure of the material, side chains also impact its solubility, which can render solution processing techniques difficult or impossible if it is too low.

The intermolecular structure of a particular polymer is similarly important in determining the material's properties, although recent studies of amorphous conjugated polymers have demonstrated that highly crystalline structures are not an absolute necessity to achieve high charge carrier mobilities^[110].

Nevertheless, intermolecular structure below the microstructural scale can heavily impact charge transport, as these structures strongly influence the transfer integrals that govern hopping transport between adjacent chains^[93,111]. Various approaches to maximising these transfer integrals have been explored, including increasing regioregularity^[112,113],

adjusting the lateral offset between neighbouring chains^[114,115] and reducing π - π stacking distance^[114]

In the broadest terms, there are two types of microstructure observed in conjugated polymers: amorphous materials without any long-range structural order and semicrystalline materials exhibiting structural order over intermolecular distances. The precise degree to which crystalline structures extend varies between materials, and even between phases of the same material, which has provided opportunities to examine the extent to which a material's microstructure influences its properties without altering its chemical composition^[99].

An excellent example of this behaviour can be found in the liquid crystalline polymer PBTTT, which exhibits three distinct mesophases depending on its processing conditions. A straightforward approach using spin coating produces an amorphous, disordered film similar to many other conjugated polymers, but thermal annealing after film formation can induce the formation of two additional phases, depending on the temperature used^[30,116].

Lower temperature annealing produces a semicrystalline microstructure of well-defined monomolecular terraces at the film's surface, with the conjugated backbones and the π - π stacking axis both parallel to the substrate, albeit with a slight tilt so the backbones are not quite edge-on^[30,117]. Higher temperature annealing causes the formation of nanoscale ribbons consisting of fully extended polymer chains stacking together along the π - π stacking axis with a few molecules branching between ribbons^[99,116].

These different microstructures in turn give rise to different electrical properties in the three mesophases. Charge carrier mobility is highest in the terraced phase, with values of $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported in the early literature^[30], followed by the ribbon phase which, once optimised, produced

values around $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[99], while the amorphous nodular phase exhibits a mobility approximately two orders of magnitude lower^[118].

The mobility values for the terraced and ribbon phases were an order of magnitude higher than most of those achieved in P3HT and similar polythiophene polymers at the time,^[30,99,119] which exhibit amorphous nodular structures similar to those observed in PBTTT prior to annealing. Even when compared to highly optimised P3HT devices, mobility values in the semicrystalline phases of PBTTT were still significantly higher^[30,120].

Both the differences in mobility between the amorphous phase and the two annealed phases and the gulf in mobility between crystalline PBTTT and previously studied materials emphasise the impact of microstructure on charge transport, and specifically the role of crystal grain boundaries, and indeed structural defects generally, as impediments to charge transport. In the terraced phase, grain boundaries are relatively infrequent, resulting in higher mobility when measured at the macroscopic scale due to the higher proportion of charge transport occurring within a single crystalline grain, while the increasingly smaller grain size in the ribbon and amorphous phases results in progressively lower mobilities^[30,99]. The same relationship between grain size and charge carrier mobility is common to inorganic semiconductors^[121].

Furthermore, work studying mobility in ribbon phase PBTTT in which zone casting was used to align the ribbons along a single axis demonstrated that mobility parallel to the ribbons' axis was significantly lower (in some cases as much as 10 times lower) than that perpendicular to their axis i.e. parallel to the extended conjugated backbones^[99]. This illustrates the relative speeds of intramolecular transport along conjugated backbones perpendicular to the ribbon and intermolecular transport via hopping along the ribbon via hopping transport in the π - π stacking direction.

The efficacy of charge transport within a single molecule and with its nearest neighbours is determined largely by the degree of order in any particular chain segment: highly ordered segments with little torsion permit both rapid charge transport along the conjugated backbone and tighter packing of adjacent chains, facilitating both intra- and intermolecular charge transport^[93].

Previous work has shown that defects within such structures act as charge traps, significantly degrading charge carrier mobilities in affected materials^[49]. Again, the precise nature of these defects varies between different materials: breaks in backbone conjugation via flexion or torsion are one possibility, but inclusion of chemical defects from exposure to air or water, or produced during synthesis, can also contribute to the number of trap states present in a particular material^[119,122–126].

Numerous reports have also shown a direct correlation between molecular weight and charge carrier mobility in conjugated polymers^[91,112,125,127,128]. The favoured explanation being that as hopping transport between adjacent chains is expected to be the bottleneck in many systems, longer polymer chains will reduce the frequency of hopping transport, making the faster intramolecular transport the more dominant mechanism^[127].

An analogous effect can be observed in crystalline or semicrystalline materials at larger length scales: as grain size increases, trap sites at grain boundaries are encountered less frequently, and overall mobility increases^[129,130]. In regioregular P3HT, increased molecular weights lead to grain boundaries becoming less of an impediment to charge transport due to some molecules acting as conjugated 'bridges' between neighbouring domains^[127]. The recent work of Gu *et al.* has made this relationship more explicit, directly relating charge carrier mobility to the fraction of polymer molecules within a population long enough to act as high mobility bridges through otherwise disordered regions of material^[131].

An alternative approach to optimising charge transport properties is to accelerate the hopping element of charge transport, generally by maximising the transfer integrals between neighbouring chains^[112,132]. The resulting higher hopping rate reduces the impact of the hopping bottleneck, again leading to higher macroscopic mobility.

While there are other approaches to enhancing a material's electrical and physical properties, doping being a widely studied example, the methods detailed above are those explored in later chapters in this work, with other possibilities left aside apart from this brief mention.

2.6 State of the Art

Over the last four decades, organic semiconductor performance has improved dramatically, from the early experiments with polyacetylene and its derivatives^[133] to modern materials close to achieving disorder-free charge transport and exhibiting mobilities on the order of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These include polymers such as IDTBT^[110], CDT-BTZ^[134] or various DPP- and poly(naphthalene diimide) (PNDI)-based materials^[101,135–137] in addition to small molecule materials such as pentacene^[138], rubrene^[70,71,139] or various benzothienobenzothiophene (BTBT) materials^[140–142].

The strategies employed to facilitate charge transport differ between systems: designing a small molecule poses different challenges than designing a polymer. Nevertheless, the goals remain the same: the production of materials with high charge carrier mobility and straightforward processing requirements.

One highly successful strategy that has been extensively employed to improve charge transport in polymeric materials is to optimise materials and fabrication techniques to produce highly ordered crystalline or semicrystalline microstructures. This approach has enhanced the charge carrier mobility in P3HT by several orders of magnitude^[91,143], and more recently prompted the development of PBTTT: a material distinguished by its highly ordered semicrystalline microstructure^[2,30,144,145]. In combination with efforts to synthesise and process higher molecular weight materials^[91,128], these efforts have yielded major progress in the development of new, high-performance polymer semiconductors.

However, some of the highest mobilities observed in recent years have been extracted from materials that either partially or entirely lack the long-range semi-crystalline microstructure observed to be so beneficial in materials such as P3HT and PBTTT^[111,134,136]. In addition, in contrast to

earlier high performance materials in which conjugated backbones assembled edge-on to the substrate, some recent D-A materials instead preferentially orient face-on^[6,146].

In particular, recent work on donor-acceptor (DA) copolymers, which incorporate alternating electron-rich and electron-deficient moieties in their conjugated backbone, have demonstrated that such microstructures are by no means a necessary condition for high mobility^[110,111,134,136]. Rather, the developing understanding of these materials has revealed that it is in fact features that are often found in highly ordered microstructures that are important to increasing mobility as opposed to the ordered microstructure itself.

For example, the presence of highly planarised conjugated backbones assists both intra- and intermolecular charge transport: the former because the removal of torsional defects from the backbone allows for more delocalised charge transport states and the latter because fully planar, particularly co-planar, backbones facilitate close intermolecular packing, minimising the π - π stacking distance and keeping transfer integrals between sites on neighbouring chains high^[6,24].

To illustrate the importance of this we can compare the charge carrier mobilities extracted from poly(9,9-dioctylfluorene-alt-benzothiadiazole) F8BT, CDT-BTZ and IDTBT: all copolymer materials with a D-A structure incorporating benzothiadiazole as the acceptor unit. In F8BT, the torsion between donor and acceptor moieties is considerably higher than that observed in the other two materials^[90,110,134]. Consequentially, while charge carrier mobilities extracted from F8BT are on the order of 10^{-3} - 10^{-2} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, values from the other materials are orders of magnitude higher, around 1-10 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.

This marked difference in charge carrier mobility between otherwise quite similar materials indicates two principal requirements to attain such performance. Firstly, the inclusion of extended planar moieties appears to

be instrumental in producing highly coplanar microstructures: laying the foundations by enforcing planarity within each moiety. Then, in order for that planarity to extend along the chain, torsion between moieties must be minimised. One approach to achieving this is to simply use smaller moieties: as Nielsen *et al.* observed, replacing phenyl groups with thienyl groups in a variety of DPP-based copolymers led to an increase in charge carrier mobility^[147].

It bears mentioning that while the prior requirements for semicrystalline order can be relaxed, a certain degree order at small length scales is still necessary. As Noriega *et al.* pointed out, the critical question is whether they have a sufficient degree of aggregation with even short-range order in combination with enough conjugated backbones to connect between the aggregate regions^[111].

An excellent demonstration of this has recently been published by Thomas *et al.*, who designed and synthesised a polymer specifically to optimise transfer integrals between adjacent chains by minimising the interchain distance at close approach and in doing so produced a system with the unusual combination of both high photoluminescence quantum efficiency and mobility^[132].

2.7 Conclusion

In summation, the charge transport properties of organic semiconductors are determined by a complex combination of factors, with perhaps the most influential being the material's structure at both the intramolecular and intermolecular scales. A wide variety of methods have been developed to optimise the aspects of physical structure that impact device performance, whether it be large, rigid moieties that encourage the formation of planar conjugated backbones to improve conjugation length and intramolecular charge transport or optimisation of side chains to influence intermolecular order or for their solubilising effects.

As the theoretical understanding of these materials has improved, so the strategies for improving their performance have changed, from the early purification of polyacetylene to the synthesis of regioregular polythiophenes to the more recent shift towards synthesis of materials incorporating particular moieties in specific arrangements.

Considerable research exists examining the relative performance of different moieties either by themselves or when combined with others in a copolymer. Combined with the improving understanding of charge transport physics, such work provides a chemical 'tool box' which can be used in what has been a long-term research goal for many years: the rational design of organic semiconductors for a wide range of applications with tunable properties, whether mechanical, electrical or optical.

It is towards this end, of exploring the design space for future organic semiconductor synthesis, that the bulk of the work described in this thesis is directed: the study of relationships between polymer microstructure, optical properties and charge transport. This is approached in two different ways: through the synthesis and characterisation of materials with similar yet distinct chemical structures to provide deeper understanding

of how such changes influence these properties, and through new, more controlled approaches to thin film fabrication and processing that can modify microstructure in order to optimise for charge carrier mobility.

Chapter 3

Experimental Methods

This chapter will details the methods used to produce and characterise the films and devices that form the basis of this project. It begins with a description of the two methods, spin coating and zone casting, used to produce films before detailing how those films were then incorporated into thin film transistors (TFTs) before discussing the various methods used to investigate device performance and film microstructure of these materials.

3.1 Thin Film Fabrication

At the outset of this project, spin coating was used to produce thin films from all of the studied materials. In terms of the deposition methods available when processing thin films from solution, it is among the quickest and most straightforward. It does however, have some drawbacks with regards to fine control of film formation conditions during deposition.

Specifically, while it is possible to pre-heat a solution before placing a droplet to be spin coated, and even use a preheated glass pipette to do so, once the droplet leaves the pipette any control over its temperature

is lost. While this is not troublesome in the case of polymers with good solvents, such as P3HT, several materials studied in this project proved difficult to keep in solution at room temperature. 2,4-dichlorobenzene (DCB) was found to be a good solvent for most of the polymers, although in some cases this required heating the solvent to assist dissolution. In the case of the fluorinated alkylthiophenes, heating to 90°C was sufficient, while several PDTTB copolymers required heating to 150°C. One of the PDTTB copolymers incorporating a thienothiophene comonomer did not fully dissolve even at this elevated temperature after heating and mixing for 24 hours. No good solvent was found for this particular material, and filtration proved difficult as well.

Another potential disadvantage of spin coating arises from the speed at which deposition takes place. If it is too fast, molecules in the solution have little time to re-arrange into a well-ordered microstructure. Given the considerable impact of microstructure on charge carrier mobility in polymer semiconductors described in the literature, what is often considered an advantage of spin coating can in fact hinder device performance.

Zone-casting is a relatively new method for producing thin films^[148] which addresses both of these potential issues. The casting solution is held in a reservoir and can be delivered to the substrate at a precisely controlled rate, while the substrate can be withdrawn with a similar degree of precision. A pair of electronically controlled heaters, one heating a plate underneath the substrate and the other heating the block enclosing the solution reservoir, allow precise control over the temperature of the solution throughout the deposition process. By modulating these four parameters, it is possible to achieve a high degree of control over the rate of solvent evaporation at the solvent-substrate-atmosphere interface where the film forms, in principle allowing for precise control over the deposition rate. This is useful because reducing the rate of crystallisation allows the molecules in solution more time to adopt a more ordered state, thereby

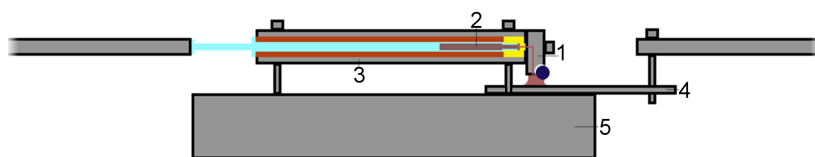


Figure 3.1: Zone-casting apparatus: (1) casting head-piece; (2) solution reservoir; (3) reservoir heater block; (4) substrate holder; (5) base heater block.

reducing structural disorder and, hopefully, improving charge carrier mobility. Of secondary interest are reports of using zone-casting to produce uniaxially aligned films^[99,149,150], a type of microstructure that is unobtainable using spin coating.

The zone-casting apparatus is shown in Fig. 3.1. It consists of five main sections: the casting headpiece; solution reservoir; reservoir heater block; substrate holder and base heater block.

The casting headpiece is a metal block with a thin channel running from its back face to its bottom face. The bottom front edge has been cut away to allow the insertion of a PTFE dowel that provides a surface for the solution to wet to both guide it to the substrate and to control the width of the zone cast area. The headpiece is attached to the reservoir heater block by a pair of bolts and a PTFE adaptor is used to pass solution from the glass syringe that serves as the solution reservoir through the headpiece. The reservoir is held within a hollow, Teflon-coated metal cylinder that is inserted inside the reservoir heater block. The temperature of the reservoir heater block is controlled by one of the heater controllers and is attached to the base heater block by four springs. The height it sits above and its inclination relative to the base heater block can be adjusted using four screws, one for each spring at a corner of the block.

The temperature of the base heater block is controlled independently of the reservoir heater block with the second heater controller. While there

is some expected interdependence between the two due to convective effects, they can both maintain stable temperatures to within 5 °C, which proved sufficient for this project. The substrate holder is simply a metal plate with a recessed rectangular area on one side which is used to hold substrates in place during zone-casting.

A significant amount of time was spent optimising the zone-casting process to produce homogeneous films. The initial zone-casting procedure involved injecting solution until it wet the substrate and then withdrawing the substrate at $40\text{ }\mu\text{m s}^{-1}$, while continuing to inject solution at a reduced rate of $0.2\text{ }\mu\text{l s}^{-1}$. This approach had produced good films previously from a variety of solutions, including DCB solutions of P3HT and PBTTT, in the latter case enabling the production of uniaxially aligned films of the material in its nanoribbon phase^[99].

Unfortunately, early attempts to replicate similar homogeneous film formation in both the fluorinated P3ATs and the PDTTB polymers failed, in each case producing a characteristic 'ridge' pattern shown in Fig. 3.2. This is a result of a combination of the speed at which the substrate is withdrawn and the temperature of the solution on the substrate. As the substrate is withdrawn, the solution wetting the surface is dragged with it, while the solution wetting the dowel remains stationary, effectively pinned by its own wetting interaction. Eventually, the free energy of the stretched droplet becomes so high that it splits, forming a separate droplet that evaporates independently, producing the observed ridges.

A higher substrate temperature counteracts this behaviour, as it causes the solution to evaporate before a separate droplet can form. It follows that solvent selection can also be used to prevent droplet formation, with higher boiling point solvents reducing the likelihood. However, the low solubility of the F-P3ATs and several of the PDTTB copolymers necessitated the use of DCB as a solvent. Producing a homogeneous film is a matter of balancing the substrate speed with the evaporation rate.

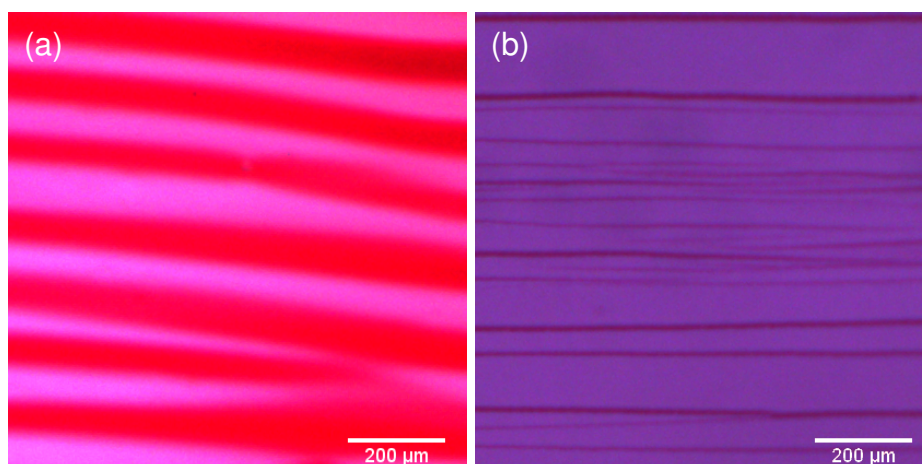


Figure 3.2: (a) Ridged film produced using high substrate extraction speed. Note the relatively wide ridges; (b) A similar film produced at low substrate extraction speed. Due to the different origin of the ridges, those in this film are considerably less regular and consistently thinner.

It is worth noting that the strength of the molecular interactions between the substrate and solution also affect this process. Stronger interactions (that is, improved wetting behaviour) will make the formation of separate droplets more unlikely due to such cases favouring the formation of wide area droplets with lower contact angles. Again, practicality limited choice in this regard, but the substrates employed had relatively strong interactions with the DCB solutions (with contact angles under 30° as measured using the sessile drop technique) leaving little room for improvement.

It is important to note that reducing the substrate speed beyond a certain critical limit can also produce a ridged film. In this case the ridges were considerably smaller and more closely packed than those produced with faster substrate speeds and ridge formation cannot be attributed to the separation of droplets. Instead, depletion of solute within the solution between the film formation interface and the reservoir resulting from faster evaporation can result in the droplet splitting. This produces a second film formation interface between the droplets, resulting in the ridge

structure.

Once optimised, the final procedure was to wet the substrate with solution, followed by extracting the substrate at $125 \mu\text{m s}^{-1}$. As the film formation front reaches the edge of the substrate, excess solution was removed using a paper towel. This produced homogeneous films that were approximately 30 nm thick.

3.2 Field Effect Transistor Fabrication

In order to extract values for charge carrier mobility from each material, field effect transistors were fabricated with the material of interest as the active layer. The devices predominantly employed a top-gate bottom-contact (TGBC) architecture, with a channel length of 20 μm and a channel width of 1,000 μm . Source and drain contacts were fabricated from gold with an adhesion layer of chromium (20 nm and 2 nm thick respectively) in the interdigitated structure shown in Fig. 3.3 via photolithography.

After source and drain contacts were patterned using thermal evaporation and the remaining photoresist was removed, the active layer was added using zone-casting as described in the previous section, followed by the dielectric layer: either electronic grade polymethylmethacrylate (PMMA) or poly(perfluoroalkenylvinyl ether) (CYTOP) *via* spin coating. Finally, gate electrodes (20 nm thick gold) were added on top of the dielectric layer through a shadow mask, again *via* thermal evaporation.

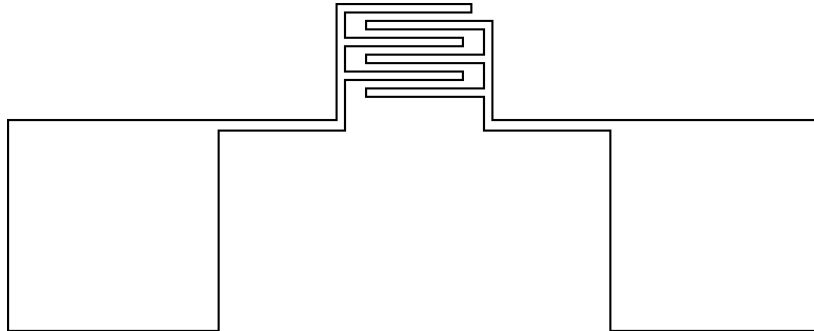


Figure 3.3: Interdigitated structure used for fabrication of FET source/drain electrodes. Each contact pad is a square 450 μm on a side. $L/W = 0.05$

Substrate Preparation

FETs were fabricated on substrates of Corning low-sodium glass, which prior to patterning was cleaned by sequential sonication in de-ionised (DI) water, acetone, then isopropyl alcohol (IPA) for 5 minutes each, followed by a 10 minute treatment in a Tegal plasma asher at a power of 250 W. Prior to zone-casting, the plasma ashing was repeated to ensure the cleanliness of the source and drain electrodes.

Photolithography

A relatively straightforward process, photolithography involves coating a target surface with a layer of photoresist, a material which either polymerises or depolymerises when exposed to certain wavelengths of light, generally in the ultraviolet range. By selectively exposing the surface to such light using a pre-patterned template fabricated by electron beam lithography, it is possible to then develop the resist chemically, removing either the exposed or the covered regions. In the former case, the resist is known as a positive resist, while in the latter it is termed a negative resist.

The approach used to fabricate the devices described in this thesis employed a dual layer of positive resists, LOR 5B and S1813. Using a dual layer, with the bottom layer composed of the more readily developed material, produces an undercut in the resist double layer, facilitating its removal once patterning is complete. The dual layer was formed by sequentially spin coating and curing the two layers.

UV exposure was performed using a Karl Suss MJB 3 HP mask aligner operating in 'soft contact' mode. The mask is held upside down using a vacuum pump beneath an optical microscope used for alignment, which is replaced by a 350 W mercury UV lamp during exposure. Substrates

are placed on a tray beneath the mask which can be moved laterally and vertically using three adjustment screws, as well as rotated about the vertical axis. During alignment, the substrate is positioned beneath the mask and brought into contact with it using the vertical adjustment screw. Exposure is automated, only requiring the specification of the exposure time. The test devices discussed in this thesis were exposed for 12 seconds.

The developer used after UV exposure was MF 319. Development was performed manually, holding each substrate still in the developer for 20 seconds and then gently shaking it for another 40 seconds to remove developed areas of the resist layers where possible. After development, films were briefly sonicated in DI water to remove whatever residual scraps of developed photoresist remained. Occasionally this sonication had to be repeated after examination under an optical microscope to ensure complete removal.

After substrates had been patterned, the undeveloped photoresist was removed by placing the substrates in *n*-methyl-2-pyrrolidone (NMP) for 1 hour. Subsequently, the resist dual layer could be removed by using plastic pipette to 'blow' currents of NMP under slightly raised sections of it. Brief sonication for 1 minute each in NMP, DI water and finally IPA served to remove any traces of remaining photoresist, while avoiding damage to the patterned structure.

Thermal Evaporation

Thermal evaporation was employed to fabricate the metallic contact electrodes for the FETs. This technique involves placing the target substrate upside down inside a bell jar that is pumped down to $\sim 10^{-7}$ bar. A tungsten or molybdenum boat containing the electrode material is placed beneath the substrate and an electric current passed through the boat to

cause resistive heating. The current is increased until the electrode material melts and then begins to vapourise. Due to the low pressure inside the bell jar, the mean free path of the vapourised gold atoms is on the order of the height of the jar, resulting in gold atoms striking the substrate almost normal to its surface.

A piezoelectric crystal mounted inside the bell jar enables measurement of the thickness of the deposited layer to sub-nanometre accuracy, permitting precise control of electrode thickness. The devices described in this thesis consisted of a 20 nm gold layer for the electrodes, with a 3 nm chromium layer to improve adhesion to the surface when fabricating on bare glass.

3.3 Electrical Characterisation

Determining the charge carrier mobility, or more accurately the charge carrier field-effect mobility, of the materials was accomplished by extraction from transfer characteristics of the devices operating in both linear and saturation regimes.

Measurements were performed in a glovebox with a nitrogen atmosphere in order to prevent the possibility of degradation of the films arising from atmospheric water or oxygen. Contacts were made to the devices using Karl Suss PH100 probes with sharp tips attached, mounted on a vacuum table. Data was collected by an Agilent HP4155C Semiconductor Parameter Analyser, which was monitored by a computer with a LabView control program. Drain, source and gate voltages could be independently controlled with the program, which also handled preliminary visualisation.

Data was collected from devices at gate voltages of 60, 80 and 100 V. This established that the materials studied in this thesis exhibit gate voltage-dependent mobility. Reported mobility values are the mean values at a gate voltage of 80 V, with measurements performed twice on each device to verify operational stability and check for any hysteretic effects. Transistor operation was near-ideal for all devices used to extract mobility, and any devices exhibiting serious non-linearities or defects were discounted from mobility evaluation to avoid the pitfalls discussed by Choi *et al.*^[25] in an effort to ensure that quoted values are representative of the materials under investigation.

Charge carrier mobilities were extracted from transistor characteristics of devices operating in the linear and saturation regimes using Eq. 3.1 and Eq. 3.2 respectively.

$$\mu_{lin} = \frac{mL}{WV_{DS}C} \quad (3.1)$$

$$\mu_{sat} = \frac{2m^2L}{WC} \quad (3.2)$$

where μ is the charge carrier mobility, m is the gradient of either the drain-source current or its square root against gate-source voltage (for linear and saturation modes respectively), L and W are the channel length and width respectively, V_{DS} is the drain-source voltage and C is the capacitance per unit area of the dielectric layer. Eq. 3.2 assumes that the contribution from any channel length modulation effects is insignificant, as values of λ , the channel length modulation parameter, extracted from transistor output characteristics were on the order of 1×10^{-9} . Even at the highest values of V_{DS} of 100 V, this produces an error of less than 1 in 10^7 .

Data was analysed in OriginLab and gradients were extracted from the top quartile of data during the voltage sweep in order to minimise the effects of non-linear behaviour near the threshold voltage after verifying that such current plots were indeed linear.

3.4 Structural Characterisation

Surface Profilometry

In the case of thicker polymer films (≥ 50 nm) and dielectric layers (~ 500 nm thick), a simple measurement with a Veeco Dektak Profilometer sufficed to determine film thickness. A small scratch is made in the material and the profilometer used to measure the height of the resultant step to find the thickness of the film.

Atomic Force Microscopy

In cases where films were too thin for profilometry to provide an accurate measure of thickness and to provide more detailed characterisation of surface microstructure, atomic force microscopy (AFM) was used. All AFM data presented in this thesis was taken with a Veeco Dimension 3100 operating in tapping mode. Such images have lateral resolution on the order of 10 nm and vertical resolution approaching 0.1 nm. The source data was visualised and processed using Gwyddion 2.35^[151].

AFM is a now ubiquitous scanning probe technique in which a cantilever, in this case fabricated from silicon, with a small pointed tip is scanned across the surface. Electrostatic interactions between the molecules in the tip and the surface cause a deflection in the cantilever, which is measured by focussing a laser on the cantilever on the opposite side to the scanning tip. This light is reflected towards a quadrature photodiode, which can determine the deflection of the tip from the deflection of the laser beam.

There are three principal modes of AFM: contact mode, non-contact mode and tapping mode. In contact mode, the tip is essentially ‘dragged’

across the surface of the sample. More accurately, either the scanner is kept at a constant height and the topographic data is extracted directly from the deflection of the laser, or the deflection of the laser is used to operate a feedback circuit that moves the scanner up and down to maintain a constant deflection. While these approaches can provide data on surface topology and have some advantages when imaging samples with very high roughness, the process of dragging the tip across a sample's surface can cause significant damage to both the surface and the cantilever tip, as well as being prone to distortion as a result of friction between the surface and tip. When imaging relatively soft surfaces such as polymer films, such damage would be even more pronounced than on harder surfaces such as silicon, making contact mode a poor choice for examining the surface morphology of organic semiconductors.

In non-contact mode, the cantilever tip is instead oscillated near to the sample surface with the amplitude of the oscillation or its frequency being held constant, again via the use of a feedback circuit. Van der Waals interactions while the tip is near the surface influence the oscillation, and this change can be used to determine the distance between the tip and the surface. While this avoids the possible damage to the samples inherent to contact mode, ambient humidity can seriously impact the measurement of the van der Waals forces. The formation of a fluid layer on the surface introduces adhesion forces in the region that the van der Waals are significant. A sufficiently thick fluid layer as a result of high humidity can render non-contact mode imaging impossible, meaning it is more often used to image surfaces in high vacuum.

Tapping mode is a variation on non-contact mode, which holds the amplitude constant, albeit with a significantly larger amplitude (~ 100 nm as opposed to ~ 1 nm). This increased amplitude allows the tip to easily overcome the adhesive effects of any fluid layer, allowing imaging in atmosphere. At the same time, allowing only intermittent contact with the

surface removes the possible distortion from friction that can be problematic in contact mode measurements, and significantly reduces damage to the film.

X-Ray Scattering

While AFM can provide some insight into the morphology of the surface of a polymer film, other approaches are necessary to probe the bulk of such materials. X-ray scattering is a technique that has been used for decades to determine the crystal structures of an enormous variety of different materials. The technique employed in these studies was grazing incidence wide-angle X-ray scattering (GIWAXS). This approach is well suited to the characterisation of thin films such as those produced via zone-casting due to the stronger interaction with such films afforded by very low angles of incidence.

GIWAXS data was gathered and analysed by Dr. Alessandro Sepe. Measurements were performed at the I22 beamline at the Diamond Light Source Synchrotron, Didcot, UK using a probe beam with wavelength of 1.15 Å and a Dectris Pilatus P3-2M-DLS-L silicon hybrid pixel detector. The q-space calibration was performed fitting the characteristic scattering signal arising from silver behenate.

The visualisations produced in X-ray scattering measurements are Fourier transforms of the sample's molecular structure into reciprocal space or q-space. That is, regular repeating patterns such as crystalline unit cells are rendered as points, and dimensions of the crystal structure are inverted. Thus, a decrease in separation of features in an X-ray scattering image is the result of an increase in the corresponding crystal lattice parameter. Higher intensity peaks and higher order peaks along an axis meanwhile, are indicative of a higher degree of crystalline order within a sample.

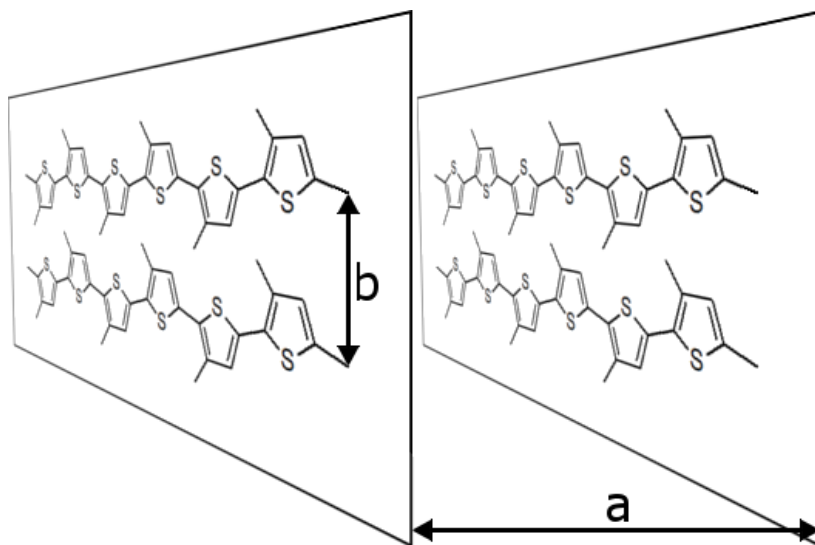


Figure 3.4: Distances probed by GIWAXS measurements of P3ATs (side chains omitted for simplicity): a is the π - π stacking distance and b the interlamellar spacing, corresponding to displacements of θ_f and α_f in q -space respectively.

Of particular interest when examining the structure-transport properties of an organic semiconductor are the π - π stacking distance between conjugated polymer backbones, which is an important mediator of interchain charge transport. To a lesser extent, the lamellar stacking distance of two neighbouring chains side by side is also of interest, as it can provide insight into to what degree the side chains of the polymers interdigitate. These two parameters are rendered as displacement along the θ_f and α_f q -space axes respectively. Given these displacements, the corresponding measurements in real space can be calculated using the equation:

$$d = \frac{\lambda}{2\sin\phi} \quad (3.3)$$

where λ is the wavelength of the x-rays and ϕ is the displacement of a given peak in q -space.

3.5 Optical Characterisation

While the optical properties of the materials studied in this work are of less interest when compared to their electrical and to a lesser extent structural properties, they can still provide useful insights. In particular, they can be used to infer information about the nature of the charge transport in these materials, or provide supporting evidence to complement structural characterisation.

Linear Absorption Spectroscopy

Absorption spectra of thin films (~ 30 nm thick) of the various materials studied in this thesis were obtained using a Hewlett Packard 8453 uv-vis spectrometer. Spectrosil was used as the substrate in order to minimise spectral response.

To a first approximation, both the energy of a spectrum's features and their bandwidth are relevant in terms of deducing the degree of disorder in the material: higher energy features suggest more localised states, indicative of lower conjugation length, while narrower bands indicate a higher degree of uniformity in length between different conjugated segments.

Beyond these qualitative observations, it is possible to produce more definite values for conjugation length from the absorption spectrum of a material. Work by Spano provides an expression for the intensity of the vibronic bands corresponding to the 0-0 and 0-1 transitions^[152]:

$$I_{0-0} = e^{-\lambda^2} \mu_{\parallel}^2 \left| \sum_n \phi_{k_{A_1^n}} \right|^2 \left(1 - \frac{W}{2E_P} e^{-\lambda^2} \sum_{\nu>0} \frac{\lambda^{2\nu}}{\nu! \nu} \right)^2 \quad (3.4)$$

$$I_{0-1} = \lambda^2 e^{-\lambda^2} \mu_{\parallel}^2 \left| \sum_n \phi_{k_{A_2^n}} \right|^2 \left(1 - \frac{W}{2E_P} e^{-\lambda^2} \sum_{\nu \neq 1} \frac{\lambda^{2\nu}}{\nu!(\nu-1)} \right)^2 \quad (3.5)$$

where λ^2 is the Huang-Rhys factor, $\mu_{\parallel}$ is the element of the polymer chain's transition dipole moment parallel to the chain's long axis, $\phi_{k_{A_1^n}}$ is the wavefunction of the vibronic excitons, W is the exciton bandwidth, E_P is the phonon energy and ν is the vibrational quantum number.

The Huang-Rhys factor is a dimensionless parameter that is related to the strength of electron-phonon coupling within a given material. More specifically, it is related to the change in nuclear equilibrium position between the ground and excited states^[36,153], often expressed in terms of Q , arbitrary nuclear coordinates, and ΔQ as illustrated in Fig. 3.5. For systems with no electron-phonon coupling ΔQ , and therefore λ^2 , is 0; the stronger the electron-phonon coupling, the larger ΔQ and λ^2 will be. When λ^2 of a system is known, it can be used to predict the lineshape of the system's absorption and emission spectra^[153,154].

Combining Eqs. 3.4 and 3.5 allows the derivation of W from the $I_{0-0} : I_{0-1}$ ratio. From equations 3.4 and 3.5, we arrive at:

$$\frac{I_{0-0}}{I_{0-1}} = \frac{\left(1 - \frac{W}{2E_P} e^{-\lambda^2} \sum_{\nu > 0} \frac{\lambda^{2\nu}}{\nu! \nu} \right)^2}{\lambda^2 \left(1 - \frac{W}{2E_P} e^{-\lambda^2} \sum_{\nu \neq 1} \frac{\lambda^{2\nu}}{\nu!(\nu-1)} \right)^2} \quad (3.6)$$

When the Huang-Rhys factor is known, this expression can be simplified by evaluating the numerical factors and the two sums, both of which converge rapidly. For P3HT, λ is commonly taken to be 1^[80,155,156]. Given that, the two sums become:

$$\sum_{\nu > 0} \frac{1^\nu}{\nu! \nu} = \frac{1}{1} + \frac{1}{4} + \frac{1}{18} + \frac{1}{96} + \dots \approx 1.316 \quad (3.7)$$

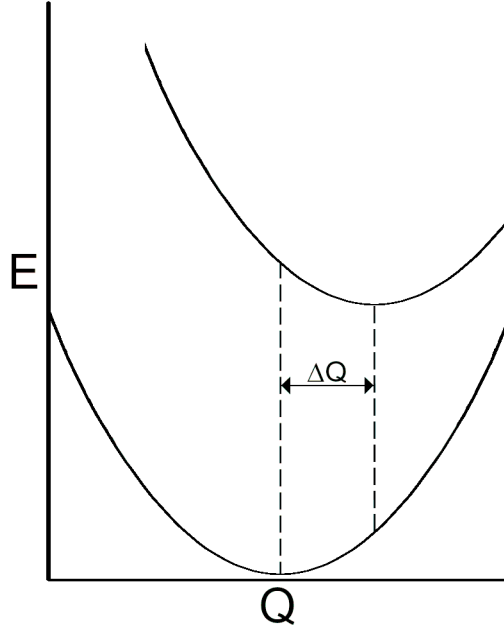


Figure 3.5: Energy-displacement diagram illustrating the effects of electron-phonon coupling.

$$\sum_{\nu \neq 1} \frac{1^\nu}{\nu!(\nu-1)} = \frac{1}{-1} + \frac{1}{2} + \frac{1}{12} + \frac{1}{72} + \dots \approx -0.403 \quad (3.8)$$

Which, when substituted into Eq. 3.10, becomes:

$$\frac{I_{0-0}}{I_{0-1}} \approx \frac{\left(1 - \frac{W}{2E_P} \times 0.368 \times 1.316\right)^2}{\left(1 - \frac{W}{2E_P} \times 0.368 \times (-0.403)\right)^2} \quad (3.9)$$

Which, when simplified, reproduces the equation provided by Spano^[152]:

$$\frac{I_{0-0}}{I_{0-1}} \approx \left(\frac{1 - \frac{0.24W}{E_P}}{1 + \frac{0.073W}{E_P}} \right)^2 \quad (3.10)$$

Which can then be rearranged to express W in terms of the ratio $I_{0-0} : I_{0-1}$:

$$W = \frac{E_P \left(1 - \sqrt{\frac{I_{0-0}}{I_{0-1}}}\right)}{0.24 + 0.073 \sqrt{\frac{I_{0-0}}{I_{0-1}}}} \quad (3.11)$$

Beljonne *et al.* reported a relation between the conjugation length N and W ^[157], which can be rearranged to provide an expression for N in terms of W :

$$W = \frac{2Nm^2}{d^3} \left(\frac{1}{1 + 2 \frac{(Nm)^2}{cd^3}} \right) \quad (3.12)$$

$$N = c \left(\frac{1 + \sqrt{1 - \frac{2W^2 d^3}{cm^2}}}{2W} \right) \quad (3.13)$$

where, m is the transition dipole moment of the monomer unit, d is the distance between molecules and c is a fitting parameter dependent on d . As N increases, W also does up to a certain conjugation length beyond which W falls as N continues to rise.

This behaviour is a result of interplay between two competing processes; the first dominant at short conjugation lengths, where the point-dipole approximation holds and an increase in N will result in an increase in W due to the increased dipole moment of the larger chain segment. As N continues to increase, the point-dipole approximation becomes invalid and the contributions from each site on both interacting chains must be considered separately, which produces Eq. 3.14, a nested sum for β .^[158]

$$\beta \approx \frac{1}{4\pi\epsilon_0} \sum_{a=1}^N \sum_{b=1}^N \frac{q_1^a q_2^b}{r_{ab}} \quad (3.14)$$

where β is the exciton coupling energy, which in thiophenes has an approximately linear relationship with W ($W \approx 4\beta$),^[152] a and b correspond to specific sites along chains 1 and 2 respectively, q_n^x is the transition electronic density at site x on molecule n and r_{ab} is the distance between sites a and b .

The diagonal terms in Eq. 3.14 (those for which $a = b$) are all positive, while the non-diagonal terms vary between positive and negative depending on the choice of sites but are cumulatively negative. As N increases, the contribution from the diagonal terms continuously decreases while the absolute value of the non-diagonal contribution falls until it reaches a minimum and begins continuously increasing, reducing β , and therefore W , as it does so.^[157]

The alternative solution of the Eq. 3.13 (found by subtracting the determinant) can be neglected as it predicts unphysically low values for N (~ 0.1) that would predict conjugation lengths shorter than a single monomer unit if they were accurate.

It bears mentioning that, for small values of W (below ~ 0.1), N is highly sensitive to changes in W . This can lead to significant variance in the predicted conjugation length for materials with especially narrow exciton bandwidths.

Raman Spectroscopy

Raman spectroscopy was performed by Dr. Tom Kehoe using a WITec Alpha 300 system. The excitation laser wavelength was chosen from 785, 633 and 532 nm depending on the material in question, and the laser power at the sample was approximately 0.2 mW. Raman spectra were obtained in the back-scattering geometry via an Olympus 50x, 0.5 numerical aperture, long working distance microscope objective. The

sample was in a continuous flow of dry nitrogen gas in a Linkham stage at room temperature.

Raman spectroscopy can provide information about a material's vibronic structure, which can in turn be used to evaluate its degree of disorder. It involves pumping a film of the sample with a laser, which excites the electrons within the targeted area. The majority of the excited electrons decay from the excited state back to the ground state as a result of Rayleigh scattering. This produces a large signal at the wavelength of the exciting laser. It is also possible for the excited electrons to decay into a vibronic state above the ground state, and then decay into the ground state via phonon emission. This photonic emission from this process is red-shifted relative to the incident light. Conversely, if an electron is already in a vibronic excited state when excited, it is most likely that it will collapse back into the ground state upon decay than to its previous vibronic state. In this case the emitted radiation is blue-shifted. These two processes are known as Stokes and anti-Stokes scattering respectively, or collectively as Raman scattering.

By measuring the relative intensity of the scattered light, it is possible to calculate the relative populations of electrons that exist in the vibronic

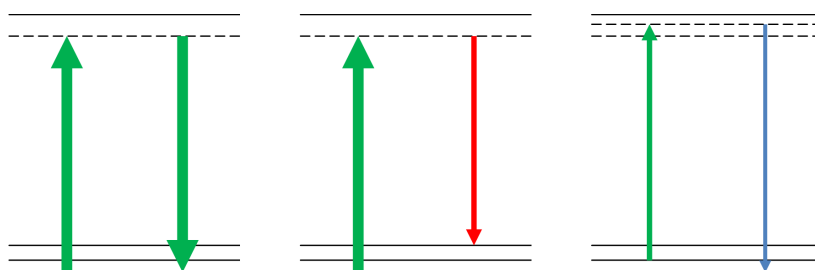


Figure 3.6: The three possible types of light scattering. (Left): Rayleigh scattering ($E_0 = E_S$); (Centre): Stokes scattering ($E_0 > E_S$); (Right): Anti-Stokes scattering ($E_0 < E_S$). The breadth of each arrow provides a qualitative representation of the likelihood of each transition.

states of a system and from their make useful predictions about molecular structure. Instead of being presented as shifts in wavelength, Raman shifts are generally referred to in terms of wavenumber. For a given excitation wavelength λ_0 and a scattered wavelength λ_S , the Raman shift, $\Delta\tilde{\nu}$, is given by Eq. 3.15

$$\Delta\tilde{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_S} \quad (3.15)$$

This can cause damage to thin films of polymeric material, so there is a balance to be struck between producing a strong signal and preserving the probed sample. However, as the laser is focussed into such a small area of the overall sample, the concern is more that degradation during the measurement might affect the results, rather than that the sample will be destroyed.

Photothermal Deflection Spectroscopy

While optical characterisation methods are both straightforward and versatile, they often encounter sensitivity problems. In order to measure absorbance they begin by measuring transmitted light, making them inherently susceptible to inaccuracies arising from light either scattered or reflected through the sample.

Photothermal deflection spectroscopy (PDS) circumvents this problem by exploiting the change in the refractive index of materials with temperature; the same effect that produces mirages on hot days^[159]. PDS measures the deflection of a laser parallel to the sample's surface as a result of the refractive index change in the heated fluid near the sample.

PDS measurements and Urbach energy extraction were performed by Dr. Aditya Sadhanala. The sample, placed on a quartz substrate, is immersed in a Fluorinert FCA72 high refractive index liquid and irradiated

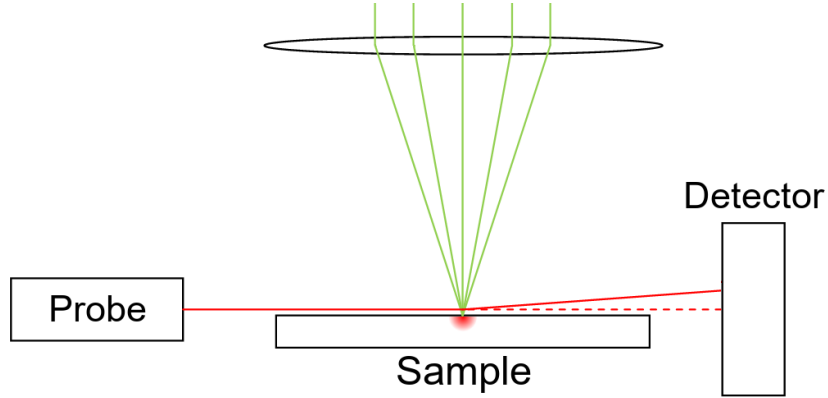


Figure 3.7: Schematic of PDS apparatus, showing the probe beam in red and the heating beam in green. The deflection in the probe beam from its incident path (dotted line) is measured by a photodiode detector.

by a monochromatic light beam. Absorption of this beam heats the sample *via* non-radiative relaxation. This in turn results in heating of the liquid near the heated region, creating a thermal gradient. Since temperature is related to refractive index, a gradient in one produces a gradient in the other. When a continuous wave probe beam passes through the refractive index gradient, it deflects by an angle related to the steepness of the gradient, which is then measured by a photodiode. The apparatus is shown in Fig. 3.7.

The deflection angle, ϕ , is given by Eq. 3.16.

$$\phi = \frac{s}{n} \left(\frac{dn}{dT} \right) \frac{dT(z, t)}{dz} \quad (3.16)$$

where s is the interaction path length, n is the refractive index of the medium, z is the height of the beam above the sample surface, t is time and T is the temperature. It is possible to expand the final term, which after some effort produces the more explicit Eq. 3.17.

$$\phi = -\frac{s}{n} \left(\frac{dn}{dT} \right) \sigma |\theta_0| \exp(i\gamma) \exp(-\sigma z) \exp(i\omega t) \quad (3.17)$$

Here the temperature term has been replaced with three components, including the phase term γ (which describes the phase between the temperature and the heating beam), the exponential decay of temperature with increasing distance from the sample and the periodic nature of the heating from the laser respectively. The new constant σ is linked to the thermal diffusion length μ via the expression:

$$\sigma = \frac{1 - i}{\mu} \quad (3.18)$$

Since PDS does not rely on transmitted light for its measurements, it is possible to obtain absorption data from both transparent and opaque samples as well as allowing the investigation of the sub-bandgap region of materials' absorption spectra. This is, in fact the most prevalent use of PDS as it offers access to a region inaccessible to more conventional spectroscopic techniques.

3.6 Theoretical Modelling

In order to aid explanation of observed structural, spectral and electrical properties of the materials, quantum chemical calculations were employed to obtain simulated structures for simplified model systems. For example, neglecting the alkyl side chains in the polyalkylthiophenes should not substantially affect the simulated geometry of a molecule in the gas phase (i.e. a single molecule by itself, neglecting intermolecular interactions), but will reduce the number of atoms in the simulation, and therefore its computational cost by more than 75%. Thus, the side chains in all of the molecules were approximated to methyl groups and backbones were truncated at 6 monomer units for the fluorinated thiophenes or 3 units of each comonomer in the PDTTB copolymers.

Simulations were conducted using GAMESS^[160,161] for the computation and Avogadro^[162] and wxMacMolPlt^[163] for molecule construction and visualisation.

Structures were initially optimised in Avogadro using the MMFF94s force field until it reached equilibrium. This structure was used to generate initial input for GAMESS. Structures were then optimised using restricted Hartree-Fock (RHF) methods with the STO-3G basis set to provide a starting point for the more reliable density functional theory method using the Becke, three-parameter functional with the Lee-Yang-Parr fit (B3LYP) with Pople's 6-31G(d) split valence basis set which was used to calculate the final equilibrium geometry.

Using the equilibrium geometries, the vibrational frequencies of each molecule were then found by way of the Hessian matrix, after which their Raman activity could be calculated.

Chapter 4

Fluorinated Polyalkylthiophenes

This chapter will discuss the study of polyalkylthiophene materials with a substituent fluorine attached at the second position on the thiophene ring. Specifically, it will compare them to their non-fluorinated counterparts and attempt to explain the differences observed between their charge transport properties arising from their molecular and macromolecular structure.

The materials used in this study, as well as their molecular weight, dispersity, regioregularity and energy levels were provided by Zhuping Fei and other members of the Heeney group at Imperial College London^[164].

4.1 Introduction

Some of the best electrical performance observed in the last two decades has been in highly crystalline or semi-crystalline materials such as regioregular P3HT^[119,165] or the liquid crystalline PBTTT.^[30] More recently however, other materials have been reported that possess mobilities in excess of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ despite possessing an amorphous microstructure. In particular, field effect transistors made with an active layer of IDTBT

Material	M _n	M _w	Đ	RR (%)	HOMO	LUMO	E _g
P3HT	39	55	1.4	97	4.64	2.73	1.91
F-P3HT	-	-	-	93	5.10	3.12	1.98
P3OT	19	26	1.4	95	4.70	2.79	1.91
F-P3OT	23	41	1.8	96	4.99	3.01	1.98
P3EHT	29	44	1.5	97	4.95	2.92	2.03
F-P3EHT	28	37	1.3	96	5.20	3.22	1.93

Table 4.1: Molecular weight (kDa), dispersity, regioregularity and energy levels (eV) of P3AT materials and their fluorinated counterparts. Molecular weight of F-P3HT could not be measured due to low solubility.

have been reported to have mobilities exceeding $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[110] While it does not possess a crystalline or semi-crystalline structure, it is notable for the extremely low degree of torsion between neighbouring units in its conjugated backbone, which was postulated to reduce the density of shallow trap states in the material, thereby improving charge transport.

In order to explore other possibilities for constructing low-torsion, high mobility organic semiconductors, a series of polymers based on the ubiquitous P3ATs were synthesised. Specifically, variants of P3HT, poly-3-octylthiophene (P3OT) and poly-3-1-ethylhexylthiophene (P3EHT) were synthesised with a fluorine atom replacing the hydrogen atom on the second carbon in each thiophene ring, as illustrated in Fig. 4.1. Regioregular structures are shown, in regiorandom segments some of the alkyl side chains exchange places with the fluorine atoms.

Polythiophenes, P3HT in particular, have been widely characterised,^[50,91,143,166–168] making them an excellent starting point for attempting to design new materials.

The rationale behind these materials' design is twofold. Firstly, it is expected that the strongly electronegative fluorine atom should produce an

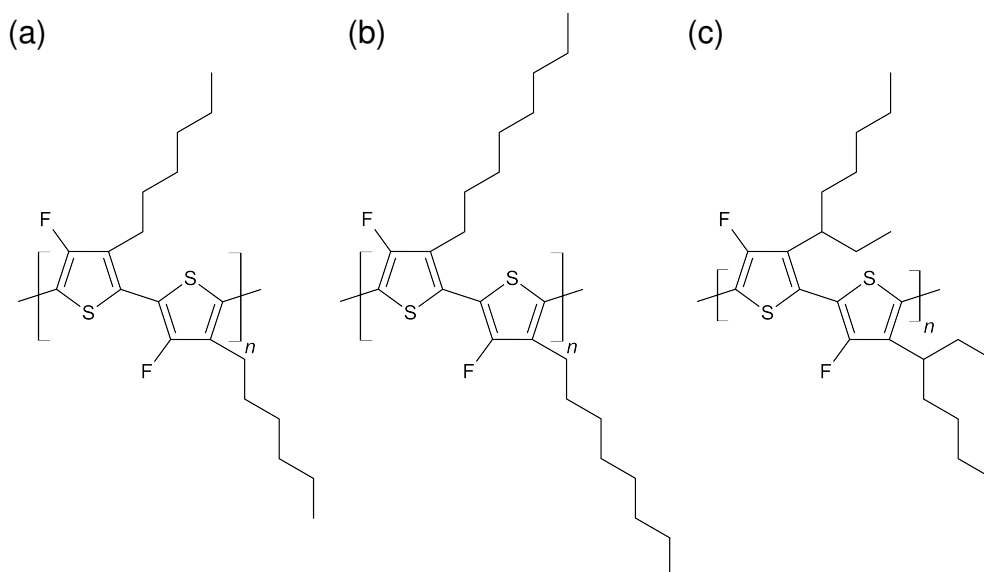


Figure 4.1: Chemical structure of regioregular (a) F-P3HT, (b) F-P3OT, and (c) F-P3EHT.

inductive electron withdrawing effect within the conjugated backbone, despite the donation of an electron lone pair via delocalisation. This should result in an increase in the ionisation energy, which enhances the stability of the compounds in atmosphere by reducing their susceptibility to oxidative doping.^[97,169]

Additionally, while the sulfur atom in a fluorinated material should retain a net positive electrostatic charge, the substitution of the fluorine for the hydrogen at the second position in the thiophene ring should replace a partial positive charge with a partial negative one. By doing so, it is hoped that the replacement of the slight repulsive force between the sulfur atom and the nearest hydrogen atom in the neighbouring ring with an attractive one between it and the substituted fluorine will act to planarise the conjugated backbone. As an aside, the relatively small size of the fluorine atom should minimise any steric hindrance the substitution introduces with regard to side-chain ordering.

In order to investigate the effectiveness of this approach, the surface and bulk morphology of thin films of the materials were examined using AFM and GIWAXS respectively. Raman spectroscopy was used to probe the vibrational modes of the systems while PDS provided an indication of the level of energetic disorder within each material, and linear absorption spectroscopy was used to examine their electronic energy levels.

To characterise charge transport within these materials, field-effect transistors were fabricated in a top-gate bottom-contact architecture as described in Section 3.2.

4.2 Field Effect Transistor Performance

Representative transfer and output characteristics for the polymer series are shown in Figs. 4.2 and 4.3. Transistor operation in devices using both the non-fluorinated materials and their fluorinated counterparts is near-ideal, with threshold voltages averaging 1.7 V and not exceeding 3.1 V and on-off ratios generally between 10^4 and 10^5 . This near-ideal operation provides a degree of confidence that extracted mobility values are useful metrics to base a comparison on, as discussed by Choi *et al.*^[25]. Linear and saturation mobilities extracted for each of the materials are summarised in Table 4.2.

There are two notable trends in this data. First, the fluorinated variant of each polymer has considerably higher mobility than its non-fluorinated counterpart, suggesting that the fluorination of the thiophene unit does improve charge transport as intended. Secondly, the branching side chains in P3EHT are seriously detrimental to charge transport, with both the fluorinated and non-fluorinated variants exhibiting much lower charge carrier mobility than their counterparts with non-branching side chains.

Changes in mobility with side chain selection are not unexpected, although existing work comparing polyalkylthiophenes with different side

Material	μ_{lin} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_{sat} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Devices
P3HT	0.088 ± 0.036	0.162 ± 0.065	18
F-P3HT	0.141 ± 0.071	0.220 ± 0.106	19
P3OT	0.148 ± 0.071	0.133 ± 0.570	26
F-P3OT	0.703 ± 0.218	0.443 ± 0.159	21
P3EHT	$4.35 \pm 2.78 \times 10^{-4}$	$6.91 \pm 2.35 \times 10^{-4}$	16
F-P3EHT	$2.46 \pm 0.89 \times 10^{-3}$	$3.07 \pm 0.49 \times 10^{-3}$	16

Table 4.2: Summary of F-P3AT Series Mobility

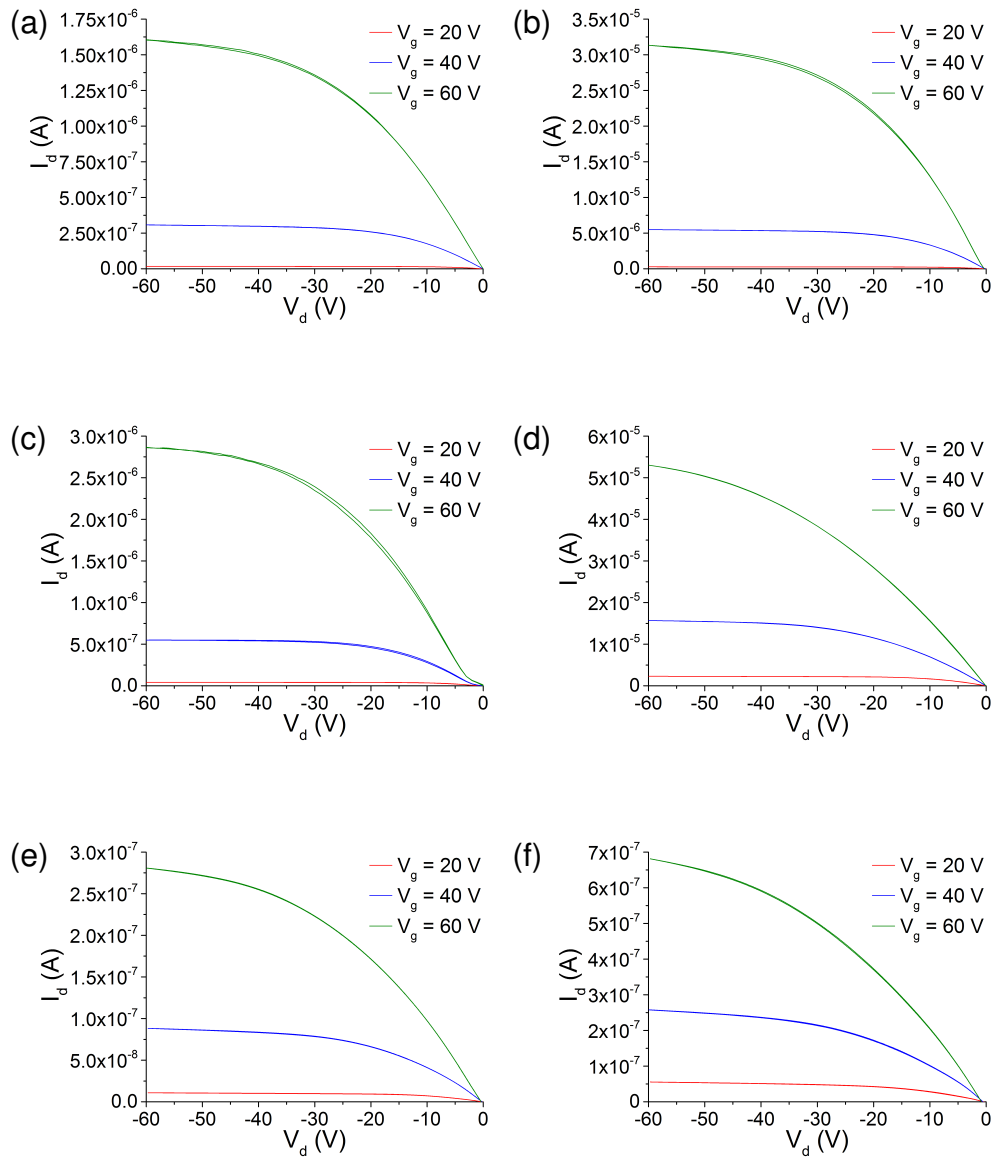


Figure 4.2: Output characteristics of (a) P3HT, (b) F-P3HT, (c) P3OT, (d) F-P3OT, (e) P3EHT and (f) F-P3EHT FETs.

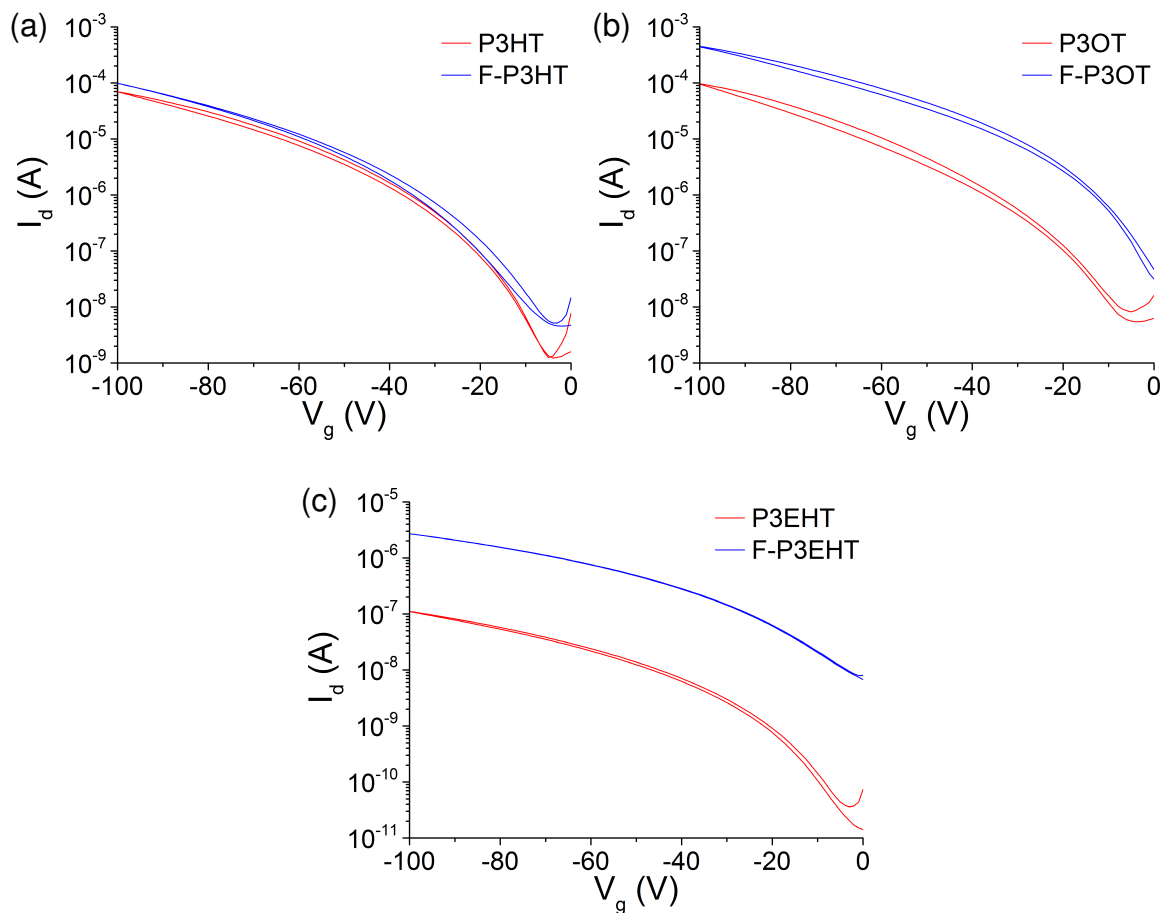


Figure 4.3: Transfer characteristics of P3AT FETs and their fluorinated counterparts.

chain lengths indicates that hexyl side chains result in higher mobilities than butyl, octyl, decyl or dodecyl side chains.^[104,170]

A possible explanation for the discrepancy between earlier results and those reported here lies in the use of different deposition methods during film formation; zone-casting in this work rather than the spin coating employed in earlier work. The lower deposition rates involved in the zone-casting method would tend to produce more thermodynamic, than kinetic, structures during film formation. This tendency could ameliorate any steric interference from the longer octyl side chains and allow P3OT to assume a more well-ordered structure, leading to improved charge

carrier mobility.

Also, due to the deeper HOMOs in the fluorinated polymers, charge injection from the gold electrodes is simplified. Each of the fluorinated materials exhibits a reduced threshold voltage in comparison with its non-fluorinated counterpart.

The decrease in mobility when moving to branched side chains is more straightforward to explain, as the increased alkyl chain density can hinder close packing, leading to an increase in intermolecular spacing and potentially reducing conjugation length as well.

A minor oddity in these results is the consistent, albeit usually small, decrease in on-off ratio upon fluorination. Normally, one would expect higher on-off ratios with deeper HOMOs^[35]. In (F-)P3EHT the difference is quite marked, the on-off ratio dropping to 10^2 in the fluorinated material. It is notable that the conjugation lengths extracted from linear absorption spectroscopy (see Section 4.5) track with these observations. Normally, higher conjugation lengths are associated with a higher HOMO and lower on/off ratio^[35]. In this case we may be observing cross-talk between the effects of increased conjugation length on the one hand and the introduction of the highly electronegative fluorine on the other producing this unexpected result.

As an addendum, before using CYTOP as the dielectric material for FET testing, P3EHT and F-P3EHT devices were fabricated using PMMA instead. While these devices actually exhibited higher mobilities with the -hexyl and -octyl variants and their fluorinated counterparts, the -ethyl-hexyl variant was found to be soluble in the n-butyl acetate used as a solvent for PMMA. This enhanced solubility arises as a consequence of the branching side-chain.

4.3 Atomic Force Microscopy

In materials such as PBTTT film morphology has been shown to correlate with measurements of charge carrier mobility,^[2] with crystalline or semi-crystalline structures exhibiting higher mobilities than their amorphous counterparts. While this trend is not universal in polymers, film morphology can still provide insight into structure-property relations.

AFM topography images of P3HT, P3OT and P3EHT and their fluorinated counterparts are shown in Fig. 4.4. Zone cast films are generally smooth, with RMS roughness values of 1.29, 1.39 and 0.96 nm for fluorinated P3HT, P3OT and P3EHT respectively. The non-fluorinated films have RMS roughness values of 0.86, 0.73 and 0.53 nm. The increased roughness in fluorinated materials reflects their increased crystallinity compared to their non-fluorinated counterparts, an observation that has been made previously elsewhere^[171].

The differences in morphology between fluorinated and non-fluorinated P3HT films are relatively obvious. While the non-fluorinated polymer forms the characteristic nodular structure seen in many other polymer films (including previous studies on P3HT),^[112,172] its fluorinated counterpart forms a semicrystalline terraced structure similar to the microstructure observed in PBTTT films.^[2,30,116] Although there are some regions which share the nodular structure of the non-fluorinated films, these appear to be the exception rather than the rule and exist on top of the terraced regions, and were therefore excluded when calculating RMS roughness.

A possible explanation for the existence of these two phases is that due to the relatively fast evaporation of residual solution after zone-casting, any excess polymer will be distributed quickly in whatever location the final droplets of solution happened to be. This would explain the relatively

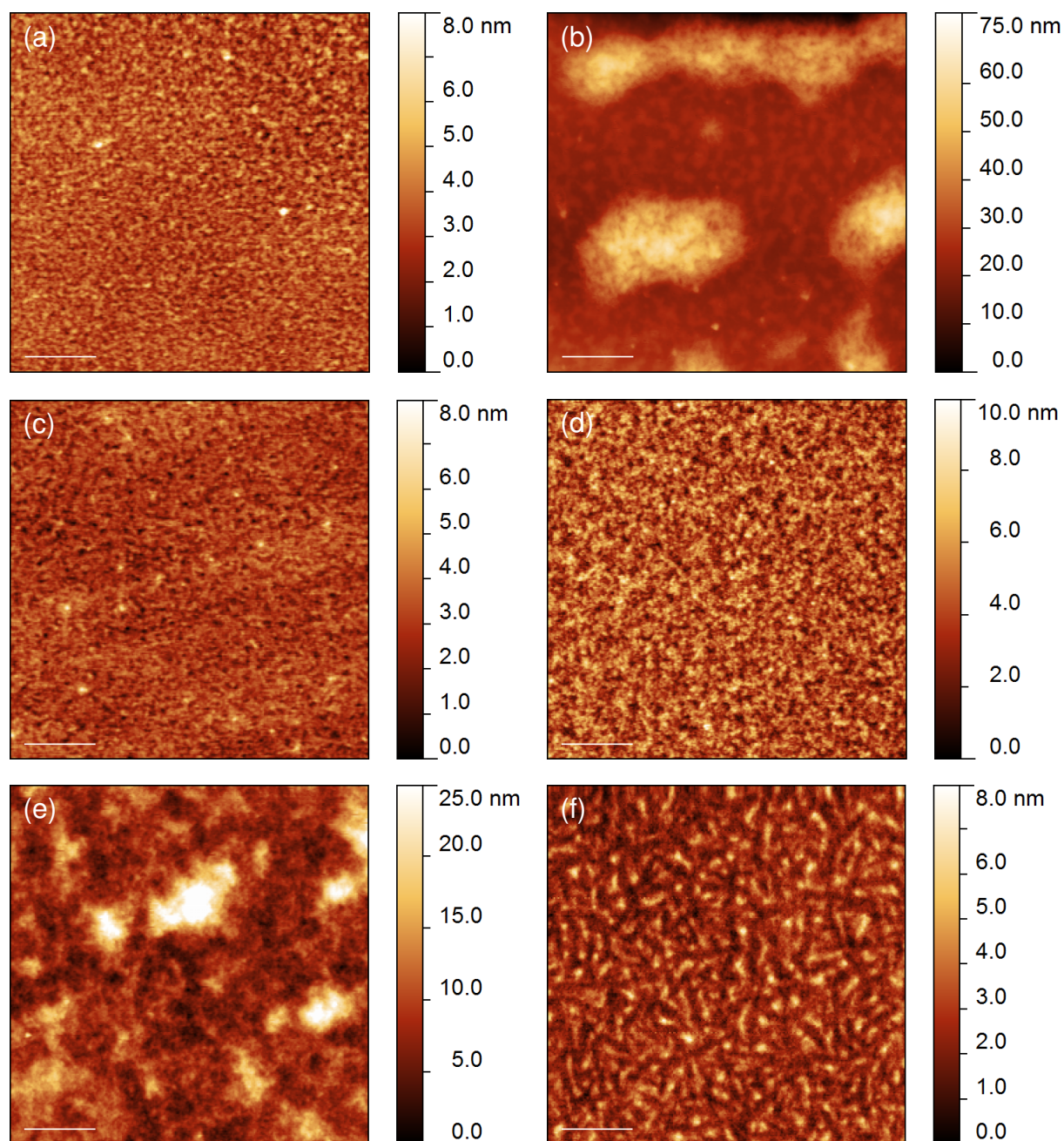


Figure 4.4: AFM images of (a) P3HT, (b) F-P3HT, (c) P3OT, (d) F-P3OT, (e) P3EHT and (f) F-P3EHT zone cast films. Scale bars represent 1 μm .

disordered nature of these regions, their apparently random distribution and their relatively large heights in comparison to the rest of the film.

Given the superior mobilities extracted from F-P3HT, the semicrystalline nature of the majority of the film and the absence of large amorphous regions, it seems reasonable to conclude that charge transport takes place through the semicrystalline regions. Indeed, contiguous regions of the nodular phase do not appear to extend much beyond a few microns (see Fig. 4.4), suggesting that while charge carriers may accumulate there as gate voltage is increased, they must either remain trapped in those regions or travel into the semicrystalline regions to achieve long-range charge transport.

By peak fitting the height distribution of the terraces in the F-P3HT topography images, it is possible to extract a value of ~ 1.6 nm for their 'step height'. This is a good match for the interlamellar spacing values reported in the literature for P3HT,^[166,168,173] which were not expected to change significantly upon fluorination. It is also in line with the expected value of ~ 1.62 nm predicted by a straightforward calculation based on the length of carbon-carbon single bonds and the geometry of the molecule reported by Kayunkid *et al.*^[168]

It is however, considerably larger than one might expect at first glance when comparing the relative lengths of the side chains to those in PBTTT, which has side chains containing between 10 and 14 carbon atoms. Given the geometry of PBTTT molecules calculated by DeLongchamp *et al.*,^[117] it is possible to calculate the expected molecular dimensions in a similar manner as for (F-)P3HT. By doing so, the expected terrace height would be ~ 3.0 nm, considerably greater than the 1.9–2.2 nm reported by various studies using AFM and X-ray techniques.^[2,30,117,144]

This discrepancy arises due to the lack of interdigitation in the side chains of form I P3HT, the more commonly observed molecular structure. Form

II P3HT, in which the alkyl side chains do interdigitate to a degree, is a thermodynamic, rather than kinetic, product of film formation^[93] which has only been observed in films prepared in specific ways involving self-seeding or extremely slow cooling in inert atmospheres.^[174,175] In form I, the areal density of alkyl chains along the P3HT backbone is so high that it would exceed that of crystalline polyethylene (PE) if it were to interdigitate; squeezing the constituent atoms significantly closer than their van der Waals radii.^[107] By contrast, the relatively larger separation of the alkyl chains along the PBTTT conjugated backbone permit interdigitation, reducing the observed step height in the terraced microstructure. It would appear that fluorinated polyalkylthiophenes, at least in films prepared *via* zone-casting, also arrange into a non-interdigitated structure.

In contrast to the materials with hexyl side chains, there is little apparent difference between P3OT and F-P3OT films (see Fig. 4.4), both having the same nodular structure observed in P3HT. Perhaps the only thing worthy of note is a slightly smaller nodule size in the fluorinated material.

Previous studies on the dependence of charge carrier mobility on film morphology in P3HT demonstrated an increase in mobility when transitioning from a nanorod structure to a nodular structure like that observed in these materials.^[112] This was attributed to better charge transport between molecules in the isotropic nodular films, due to the relative difficulty of hopping transport between molecules in different nanorods in such films. It seems reasonable to suggest that a decrease in the size of the nodules as observed here could be an indication of greater isotropy in the bulk of the film, leading to better long-range transport due to the presence of more charge transport pathways.

The branched side-chain materials on the other hand are markedly different from each other. The P3EHT films are considerably rougher than those of the other materials, although it appears to possess a similar nodular structure. Its fluorinated counterpart has an entirely different

structure composed of apparently randomly oriented fibrils. In a similar fashion to the terraced structure observed in F-P3HT, changes in height across the sample appear to take place in discrete steps of ~ 1.8 nm.

The increased roughness of P3EHT likely indicates lower crystalline order in comparison to the other materials, which offers an explanation for the considerably lower charge carrier mobilities observed in this material. Alternatively, the relatively poor electrical performance of F-P3EHT could be a result of its fibrillar microstructure: as with the nanorod structures described by Kline *et al.*^[112], charge transport within a single fibril should be relatively fast as a result of the high degree of local structural order. Charge transport between fibrils however, would be considerably hindered by the poor orbital overlap between molecules in separate fibrils.

The increased step height observed in these films is likely due to the branched side chain, which will further increase the already high areal density of alkyl chains along the conjugated backbone. Given previous evidence correlating areal side chain density with side chain tilt angle,^[107] materials with branched side chains would be expected to have a higher tilt angle than the unbranched side chains in the other materials, which would account for the increase in step height.

4.4 X-Ray Diffraction

Grazing incidence wide angle X-ray scattering (GIWAXS) was employed to examine the bulk microstructure of the films, to expand on the information provided by AFM about their surface morphology. The 2D GIWAXS images for P3HT, F-P3HT and F-P3OT are shown in Fig. 4.5.

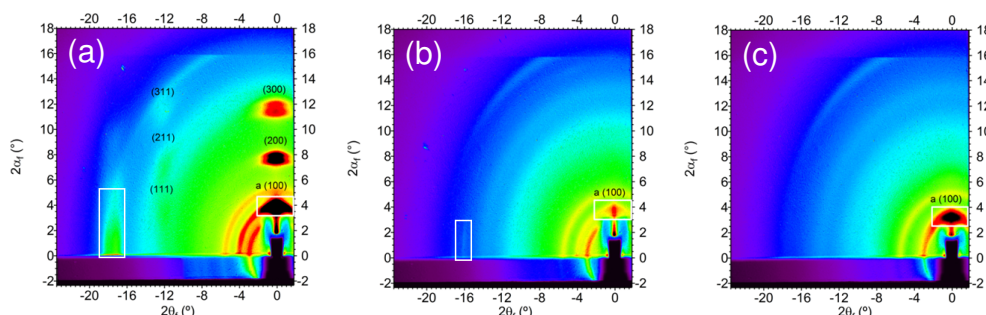


Figure 4.5: 2-D GIWAXS plots of (a) P3HT, (b) F-P3HT, (c) F-P3OT. Scattering intensity is indicated by a colour scale with red indicating the most intense scattering and purple the least. Black regions have been occluded to better view the intensity patterns in the rest of the figure. White boxes highlight the peaks corresponding to lamellar and π - π stacking.

The two features of principal interest are the relative positions of the peaks along the α_f and θ_f axes in each material. The former corresponds to the separation of the polymer chains in the plane of the conjugated backbone: the interlamellar spacing which we would expect to correlate with the step heights obtained from AFM data (see Fig. 4.4). The latter, meanwhile, corresponds to the distance between the backbones in the π - π stacking direction (see Fig. 3.4).

No difference was observed in interlamellar spacing between the non-fluorinated materials and their fluorinated counterparts, although the distance between the backbones increased in P3OT and F-P3OT relative to F-P3HT, from 1.6 to 1.9 nm.

Material	a (Å)	b (Å)
P3HT	3.8	16
F-P3HT	4.1	16
F-P3OT	-	19

Table 4.3: Summary of lattice parameters (see Fig. 3.4) for selected F-P3AT materials. F-P3OT π - π stacking distance could not be determined from diffraction pattern.

This is in reasonable agreement with the expected value given the increase in side-chain length. If we assumed precisely the same structure as P3HT, the anticipated value would be slightly higher, approximately 2.05 nm. This suggests that the longer side chains in (F-)P3OT either are more likely to interdigitate than those in (F-)P3HT, that they have a reduced tilt angle or that they are more prone to disorder. Considering that the areal density of the side chains along the conjugated backbone is the same in (F-)P3OT as in (F-)P3HT, we would not expect them to interdigitate any more readily. Likewise, the similar configuration around the backbone would be expected to keep the tilt angle of the side chains constant as well. However, the ends of the octyl chains will be less limited in their configurations than the ends of the hexyl chains, due to the greater distance from the conjugated backbone, leading to the conclusion that the ends of the octyl chains form a more disordered region between conjugated backbones, effectively reducing the interlamellar spacing.

It is also in good agreement with the variation in height observed in AFM measurements of F-P3HT (see Fig. 4.4), supporting the conclusion that the structure observed there is indeed comparable to that seen previously in PBTTT; molecules oriented edge-on to the substrate, with π - π -stacking in the same plane as the terraces.

A notable difference between the non-fluorinated and fluorinated materials is the change in position of their π - π stacking peaks, indicating an increase in interchain separation along this axis from 3.8 Å in the former

to 4.1 Å in the latter. Given the higher charge carrier mobilities observed in these materials this is slightly surprising. A reduction in π - π stacking distance generally correlates with higher charge carrier mobility as a result of improved interchain charge transport due to the larger charge carrier transfer integrals between different conjugated backbones.^[93,176]

This suggests that the improvements in charge carrier mobility in the fluorinated materials is due to enhanced planarisation of the conjugated backbone leading to improvements in intrachain transport as charge traps between conjugated backbone segments are removed. A sufficiently large improvement could counteract the expected impediment to interchain charge transport resulting from a larger π - π stacking distance, resulting in a higher overall mobility. Indeed, materials with the same π - π stacking distance have been demonstrated to have different charge carrier mobilities previously, including samples of P3HT with different degrees of regioregularity,^[113] and certain isoindigo-dithiophene copolymers with different side chain branching patterns.^[105]

Also of note is the reduced intensity of peaks in the fluorinated materials, indicating a lower overall degree of crystalline order in comparison with their non-fluorinated counterparts. This offers further evidence that high crystallinity is not a sufficient condition to guarantee high charge carrier mobility. It is possible that by enforcing a higher degree of backbone planarity, fluorination impedes the formation of long-range crystalline structures but provides the long tie chains shown to be so important to macroscopic mobility by Gu *et al.*^[131].

4.5 Linear Absorption Spectroscopy

There is a considerable amount of existing work regarding the optical properties of P3HT,^[91,152,177–179] which provides an excellent starting point for optical characterisation of both the other polyalkylthiophenes and their fluorinated counterparts. The absorption spectrum of aggregated P3HT is characterised by a pair of well-defined peaks, A_{0-0} and A_{0-1} , corresponding to the excitation of an electron from the ground state to the first or second vibronic band (see Fig. 4.6).

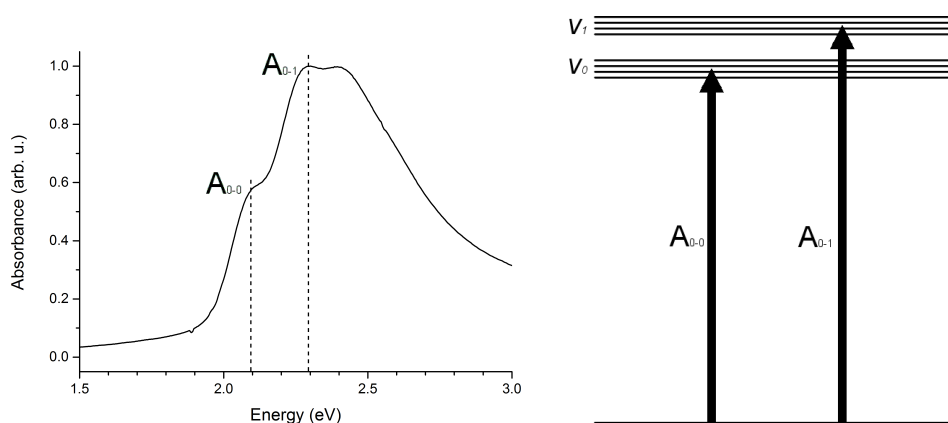


Figure 4.6: Summary of the primary absorption modes in P3HT: (*left*) absorption spectrum of P3HT indicating A_{0-0} and A_{0-1} modes; (*right*) partial Jablonski diagram illustrating excitation from the ground state into vibronic bands.

The absorption spectra for zone-cast thin films of P3HT, P3OT, P3EHT and their fluorinated counterparts are shown in Fig. 4.7. The spectra for the hexyl and octyl side chain materials are almost identical, which is unsurprising given their highly similar molecular structures, while the branched side chains in P3EHT alter the structure enough to produce more notable changes in the absorption spectrum. Of the non-fluorinated materials, P3OT has the most well-defined spectrum and is also slightly

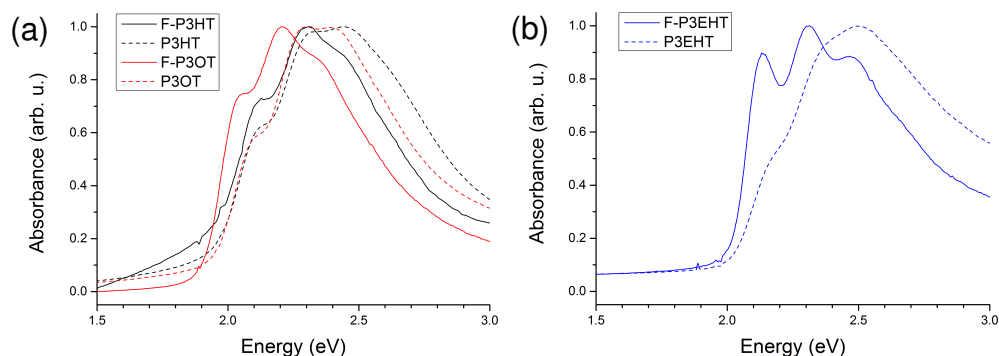


Figure 4.7: Normalised absorption spectra of (a) P3HT and P3OT and (b) P3EHT (dashed lines) and their fluorinated counterparts (solid lines).

red-shifted compared to P3HT and P3EHT, while P3EHT has a considerably broader spectrum that is blue-shifted with respect to the others. P3HT occupies a position between the other two in terms of feature energy and breadth.

As observed by Brown *et al.*, blueshifts and redshifts in the spectral features of P3HT correlate with decreases and increases in conjugation length respectively.^[177] On a qualitative level, this can be understood by considering the prototypical one-dimensional potential well and noting that a reduction in the width (analogous to the conjugation length in a polymer chain) will result in an increase in the energy levels of the system, and vice versa. They also noted that the broadening of absorption peaks can be explained by an increased variation of the absorption bandwidths resulting from greater variance in conjugation length.

These observations are in good agreement with expectations given the relative charge carrier mobilities of these materials, with P3OT having the highest mobility, the lowest energy spectral features and the most well-defined spectrum, with P3HT and P3EHT having progressively higher energy features and broader spectra.

The spectra of the fluorinated materials all follow a similar pattern, each red-shifted relative to and better-defined than the spectrum of its non-fluorinated counterpart, suggesting that they have longer conjugation lengths and less variance in the sizes of their chromophores in comparison to those counterparts. As would be expected from their relative charge carrier mobilities, the spectrum of F-P3HT is blue-shifted and has broader spectral features when compared to F-P3OT, indicating shorter conjugation length and higher structural disorder. Likewise, the spectrum of F-P3EHT is blue-shifted even further, suggesting an even shorter conjugation length than F-P3HT, in line with its lower mobility. However, its A_{0-0} and A_{0-1} peaks are in fact narrower than those observed in the other fluorinated materials, which perhaps somewhat oddly indicates a relatively high degree of structural order^[80,157,180].

Similar results have been reported in P3HT nanofibres,^[181] which is relevant in light of the fibrillar microstructure observed via AFM. It may be that the branching side chains in F-P3EHT reduce inter-chain interactions as a result of the increase in alkyl chain density discussed in section 4.3, allowing fluorination to extensively planarise the conjugated backbone. While this would enhance intramolecular charge transport, the relatively weak interchain coupling resulting from the increased intermolecular spacing and segregation of the fibrils would render long-range interchain charge transport considerably more difficult.

Also of interest is the higher intensity of the I_{0-0} peak relative to the I_{0-1} peak in the fluorinated materials, again indicative of increased conjugation length. In order to obtain estimates of conjugation length using Eq. 3.13, an appropriate value for c is required. These correspond to the values of d obtained from GIWAXS measurements. Beljonne *et al.* do not provide a precise relation between the two, but provide some pairs of values that, combined with the stipulation that $c \rightarrow 0$ as $d \rightarrow \infty$,^{*} can be

^{*}As c represents the evolution of W with N , due to the absence of Davydov splitting in the limit of an isolated chain (where $d \rightarrow \infty$), c will approach 0 as W does.

used to arrive the following relation via curve fitting:

$$c = 24d^{-0.83} \quad (4.1)$$

For c measured in eV and d measured in Å. Using the values extracted from the GIWAXS data discussed in the previous section, this produces values for c of 7.62 and 7.27 eV when $d = 3.8$ and 4.1 Å in the non-fluorinated and fluorinated materials, respectively.

The resulting relation between N and W based on Eq. 3.12 for fluorinated and non-fluorinated P3HT is shown in Fig. 4.8. To obtain this curve, m was taken to be 3.8 D in line with the results published by Deckers *et al.* for P3HT.^[182] While this is not likely to be as accurate for the fluorinated materials, N is only weakly correlated with m unless one or the other is very small ($N \lesssim 10$, $m \lesssim 1$). Calculated values for W and N based on the $I_{0-0} : I_{0-1}$ ratio of each material are summarised in Table 4.4.

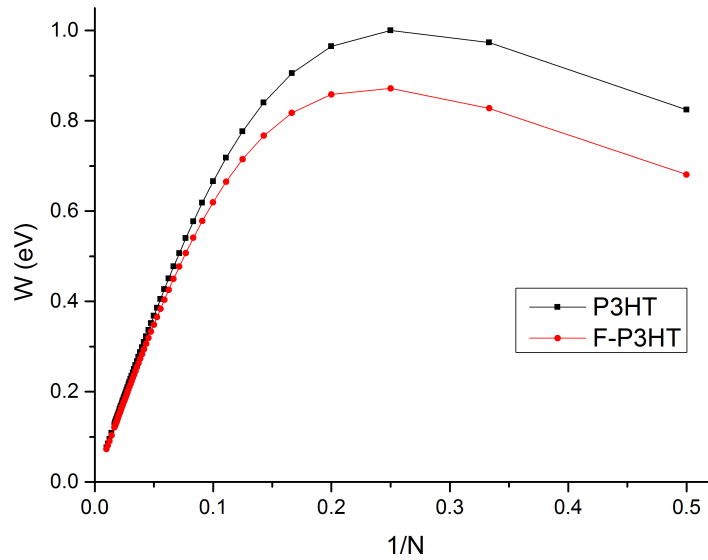


Figure 4.8: Exciton bandwidth plotted against $1/N$ for P3HT and F-P3HT.

Material	$\frac{I_{0-0}}{I_{0-1}}$	W (eV)	N	M_n	M_w
P3HT	0.644	0.126	60	39	55
F-P3HT	0.730	0.086	84	-	-
P3OT	0.613	0.135	56	19	26
F-P3OT	0.742	0.070	103	23	41
P3EHT	0.524	0.182	41	29	44
F-P3EHT	0.898	0.029	249	28	37

Table 4.4: Exciton bandwidth and conjugation lengths of the F-P3AT series. M_n and M_w are given in kDa.

The estimates for hexyl and octyl side chain materials match with expectations given the previously discussed results of the transistor and X-ray measurements; the increased charge carrier mobility in spite of the increased π - π stacking distance strongly suggested higher conjugation lengths in the fluorinated materials to compensate for their impeded intermolecular charge transport with enhanced intramolecular transport.

Given the molecular weight of the various materials, these values suggest that F-P3OT is composed of almost fully extended chains, made of at most two conjugated segments (given the molecular weights for F-P3OT, and that each monomer unit masses 212 a.m.u., average chain length would be ~ 108 -193). The other materials have considerably shorter conjugation lengths, with the exception of F-P3EHT. In this case, the predicted value is unphysically large, illustrating a limitation of this approach to estimating conjugation length. As the ratio between the two absorption peaks approaches 1, the predictions of N diverge towards infinity before becoming negative as the ratio exceeds 1. This is of course, based on the assumption that the Huang-Rhys factor is 1. If this approach could be generalised to materials with arbitrary Huang-Rhys factors, it would provide a straightforward approach for estimating conjugation length.

There are however, some oddities in the specifics of these data. Firstly, despite P3OT having higher charge carrier mobility than P3HT, its calculated exciton bandwidth and conjugation length are lower, albeit only slightly. Combined with the relatively minor difference in mobility and conjugation length, and accounting for the various uncertainties in the measurements, the calculated conjugation lengths are within the margin of error.

The projected values for the conjugation length in F-P3EHT reinforce the hypothesis advanced earlier: F-P3EHT forms assumes a fibrillar structure during zone-casting that, while providing significant improvements in conjugation length and intramolecular charge transport, do so at the expense of long-range transport between fibrils. The final result is a material that, despite its high conjugation length, suffers from low charge carrier mobility as a result of poor transport between conjugated backbones in different fibrils.

4.6 Raman Spectroscopy

When examining the Raman spectra of the two sets of materials, P3HT is once again a useful starting point as it has been studied previously in considerable detail.^[82,183,184] The principal features of the spectrum are a pair of peaks centred at approximately 1380 and 1445 cm^{-1} and a third, considerably less intense peak around 720 cm^{-1} which are assigned to stretching of the single bond between the two β carbon atoms, stretching of the double bond between the α and β carbon atoms and deformation of the thiophene ring due to bending of the bonds between the sulfur atom and the two α carbon atoms respectively, as illustrated in Fig. 4.9.

The Raman spectra of the polyalkylthiophenes and their fluorinated counterparts are shown in Fig. 4.10 and summarised with their assigned Raman modes in Table 4.5. All spectra for shown were produced using 785 nm excitation. In the spectrum of zone-cast P3HT the two primary Raman modes are observed at 1380 and 1445 cm^{-1} as expected, with secondary peaks at 725, 1003, 1087, 1180, 1206, and 1512 cm^{-1} . These results are similar to values reported by Tsoi *et al.*,^[82] the only difference being a small shift to lower wavenumber in the symmetric $\text{C}_\alpha=\text{C}_\beta$ stretching mode and antisymmetric $\text{C}_\alpha\text{-S-C}_\alpha$ deformation mode.

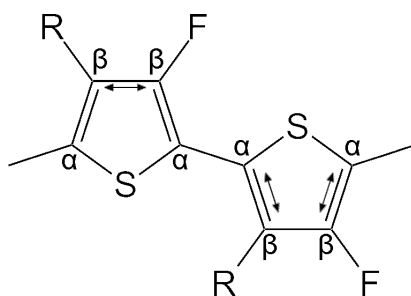


Figure 4.9: Diagram of (F-)P3AT molecule with arrows indicating the vibrations corresponding to the principal Raman modes: the $\text{C}_\beta\text{-C}_\beta$ intra-ring stretching mode on the left ring and the $\text{C}_\alpha=\text{C}_\beta$ stretching mode on the right.

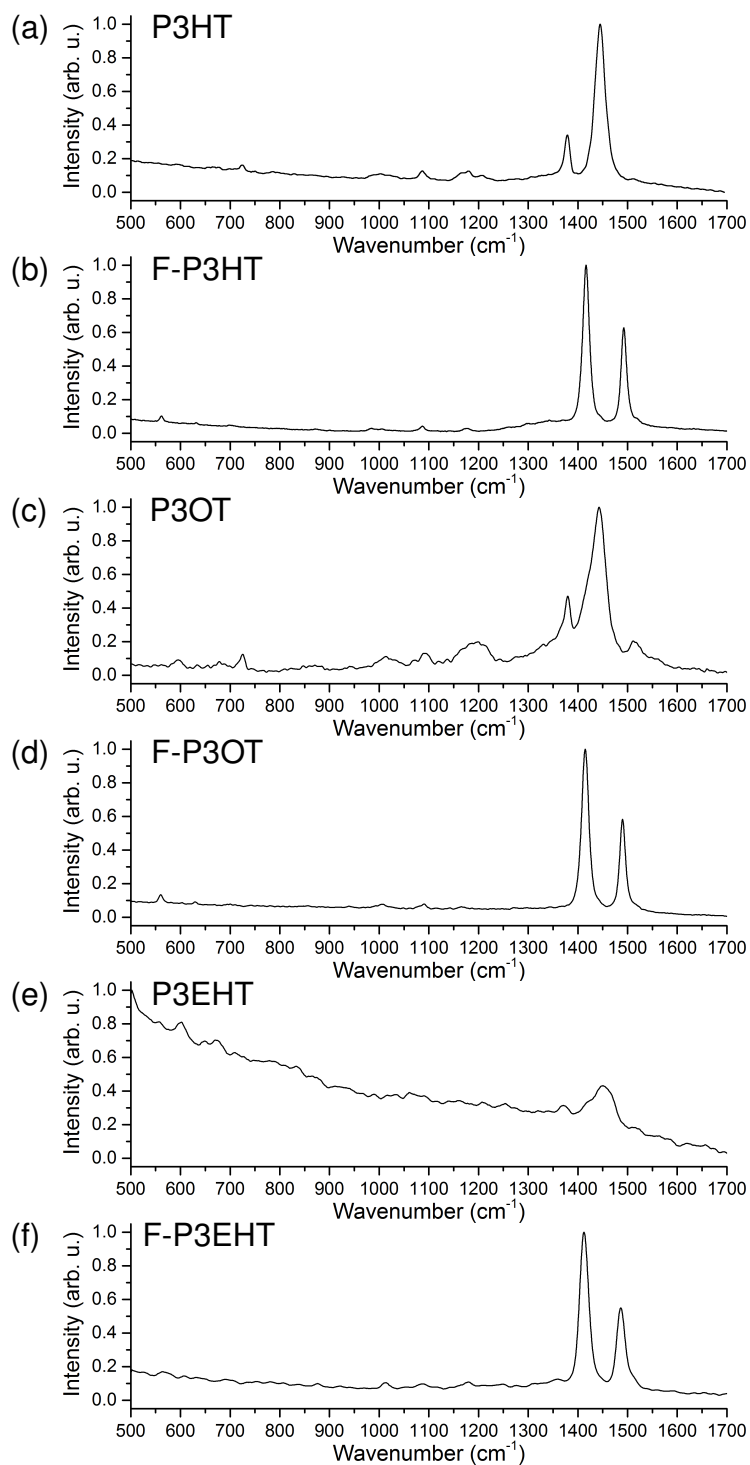


Figure 4.10: Normalised Raman spectra of (a) P3HT, (b) F-P3HT, (c) P3OT, (d) F-P3OT, (e) P3EHT, (f) F-P3EHT.

Vibronic Mode	P3HT	F-P3HT	P3OT	F-P3OT	P3EHT	F-P3EHT
C_{α} -S- C_{α} deformation	592	562	593	561	600	563
C_{α} -S- C_{α} symmetric deformation	677	-	678	-	675	-
C_{α} -S- C_{α} anti-symmetric deformation	725	-	726	-	-	-
C_{β} -alkyl stretch	1003	1005	1013	1006	-	1013
C_{β} -H(F) bend	1087	1087	1090	1090	1061	1088
C_{α} - C_{α} symmetric stretch	1180	1178	1186	1165	1163	1180
C_{β} -H(F) stretch	1206	-	1201	-	1210	-
C_{β} - C_{β} intra-ring stretch	1379	1416	1380	1415	1373	1412
$C_{\alpha}=C_{\beta}$ stretch	1445	1493	1443	1490	1451	1487
$C_{\alpha}=C_{\beta}$ antisymmetric stretch	1512	1519	1511	1524	1515	1520

Table 4.5: Summary of F-P3AT series Raman spectra. All Raman modes are given in wavenumber (cm^{-1})

The immediately obvious difference between the fluorinated materials and their non-fluorinated counterparts is the shift of the C_{β} - C_{β} and $C_{\alpha}=C_{\beta}$ stretching modes to higher wavenumbers in the fluorinated materials. The shift is very similar in the hexyl and octyl side chain materials, with 36.5 and 47.5 cm^{-1} shifts in the C_{β} - C_{β} and $C_{\alpha}=C_{\beta}$ peaks respectively, but slightly different in the ethyl-hexyl side chain materials, where the same modes are shifted by 40 and 34 cm^{-1} , respectively.

Also of note are the width of the peaks in each material. For the most part, peaks are quite well-defined with small FWHM which decrease when moving from non-fluorinated material to fluorinated counterpart. The spectra of P3OT and P3EHT however, both have considerably broader peaks than the other materials. In the case of P3EHT this is not entirely surprising: the same homogeneous broadening was observed in absorption spectroscopy and points to the higher levels of disorder in the material. In the case of P3OT this observation is more unexpected: its absorption spectrum was practically indistinguishable from P3HT. If anything, P3OT had marginally narrower spectral features.

In addition to the frequency of each mode, the ratio between the intensities of the C_{β} - C_{β} and $C_{\alpha}=C_{\beta}$ modes is significantly higher in the fluorinated materials. The relative intensities of the C_{β} - C_{β} and $C_{\alpha}=C_{\beta}$ modes

are summarised in Table 4.6.

Tsoi *et al.* observed that this ratio was considerably larger in regioregular P3HT than in regiorandom P3HT, interpreting the change as correlated with molecular order^[82]. This conclusion was supported by their own simulations and those of others which predicted an increase in this ratio with increasing conjugation length or reduced backbone torsion.^[82,185]

The experimental data are in reasonably good agreement with the theoretical spectrum calculated for hexa-3-methylthiophene (H3MT) and a fluorinated variant (F-H3MT) shown in 4.11. The peaks corresponding to the primary Raman modes appear at higher wavenumbers than their counterparts in the experimental spectrum, but this is a well-documented phenomenon in such theoretical modelling and is commonly corrected by scaling the wavenumbers of each data mode by an appropriate multiplicative factor.^[82,186,187] The increase in the peak intensity ratio in fluorinated materials is also anticipated, but appears to be overestimated in the simulations.

A wide-ranging study by Merrick *et al.* provides a scaling factor of 0.9613 for the B3-LYP functional using the 6-31G(d) basis set,^[187] which in fact

Material	FWHM _{C-C}	FWHM _{C=C}	$\frac{I_{C-C}}{I_{C=C}}$
P3HT	13.3	24.6	0.272
F-P3HT	16.3	13.8	1.629
P3OT	27.5	41.7	0.424
F-P3OT	17.3	14.2	1.739
P3EHT	32.0	61.0	0.329
F-P3EHT	22.1	21.3	1.890

Table 4.6: Summary of primary peak intensity ratios.

over-corrects the theoretical results, placing the primary $C_{\alpha}=C_{\beta}$ peak at $\sim 1420\text{ cm}^{-1}$ rather than the empirical value of 1445 cm^{-1} . However, it should be mentioned that their analysis was confined to fairly small molecules, no larger than 10 atoms. In contrast, even the smallest of the oligomers modelled in this work was comprised of 62 atoms which could explain the discrepancy. It bears mentioning that other theoretical work on the Raman modes of oligothiophenes has also used larger scaling factors,^[82] so similar corrections are not without precedent.

For the simulated Raman spectrum of H3MT, a scaling factor of 0.98 produces reasonable predictions for the frequencies of the principal modes: 1447 cm^{-1} for the $C_{\alpha}=C_{\beta}$ mode and 1378 cm^{-1} for the $C_{\beta}-C_{\beta}$ mode. Lower frequency modes are still over-corrected with this scaling factor however, with some peaks appearing at lower frequencies than those observed experimentally, in some cases even before applying the scaling factor. Normalised experimental and (rescaled) simulated spectra, as well as those of F-P3HT and fluorinated hexa-3-methylthiophene (F-H3MT) are shown in Fig. 4.11.

Given the fairly accurate prediction of the Raman spectra, it seems reasonable to accept the calculated equilibrium geometries, shown in Fig. 4.12, as broadly representative of the actual materials. This suggests average interring torsion angles of 2.1° and 7.9° in the fluorinated and non-fluorinated materials respectively, which jibes well with previously discussed results suggesting that the fluorinated materials have more planar conjugated backbones resulting in improved intramolecular charge transport.

In contrast to prior work, which correlated increased conjugation length with shifting of the primary Raman modes to lower wavenumbers,^[185] both experimental and simulated spectra shift to higher wavenumbers on fluorination. A possible explanation for this discrepancy lies in the choice of fluorine as the substituent for hydrogen.

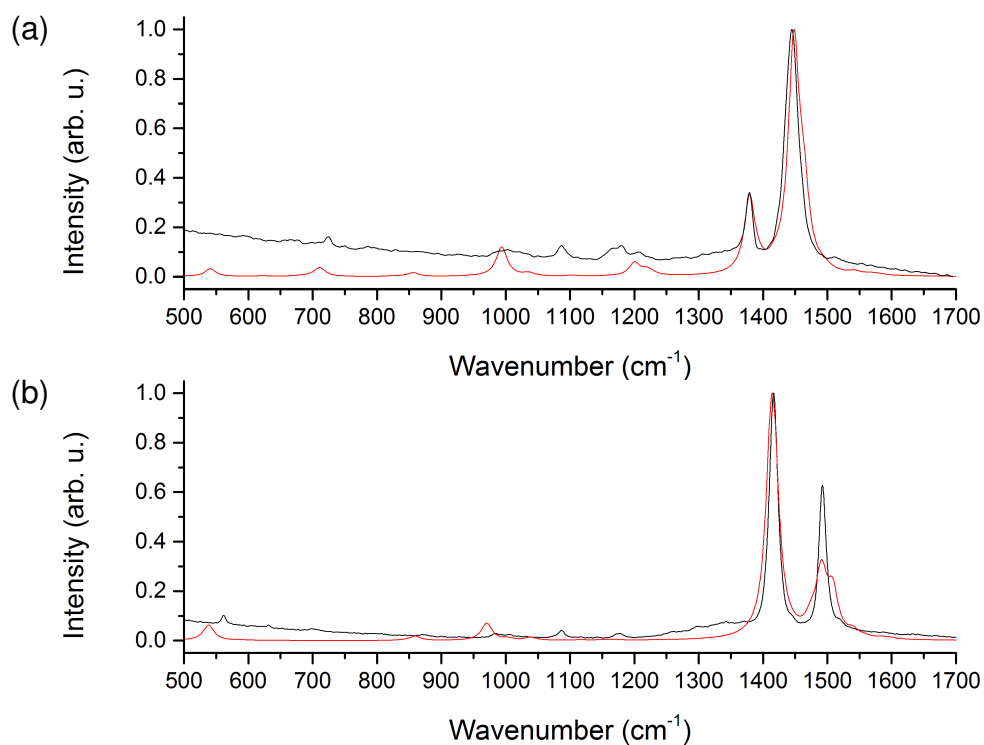


Figure 4.11: Experimental (black) and simulated (red) spectra of (a) P3HT and H3MT and (b) F-P3HT and F-H3MT.

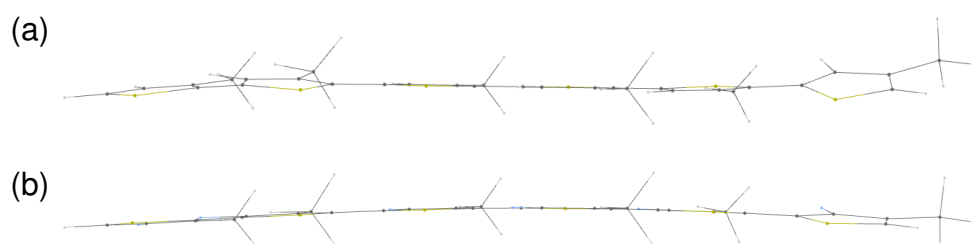


Figure 4.12: Equilibrium geometries of (a) hexa-3-methylthiophene and (b) fluorinated hexa-3-methylthiophene rendered as wireframes from an edge-on perspective.

Agosti *et al.* noted in a comparison of oligo-thiophenes, -pyrroles and -furans (which replace the sulfur atom in the thiophene ring with an amine group and an oxygen atom respectively) that electronegativity of the substituent, rather than mass, was the primary determinant of wavenumber shift of the primary ring breathing modes.^[188] They observed that the more electronegative substituents produced a significant increase ($\sim 140\text{ cm}^{-1}$ from thiophene to furan) in frequency of the primary Raman modes. While the fluorine substitution in this case is not within the ring itself, it is expected to influence electronic structure of the backbone. As the most electronegative element, a similar effect as a result of fluorination would be expected to be more pronounced than other possible substituents.

In addition to the position of the peaks, their full width at half maximum (FWHM) is reduced in the fluorinated materials, mirroring the trend observed in regioregular P3HT compared to regiorandom P3HT^[82]. With the exception of the C_β - C_β peak in F-P3HT, the FWHM of the two major peaks are at least 30 % narrower in the fluorinated materials, further evidence of a higher degree of molecular order.

4.7 Photothermal Deflection Spectroscopy

Due to its superior electrical performance and the similarity of the three types of material, PDS characterisation was restricted to P3OT and F-P3OT. The photothermal deflection spectra for these materials are shown in Fig. 4.13.

The main feature of interest in these spectra is the band edge at ~ 1.8 eV, and the Urbach energy (E_u) extracted from its gradient. The values extracted from this data are 40.0 meV and 31.5 meV for P3OT and F-P3OT respectively. As discussed in chapter 2, a lower Urbach energy correlates directly to a lower level of energetic disorder within the material, adding support to the conclusion that fluorination produces an enhanced degree of order in these materials. For context, E_u in PBTTT and IDTBT is 47 and 24 meV, respectively^[110].

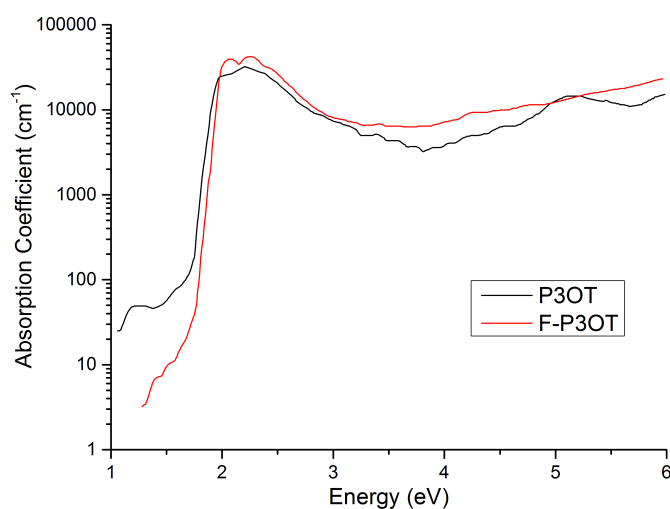


Figure 4.13: PDS spectra of P3OT and F-P3OT.

Another point of interest in the spectra is the sub-bandgap region. In P3OT there is a peak in this region that is notably absent in F-P3OT.

Features in this region are generally attributed to defects in the film. In organic semiconductors, these are likely a result of oxidative doping. For example, similar differences can be observed between the PDS spectra of P3HT and PBTTT which have been compared previously in the literature,^[96] with PBTTT being demonstrated as less prone to oxidative doping in air. While it does not directly relate to the electrical performance of the materials, enhanced environmental stability is a benefit when considering potential applications due to better device longevity, and therefore bears mentioning.

This observation jibes nicely with the lower HOMO observed in F-P3OT, which has previously been demonstrated to enhance oxidative stability^[97,169]. As the HOMO in each fluorinated polymer is suppressed relative to its non-fluorinated counterpart, this suggests that fluorination, in addition to enhancing charge carrier mobility, may also be a viable route to enhancing device stability.

4.8 Concluding Remarks

In closing then, fluorination of polyalkylthiophenes appears to increase conjugation length by eliminating torsional defects within the backbone, a conclusion evidenced by linear absorption spectroscopy and Raman spectroscopy, in conjunction with DFT simulations. Mobility values extracted from transistors support this conclusion, with fluorination producing up to a fivefold increase in charge carrier mobility, as do PDS measurements indicating lower energetic disorder in the fluorinated materials and AFM images which suggest a low degree of structural disorder. It is also likely that the deeper HOMOs in the fluorinated polymers would likewise lead to higher mobilities due to the reduced barriers to charge injection from the gold electrode (work function 5.1 eV)^[189].

GIWAXS measurements do reveal a small increase in intermolecular spacing along the π - π stacking direction in the fluorinated materials, which would be expected to hinder intermolecular charge transport mediated by hopping, often a bottleneck in highly conjugated systems. Given the mobility values extracted from transistor performance however, it seems that the enhanced intramolecular transport in the fluorinated materials attained by the reduction of torsional defects is sufficient to counteract any reduction as a result of this increased hopping distance.

It is interesting to note the difference in mobility between these materials and other recently developed systems with similar highly planar molecular structures. Specifically, systems based upon an indacene core with benzothiadiazole sub-units and selenium-substituted thiophenes, which share the same highly planar conjugated backbone as the fluorinated polyalkylthiophenes, have been reported to have mobilities in excess of $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[110] The obvious question arises: what restricts mobility in the fluorinated thiophenes relative to these other materials?

The most obvious explanation may be the correct one in this case: despite the fluorinated polyalkylthiophenes having reduced backbone torsion when compared to their non-fluorinated counterparts, DFT simulations indicate that they are not completely torsion free. The authors noted that one of the design criteria for disorder-free transport was the removal of intramolecular bonds that permit torsion wherever possible. Clearly this is not the case here, as polythiophenes contain none of the extended fused moieties such as indacene or thienothiophene, allowing the possibility of torsional defects between each thiophene ring.

Nonetheless, the substitution of hydrogen for fluorine on the second carbon in the thiophene ring appears to provide significant benefits to charge transport in polythiophenes; reducing though not eliminating backbone torsion, making it another potential candidate in the expanding array of tools available for the synthesis of novel organic semiconductors.

Additionally, these results provide considerable evidence to support the conclusion that the planarity of a conjugated polymer's backbone is more important than its crystallinity in determining charge carrier mobility. While if anything, GIWAXS suggests the fluorinated materials are less crystalline, their absorption spectra indicate a significantly higher conjugation length. This conclusion correlates well with findings in other materials, which despite lacking crystalline microstructures have superior charge carrier mobility^[110].

Chapter 5

PDTTB Copolymer Series

This chapter will discuss the properties of a PDTTB homopolymer and five 1:1 alternating copolymers with it as one of their comonomers in order to examine the effects of the different component moieties on inter- and intramolecular structure, optoelectronic properties and on charge transport.

The materials used in this study, as well as their molecular weight, dispersity and energy levels were provided by Hongliang Zhong and other members of the Heeney group at Imperial College London.

5.1 Introduction

There are several examples of organic semiconductors that employ fused aromatic structures containing relatively few single inter-ring bonds found in polythiophenes. Since the thiophene sections of such molecules are planar by nature, torsional defects tend to occur at these single bonds. By reducing their relative frequency within the backbone, it is hoped that the frequency of torsional defects is can be reduced.

Material	M _n	M _w	Đ	HOMO	LUMO	E _g
PDTTB	65	171	2.6	5.04	2.84	2.2
C-T	68	133	2.0	5.16	3.06	2.1
C-TT	40	66	1.6	5.16	3.16	2.0
C-TPD	24	28	1.2	5.38	3.48	1.9
C-BT	66	173	2.6	5.17	3.47	1.7
C-DPPDT	37	110	3.0	5.12	3.82	1.3

Table 5.1: Molecular weight (kDa), dispersity and energy levels (eV) of PDTTB materials.

Particularly well-known examples include various derivatives of fluorene such as poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-bithiophene] (F8T2) and F8BT, which have seen considerable success as active layers in both FETs and LEDs,^[14,120,190] but more recently materials like IDTBT have been reported to have impressive charge transport properties attributed to extremely low structural disorder^[110].

The PDTTB monomer is based on a single fused aromatic unit of two thienothiophene groups fused to a central benzene ring, with a pair of dodecyl side chains to enhance solubility. The copolymers include a variety of widely used moieties as comonomers: thiophene (T), thienothiophene (TT), benzothiadiazole (BT), thienopyrroledione (TPD) and diketopyrrolopyrrole-dithiophene (DPPDT). For brevity, the copolymers will be referred to using the nomenclature C-X, where X is the abbreviation for their comonomer.

The variation around a common theme provides an excellent opportunity to study the effects of these groups on various properties of the resulting copolymers, both in isolation and in comparison with each other. Their chemical structures are shown in Fig. 5.1 and their chemical properties are summarised in table 5.1.

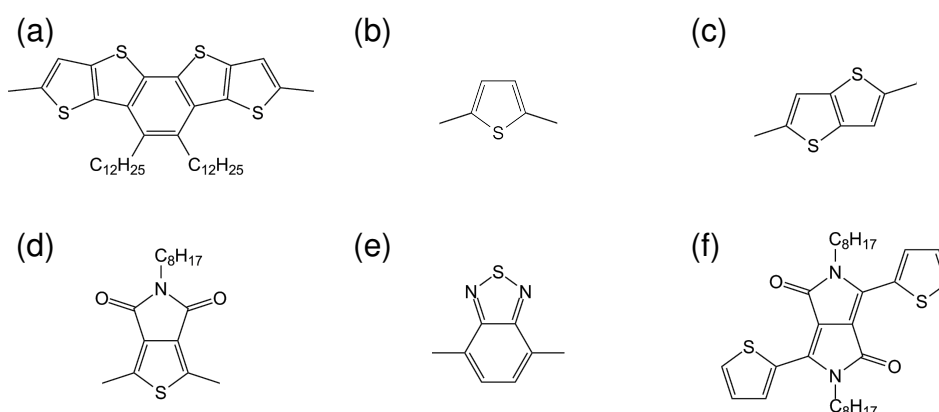


Figure 5.1: Schematics of (a) dithienothiophenebenzene (DTTB), (b) thiophene (T), (c) thienothiophene (TT), (d) thienopyrroledione (TPD), (e) benzothiadiazole (BT) and (f) diketopyrrolopyrrole-dithiophene (DPPDT) moieties.

Moieties like T and TT, and to a lesser extent BT, have the advantage of being relatively small, and are therefore expected to produce fairly minor changes in backbone structure.

While each of the comonomers is formed from aromatic rings, the TPD and BT moieties are distinguished by extending out orthogonal to the backbone rather than along it as is the case in the others. This difference may be crucial in terms of the effects of the substitution on backbone torsion, as observed previously with the TT moiety in PBTTT compared to other polythiophenes^[116].

The TPD, BT and DPPDT moieties provide electron-withdrawing groups to produce a donor-acceptor or ‘push-pull’ electronic structure, which has seen considerable use in a variety of optoelectronic devices: whether in FETs where the decreased bandgap lowers the barrier to charge injection^[12,90,95,108,114] or photovoltaics where it allows absorption of a broader segment of the solar spectrum^[101,191]. The combination of this property with a variety of differently structured comonomers will hopefully shed

light on how donor-acceptor materials perform within a family of similar yet distinct materials.

5.2 Field Effect Transistor Performance

Transfer and output characteristics for the PDDTB and C-T, C-BT, C-TPD and C-DPPDT copolymers are shown in Fig. 5.2, and extracted mobilities from linear and saturation modes for the entire series are summarised in Table 5.2. Characteristics for C-TT devices are omitted due to them suffering dielectric breakdown at gate voltages higher than approximately 20 V. While mobilities could be extracted from the linear regime in this material, the lack of data from higher gate voltages rendered extraction of mobility in the saturation regime impossible and meant insufficient data was available to produce meaningful characteristics.

Transistor operation was quite mixed. On-off ratios for materials aside from C-TPD and C-DPPDT were low, on the order of 10 - 10^2 , with C-DPPDT and C-TPD exhibiting higher values of 10^3 and 4 respectively. However, even these numbers are relatively low in comparison to materials reported elsewhere^[35], suggesting that further work on device fabrication is needed to produce ideal transistors. Threshold voltages however, were very small in all materials, never exceeding 0.8 V.

The mobility values are of PDDTB and C-T are fairly unremarkable, on the order of 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is comparable with other commonly

Material	μ_{lin} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_{sat} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Devices
PDDTB	$3.64 \pm 0.95 \times 10^{-3}$	$3.73 \pm 0.89 \times 10^{-3}$	9
C-T	$2.77 \pm 1.03 \times 10^{-3}$	$4.08 \pm 1.11 \times 10^{-3}$	11
C-TT	$5.81 \pm 5.13 \times 10^{-3}$	-	4
C-TPD	$4.51 \pm 0.19 \times 10^{-5}$	$1.10 \pm 0.29 \times 10^{-4}$	11
C-BT	$4.48 \pm 4.11 \times 10^{-4}$	$1.60 \pm 0.70 \times 10^{-4}$	5
C-DPPDT	0.127 ± 0.029	0.200 ± 0.072	8

Table 5.2: Charge carrier mobility in PDDTB materials.

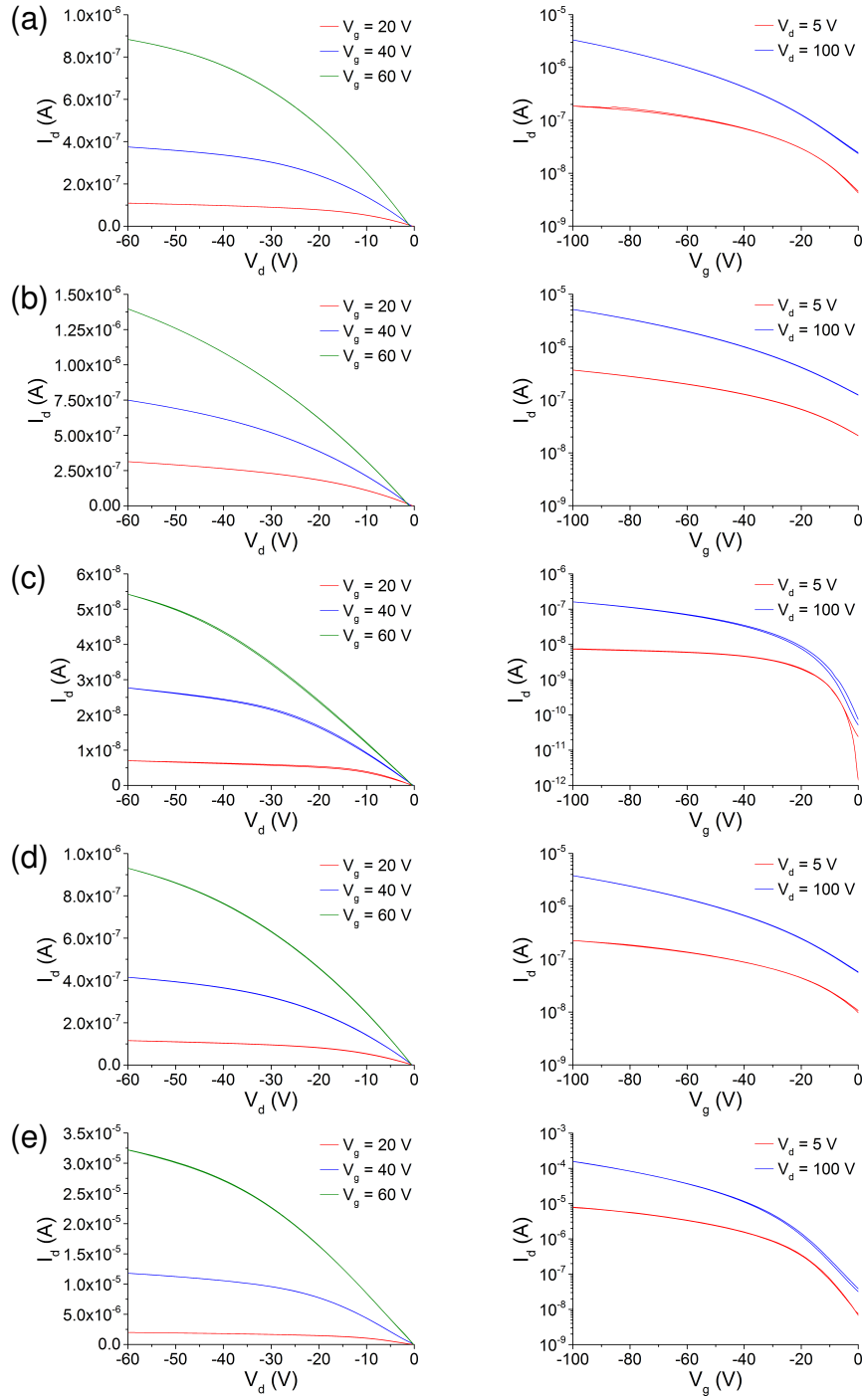


Figure 5.2: Output (*left*) and transfer (*right*) characteristics from FETs with active layers of (a) PDTTB, (b) C-T, (c) C-TPD, (d) C-BT and (e) C-DPPDT.

studied materials such as spin-coated P3HT or F8T2^[112,192]. Given their similar molecular weights, there is a possibility that the thiophene moiety, while not impeding charge transport in such a D-A copolymer, also does little to enhance it.

Conversely, C-TPD and C-BT exhibit considerably lower mobilities, on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is somewhat unexpected given the far superior performance of other materials incorporating these or similar moieties^[11,32,35,193], but illustrates the complexity of designing new organic semiconductor materials.

The precise reasons for their low performance will be discussed throughout the rest of the chapter, but based purely on their chemical structure, one hypothesis would be that a higher degree of torsion between copolymer units in these materials acts to disrupt charge transport. As noted previously, these materials are the only ones whose copolymer moieties extend orthogonally from the backbone. In the case of C-TPD the situation is exacerbated by the presence of relatively long alkyl side chains. Previous work has shown the importance of side chain density in polymeric materials^[107], with specific reference to the obstacles produced by high side chain density to efficient molecular packing. Due to the compact nature of the TPD moiety, side chain density in *trans* C-TPD (with side chains extending from the opposite side of the backbone than those of the DTTB moieties) would be comparable with regioregular P3HT, which can assume a variety of packing conformations depending on processing conditions. In the *cis* configuration however, side chain density would increase by more than 50%, with potentially serious implications for interchain order.

C-TPD also has the lowest molecular weight of any of the materials by a considerable margin, almost a factor of 3 less than the homopolymer. It bears mentioning that a similar difference in M_n in studies on the effect of molecular weight by Kline *et al.* accounted for anything between 1-2.5

orders of magnitude difference in mobility^[112]. However, even allowing for such a dramatic improvement in mobility with molecular weight, C-TPD would still be expected to underperform relative to the homopolymer at comparable values of M_n .

Another possible reason for the low mobility of C-TPD could be larger injection barriers resulting from its relatively low HOMO relative to the other materials.

C-BT, meanwhile, M_n almost identical to the homopolymer despite exhibiting mobilities an order of magnitude lower, suggesting that the low mobility in this material is more intrinsic to the copolymer itself than related to its molecular weight.

In spite of the aforementioned frequency of dielectric breakdown in C-TT, mobilities extracted from the linear regime are higher than those of PDTTB and C-T by approximately a factor of 2. However, given the variance these mobilities, caution must be exercised in drawing definitive conclusions. At the very least, the fact that the higher mobilities extracted from these devices approach or even exceed $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, even though C-TT has one of a considerably lower M_n than the other materials, suggests that further research focussing on the processing of this copolymer would be a worthwhile effort. Indeed, it would not be entirely surprising if incorporation of the TT moiety enhanced charge carrier mobility. Its inclusion in materials such as PBTTT produced significant increases in mobility due to the reduced backbone torsion and increased conjugation length resulting from its rigid, planar nature^[30].

The cause of the frequent dielectric breakdowns lies in the extreme difficulty of producing smooth films from these polymers. Due to its extremely low solubility, even across a variety of solvents, at elevated temperatures and after mixing for over 48 hours, undissolved aggregates of polymer

remained which could not be removed by filtration. Attempts to do so resulted in solutions with such low concentrations that films produced with them did not fully coat a substrate.

Undissolved aggregates in unfiltered solutions were deposited during film formation, leading large clumps of disordered aggregate material being deposited across the substrate. These clumps, often as much as an order of magnitude thicker than the rest of the film, effectively reduced dielectric thickness to the point that breakdown became all but unavoidable at even moderate gate voltages. The same issue affected C-BT, although in its case the aggregate clumps were considerably smaller and thus dielectric breakdown was generally not a problem. A possible reason for the low solubility of C-TT is the geometry of the moiety. While the other fused moieties have an angle incorporated into their structure, allowing copolymer chains containing them to curve to a certain degree, TT is by contrast entirely linear. As seen reported by Rieger *et al.*, this can seriously impact both solubility, microstructure and charge carrier mobility^[194].

Given the difference in mobility values extracted from C-TT and C-BT, it seems dubious to blame these difficulties for the poor performance of the latter when the former outperforms the baseline homopolymer by a considerable margin in its better devices. Instead, it may be that the relative isolation of the disordered regions from each other causes current to flow around them, instead travelling through the more ordered regions.

By far the highest performance was observed in C-DPPDT, with mobility values above $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, on par with some of the higher values observed in semicrystalline polymer materials to date^[2,91]. It is of particular note that it is the only copolymer with a donor-acceptor structure to have outperformed the homopolymer, C-T and C-TT, with both C-TPD and C-BT performing extremely poorly by contrast. The fact that M_n in C-DPPDT is relatively low, only a little over half that of the homopolymer, strongly

suggests that further research into producing higher M_n samples of the material, in addition to optimisation of material processing and device fabrication, would be fruitful in exploring the limits of its mobility in order to determine if it is a member of the growing family of high-mobility D-A copolymers that rely on well interconnected ordered aggregates rather than extended range semicrystalline structure to achieve efficient charge transport^[6,24].

5.3 Low-Temperature Field Effect Transistor Performance

Mobility values were also extracted from the PDDTB and its copolymers over a range of temperatures from 200-340 K in order to calculate the activation energy for electron transport (E_a). The extracted values are shown in table 5.3. Unfortunately, values for C-BT and C-TT could not be extracted due to the devices suffering dielectric breakdown before sufficient data points at different temperatures could be acquired to produce a meaningful value. Activation energy is correlated with structural disorder^[26], so it is expected that higher mobility materials will have lower activation energies.

Transfer characteristics for the PDDTB copolymers at 200 and 300 K are shown in Fig. 5.3. Arrhenius plots illustrating the relationship between mobility and temperature in each material are shown in Fig. 5.4.

The extracted values for E_a correlate reasonably well with the mobilities of each material, with C-DPPDT having by far the lowest activation energy, in line with its high charge carrier mobility. The PDDTB homopolymer and C-T and C-TPD have progressively higher activation energies, tracking with the reduction in mobility.

Material	E_a (meV)
PDDTB	174
C-T	216
C-TPD	230
C-DPPDT	109

Table 5.3: Summary of activation energies extracted from cryogenic FET measurements for the PDDTB series.

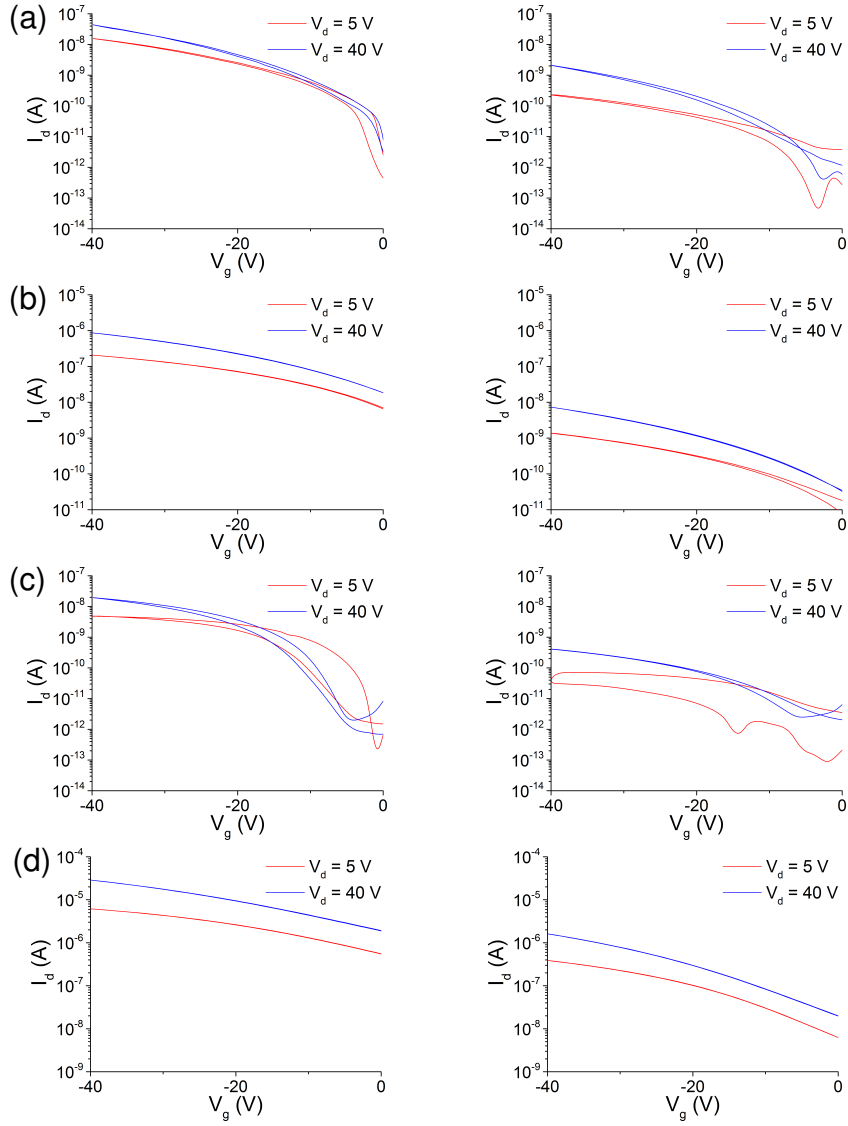


Figure 5.3: Room temperature (300 K) (*left*) and low-temperature (200 K) (*right*) transfer characteristics from FETs with active layers of (a) PDTTB, (b) C-T, (c) C-TPD and (d) C-DPPDT.

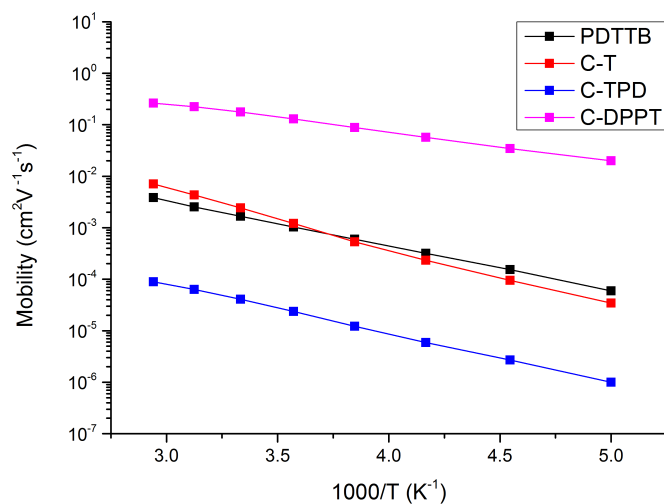


Figure 5.4: Arrhenius plot showing the relationship between mobility and temperature for the PDDTB and its copolymers.

The outlier in this data set is C-T, which possesses a somewhat higher mobility than its activation energy would suggest.

A possible explanation for the discrepancy can be found in the absorption spectrum of C-T which despite many similarities to the homopolymer exhibits a significant amount of broadening in its spectral features, suggesting a higher degree of variability in its structure than the homopolymer and offering a plausible explanation for its unexpectedly high activation energy.

5.4 Atomic Force Microscopy

AFM topography images from PDTTB and the various copolymers are shown in Fig. 5.5. By and large the structures observed in these images do not differ greatly from those seen in the alkylthiophenes presented in the previous chapter and other materials reported elsewhere in the literature, with the same nodular structure in evidence, in PDTTB, C-T and C-TPD (Fig. 5.5 (a), (b) and (e))

The topology of C-TT shows the aggregate deposits discussed in Section 5.2. While there are similar regions in some of the other materials, the areas on the C-TT film are considerably higher than on the others, protruding more than 100 nm from the film's surface, resulting in a thinner dielectric layer and therefore a higher likelihood of dielectric breakdown.

Interestingly, aside from these regions the film appears very well ordered, possessing a terraced microstructure similar to that observed in PBTTT^[30], offering an explanation for its relatively good performance prior to dielectric breakdown. This suggests that if a good solvent could be found for the TT copolymer and film formation were optimised in order to eliminate the deposits of undissolved polymer the material might enjoy higher charge carrier mobilities.

Like the F-P3HT films discussed in Section 4.3, charge transport through the C-TT layer is expected to take place through the semicrystalline regions beneath the aggregate deposits

Given that charge transport is expected to be confined to the well-ordered regions at the substrate level due to the TGBC architecture, such increases might be small, but device stability should be drastically improved.

The surface of C-BT films also exhibits a microstructure consisting of a network of fibrils like those observed in F-P3EHT and in some carefully

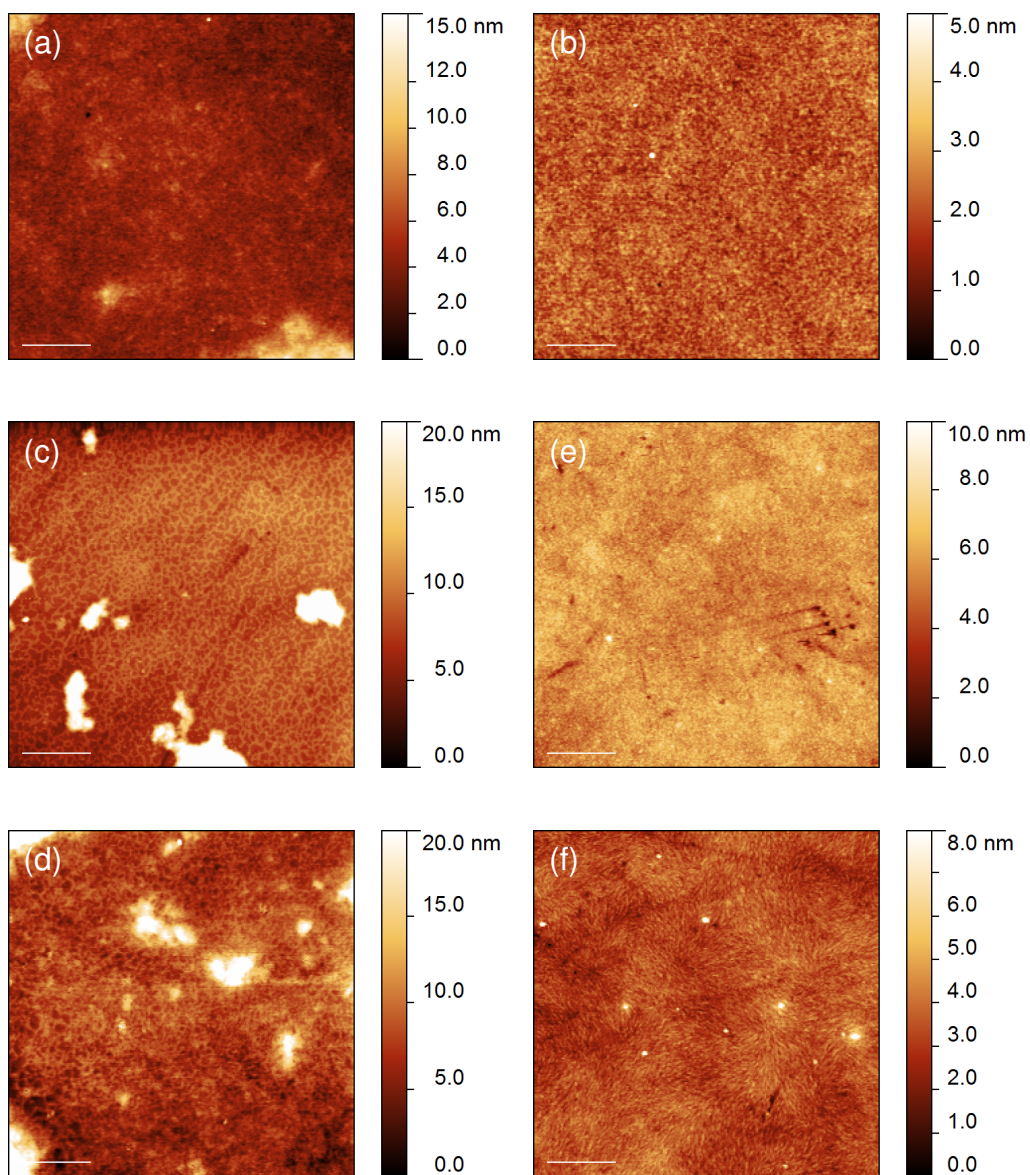


Figure 5.5: AFM topography images of (a) PDDTB, (b) C-T, (c) C-TT, (d) C-TPD, (e) C-BT, (f) C-DPPDT. Scale bars represent 1 μm.

prepared films of P3HT^[181]. Generally, these fibrillar microstructures have poor charge carrier mobilities, at least at the macroscopic scale. Charge transport within a particular fibril can be relatively good but charge transfer between fibrils tends to be extremely slow, resulting in the poor bulk performance. Like C-TT, C-BT films contained a certain amount of undissolved polymer aggregates, though not as much as the former. In some cases this did lead to dielectric breakdown, but not approaching the near-universal problem that it was in the other copolymer.

Finally, there is the somewhat unusual microstructure of C-DPPDT which has a set of regions at apparently discrete heights like the terraced structures observed in other materials but that appear to be composed of fibrils similar to those observed in materials such as nano-ribbon phase PBTTT^[144], albeit smoother and with a smaller characteristic length scale. In contrast to PBTTT however, the fibrils in C-DPPDT are too wide to be a line of fully chain-extended polymer chains: their approximate width of 30nm would suggest a chain length of over 100 copolymer units, while their molecular weight places the upper limit slightly over 30. Moreover, its superior charge carrier mobility suggests that interchain charge transport is considerably faster than that observed in ribbon-phase PBTTT.

Overall, the PDTTB copolymers possess microstructures comparable with existing materials which broadly correlate with their extracted mobilities. Specifically, the terraced previously observed in PBTTT and seen in C-TT appears to correlate with faster charge transport, but here the link was obscured by the material's poor solubility leading to the formation of films with large areas of disordered aggregates. The microstructure of C-BT shares similarities with fibrillar structures observed in other materials, and appears to suffer from the same intermolecular bottlenecks to charge transport. C-DPPDT has a somewhat unusual microstructure with similarities to both fibrillar and terraced structures observed elsewhere, though with notable differences that distinguish it from both.

Nonetheless, the larger domains (relative to the other copolymers) do broadly correspond with the material's higher charge carrier mobility.

5.5 Linear Absorption Spectroscopy

As with the fluorinated polythiophenes, studying the linear absorption spectra of the PDTTB copolymer series can provide indications of the structural disorder of in each material. While there is no pre-existing body of work as extensive as that available for P3HT, certain spectral features are relatively general. Specifically, the intensity ratio of the A_{0-0} and A_{0-1} peaks is still relevant in producing an estimate of backbone conjugation length in several of the copolymers, while changes in bandwidth or frequency of the absorption spectrum provide similar indicators of disorder.

The absorption spectra of the homopolymer and each copolymer are shown in Fig. 5.6. In contrast to the polythiophenes discussed in the previous chapter, there are considerable differences between the spectra due to the far more pronounced differences in their chemical composition and structure.

The spectra of the homopolymer and C-T are quite similar, exhibiting the same double peak observed in the polythiophenes corresponding to absorption from the ground state to the first or second vibronic band. The homopolymer's spectrum is more well-defined than that of C-T, suggesting less variation in conjugation length in the former, though the $I_{0-0} : I_{0-1}$ ratio suggests a higher average conjugation length in the latter. The differences are relatively minor however, which meshes well with the similar charge carrier mobility extracted from the two materials.

C-TT possesses a similar spectrum, but is slightly red-shifted compared to the homopolymer and C-T and has a higher intensity ratio, both suggestive of a higher conjugation length, bearing out the higher mobilities extracted from this material. Its broader spectral features indicate a higher variation in chain conjugation lengths, which would generally be associated with more disordered materials. However, in C-TT there

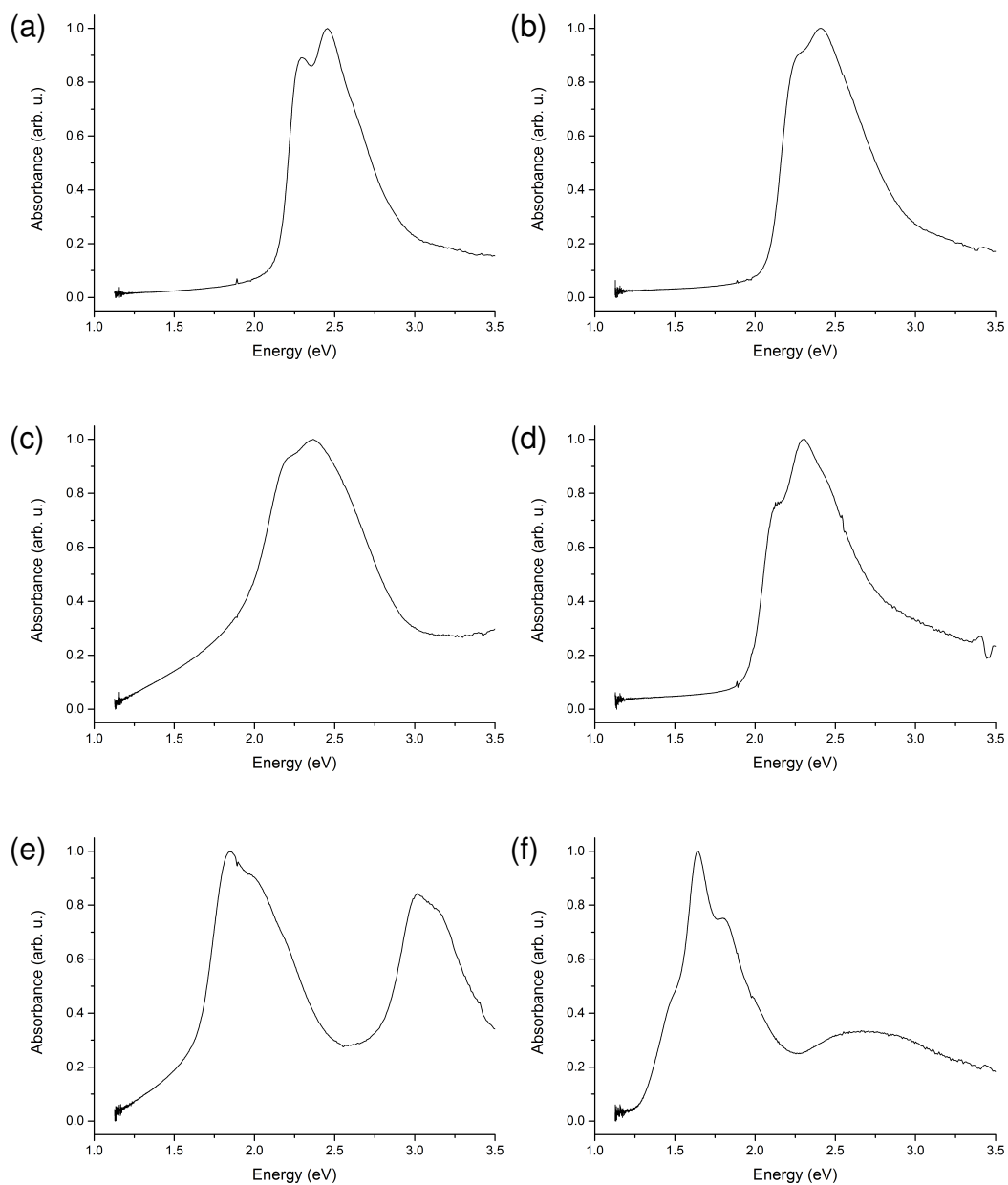


Figure 5.6: Linear absorption spectra of (a) PDDTB; (b) C-T; (c) C-TT; (d) C-TPD; (e) C-BT; (f) C-DPPDT.

are two different microstructures: ordered terraced regions and disordered aggregate deposits. The broadened absorption spectrum can be attributed to the disordered regions of undissolved polymer which are expected to contain both shorter conjugation lengths than the terraced areas and a wider distribution of conjugation lengths.

C-TPD shares several similarities with C-TT, with peaks at much the same energies and the same characteristic peak pair. The crucial difference lies in the ratio between the intensities of the two peaks, which is considerably lower than in the other materials. The implication of a reduced conjugation length correlates well with the relatively poor charge carrier mobility noted in Section 5.2.

In contrast to the fairly similar spectral features of the other four materials, the spectra of C-BT and C-DPPDT are markedly different, both with peaks at significantly lower energies. The analysis applied to the other copolymers seems unlikely to apply to these materials due to their strong donor-acceptor characteristics. The addition of the electron accepting BT or DPPDT moieties is expected to lower the bandgap, and hence the absorption edge, before any consideration of the effects of conjugation length on the chromophores. However, characterisation via other spectral features is more generally applicable.

First, C-DPPDT has the narrowest spectral features of the entire series, indicating a relatively high uniformity in its structure. Secondly, as described in the previous chapter, the $I_{0-0} : I_{0-1}$ intensity ratio in a material can be used to estimate its conjugation length. Precise calculation in this case proved less useful, as the method used previously contained several assumptions which while reasonable for polythiophenes are less so in these materials. Consequently, applying the same analysis here produces estimates of conjugation length greater than the chain length of the polymers given their molecular weight. We can, however, examine the relative ratios to draw some qualitative conclusions along similar

Material	$I_{0-0} : I_{0-1}$
PDTTB	0.890
C-T	0.898
C-TT	0.932
C-TPD	0.766
C-BT	1.118
C-DPPDT	1.330

Table 5.4: $I_{0-0} : I_{0-1}$ ratios of the PDTTB copolymers.

lines. Intensity ratios for the various materials are summarised in Table 5.4.

The ratios in PDTTB and C-T, C-TT and C-TPD correlate well with the relative extracted mobility values, with the PDTTB and C-T producing comparable values, C-TT being slightly higher and C-TPD the lowest, all of which aligns with the extracted mobilities of those materials. In the case of C-TT, this suggests that the aggregate deposits that hindered electrical characterisation do not dominate the spectral properties of the film, although it's considerably broader spectral features do indicate wide variation in chromophore size within the film, which is expected given the existence of these disordered regions.

The inversion of the $I_{0-0} : I_{0-1}$ ratio in C-BT and C-DPPDT suggests that these materials behave more like J-aggregates than the other materials. That is, the intrachain coupling is relatively stronger in these materials compared to their counterparts^[195]. Similar observations have been made in certain mesophases of P3HT, where a nanofibre structure with improved intrachain order, thereby reducing the relative strength of interchain coupling^[181]. However, it is also possible that the shift to J-aggregate spectral features is a result of a reduction in interchain order and coupling, rather than an increase in intrachain interactions.

Indeed, given the mobilities observed in each material, C-BT and C-DPPDT appear to be examples of the latter and former cases respectively, with C-DPPDT exhibiting the higher mobilities that are expected in materials with higher intrachain order, while the lower values of C-BT suggest that the spectral changes are more likely a result of inferior interchain order. AFM data supports this conclusion, given the contrast between the relatively ordered, fibrillar structure of C-DPPDT and the more disordered C-BT which includes an amount of disordered aggregate material, albeit less than observed in C-TT films. Additionally, the calculated structure for C-BT (see Section 5.6) exhibits considerable torsion between comonomer units, which offers an explanation for the inferior interchain order.

5.6 Raman Spectroscopy

Despite lacking a prototypical example as widely studied as P3HT as a reference, PDTTB and its copolymers share several features of their Raman spectra with many other organic molecules, including the fluorinated polythiophenes discussed in the previous chapter. Specifically, the characteristic peak in the region of 1450 cm^{-1} corresponding to the $C_{\alpha}=C_{\beta}$ stretching mode is observed in the spectra of all of the materials, as well as the usually less intense $C_{\beta}-C_{\beta}$ stretching modes around 1390 cm^{-1} . Additionally, the ratio between the two principal carbon bond peaks may still act as an indicator of structural order. The ratio for each material is listed in Table 5.5.

The Raman spectra of the PDTTB copolymer series are shown in Fig. 5.7. Due to their varied optical properties discussed in the previous section, the wavelength of the excitation laser had to be carefully chosen in order to avoid fluorescence swamping the Raman signal. For the homopolymer, C-T, C-BT and C-DPPDT this was relatively straightforward: the first two could be probed with the same 785 nm laser used for the F-P3AT materials discussed in the previous chapter, while the latter two could be probed with a 532 nm laser, the energy of which ($\sim 2.3\text{ eV}$) falls in a local minimum of their absorption spectra (see Fig. 5.6).

The remaining materials (C-TT and C-TPD) however, posed more of a challenge. Both produced extremely weak Raman signals under 785 nm excitation, necessitating a shift to shorter wavelengths. Unfortunately, due to the slight redshift in their absorption spectra relative to the homopolymer, both the 633 nm and 532 nm lasers produced a fluorescence signal. As 532 nm excitation produced much better Raman signal strength, with practically nothing discernible in the 633 nm spectra, Raman spectra from these two materials were produced using 532 nm excitation as well.

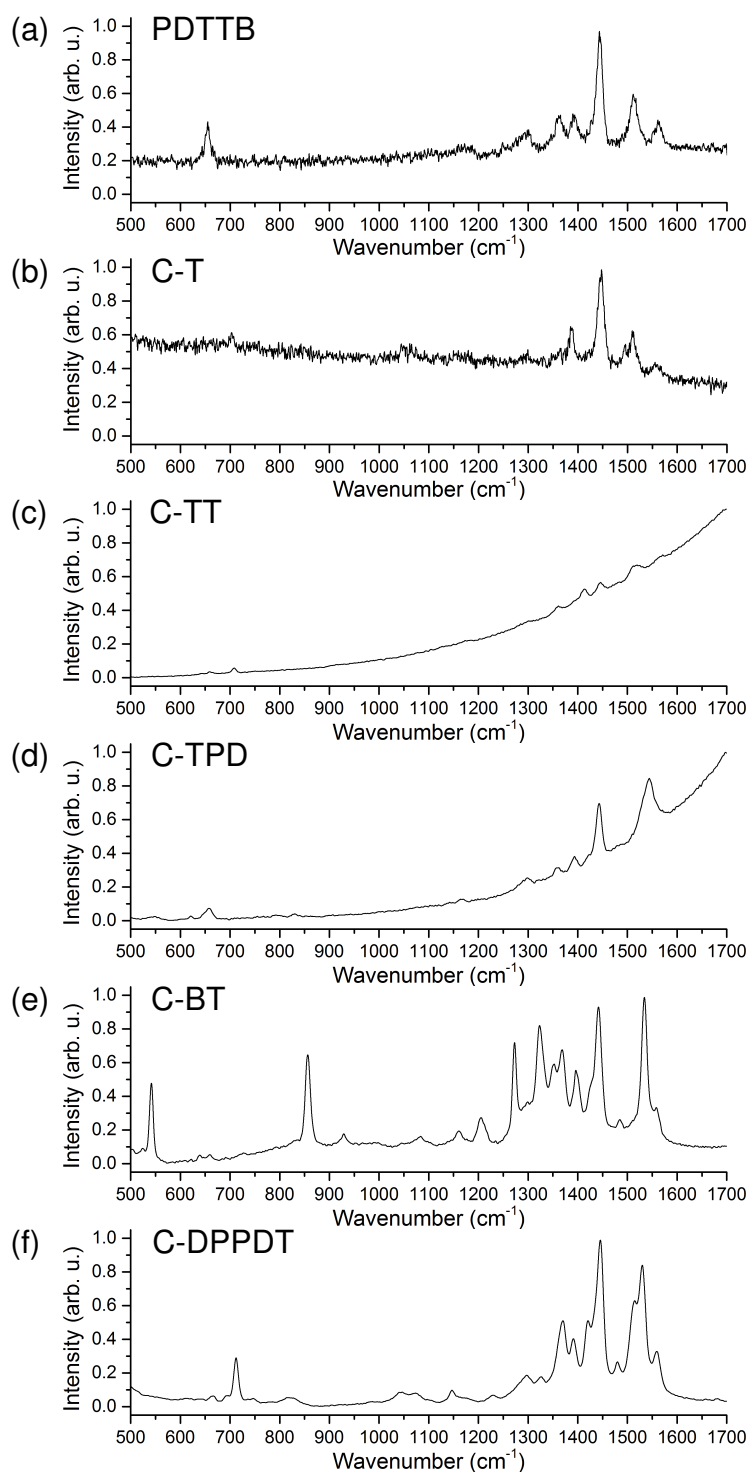


Figure 5.7: Raman spectra of (a) PDDTB; (b) C-T; (c) C-TT; (d) C-TPD; (e) C-BT; (f) C-DPPDT.

The principal peak intensity ratios, like some of the other results discussed in this chapter, are somewhat mixed in terms of how well they correlate with the mobility measurements discussed in Section 5.2. Specifically, while the intensity ratios in the homopolymer, C-TT, C-TPD and C-DPPDT align with their respective mobilities and other indicators of disorder, C-T and C-BT are somewhat more difficult to interpret with the same straightforward approach.

For C-T, the higher intensity ratio does correlate with the analysis in Section 5.5, which also indicated a higher degree of order than in the homopolymer, although the difference obtained *via* Raman spectroscopy is considerably higher.

The relatively higher likelihood of torsional defects in materials containing the smaller thiophene moiety than those with larger fused copolymer groups offers a potential explanation for this, while another explanation could be poor intrachain transport in C-T relative to the other materials, counteracting an otherwise improved interchain mobility.

In C-BT, the same trend is observed as in absorption spectroscopy: narrow spectral features that appear to suggest that the material should have

Material	$\frac{I_{C-C}}{I_{C=C}}$
PDTTB	0.261
C-T	0.401
C-TT	0.575
C-TPD	0.227
C-BT	0.583
C-DPPDT	0.406

Table 5.5: Summary of carbon peak intensity ratios.

a higher mobility than it in fact does. However, results previously published by Donley *et al.* note that in F8BT a characteristic peak at $\sim 1360\text{ cm}^{-1}$ associated with the carbon-carbon stretching mode between the benzene ring and thiadiazole moiety becomes more intense for molecular structures with higher torsion angle between the BT moiety and the conjugated backbone^[90]. More specifically, They linked torsion angle to the relative intensity of this peak to the primary ring stretching mode of the BT moiety at $\sim 1545\text{ cm}^{-1}$.

While peaks do appear at these wavenumber in the other copolymers (a characteristic thiophene ring-breathing mode exists in the range, see Section 4.6), the relative intensity in C-BT is markedly higher. While direct comparison to existing literature is somewhat problematic due to the differences in the structures involved, the increased intensity and distinct character of the BT stretching modes in conjunction with similar indications from absorption spectroscopy and the results of quantum chemical simulation give more weight to the interpretation that the intensity of these peaks is indicative of high torsion between the PDTTB and BT copolymer moieties.

While a similar analysis could be hypothetically applied to C-TPD given the similarities between its structure and that of C-BT, extracting much useful data from its Raman spectrum is difficult due to large fluorescence signals that were present at all available excitation wavelengths.

It seems unlikely however, that the same comparison of ring-stretching mode intensities would be applicable to C-DPPDT. While the DPP moiety does possess the same fused ring structure as BT, the crucial difference is that this moiety does not extend orthogonally from the conjugated backbone as noted previously. Thus, while the intensity of these modes can be expected to increase with backbone torsion in C-BT due to the reduced steric hindrance from the rest of the backbone in high torsion conformations, the related stretching modes in C-DPPDT would be in the

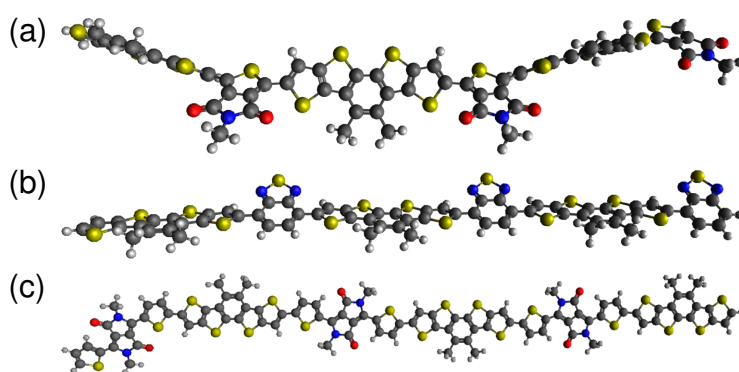


Figure 5.8: Simulated structures of (a) C-TPD; (b) C-BT and (c) C-DPPDT

same axis as the backbone and therefore less likely to be affected by changes in torsion. The narrow spectral features and relatively high ratio between the principal carbon-carbon stretching modes however, do offer further evidence to support the characterisation of this copolymer as a low disorder material.

This analysis correlates well with quantum chemical modelling of the various materials, contrasting the significant intrachain torsion within C-BT and C-TPD with the relatively torsion-free C-DPPDT (Fig. 5.8).

5.7 Photothermal Deflection Spectroscopy

Photothermal deflection spectroscopy (PDS) provides an alternative, more direct method to probe energetic disorder in materials, making it a useful complement to the methods discussed thus far. Spectra obtained from the PDS measurements of PDDTB and its copolymers are shown in Fig. 5.9 with extracted Urbach energies shown in Table 5.6.

As before, the results are somewhat varied in terms of how straightforward they are to interpret in light of the charge carrier mobilities extracted from field effect transistor measurements. C-DPPDT has the lowest Urbach energy, which correlates well with its relatively high mobility and the analysis of its absorption and Raman spectra discussed previously. It is lower than values extracted from PBTTT, and comparable with other polymers containing the DPP moiety, but not as low as in materials such as IDTBT or diketopyrrolopyrrole-thiophene-thienothiophene (DPPTTT) with much higher charge carrier mobilities^[110].

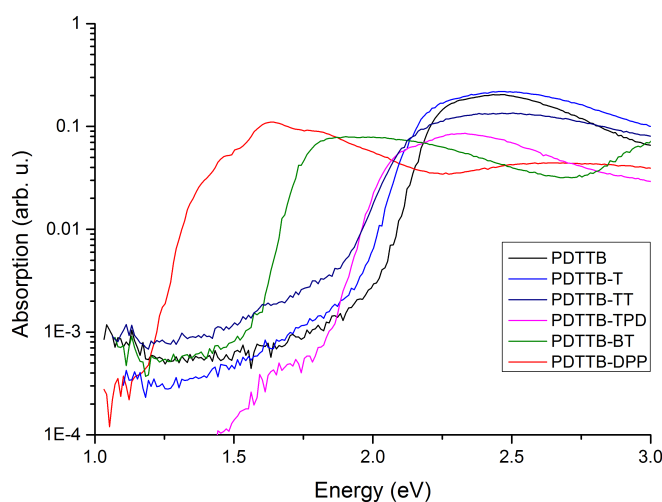


Figure 5.9: PDS spectra of PDDTB and its copolymers.

Material	E_U (meV)
PDTTB	49
C-T	54
C-TT	75
C-TPD	49
C-BT	40.5
C-DPPDT	40

Table 5.6: Urbach energies of PDTTB materials.

While the similar values for PDTTB and C-T correspond well to their similar mobilities and microstructures, the Urbach energies of the other copolymers are less straightforward to explain if working under the assumption that lower energetic disorder results in higher charge carrier mobilities.

Despite its poor electrical performance, C-TPD exhibits the same Urbach energy as PDTTB while C-BT has an Urbach energy almost identical to C-DPPDT, despite having one of the lowest mobilities of the entire series. This type of anomalous behaviour has been seen previously in polytriarylamines^[96], implying that low energetic disorder in and of itself is not sufficient to guarantee high charge carrier mobility. Referring to the analysis in Section 5.6 serves to resolve this incongruity. As noted there, torsion between copolymer units, expected to be more pronounced in C-TPD and C-BT, acts to disrupt intermolecular packing, hindering charge transport above the molecular level. Such behaviour would not necessarily lead to higher energetic disorder, but would manifest in lower mobility in FET devices.

The extremely high Urbach energy extracted from C-TT is also at odds with a mobility slightly higher than that extracted from PDTTB. The disparity can be attributed to the undissolved polymer deposits on the surface

of the film. As the deposits are expected to contain largely disordered material due to the lack of opportunity to reorder during film deposition, and since PDS cannot selectively target the more ordered regions, a high energetic disorder is straightforwardly explained as the higher disorder deposits dominating the measured response.

5.8 Concluding Remarks

As research continues to expand the collective understanding of more and more organic semiconductors, the capacity for rational design of future materials expands. This is equally true of work focussing on detailed characterisation of a particular moiety, or more general work developing theoretical frameworks to predict the behaviour a wide variety of systems. Indeed, the two approaches support one another, with the former either confirming or disconfirming the existing framework and in either case offering more data to refine the theories as necessary.

The work discussed in this chapter presents a detailed examination of a specific set of copolymers, but their shared DTTB copolymer moiety provides an opportunity to discuss each material in the context of the entire series.

The homopolymer is in many respects fairly unremarkable: it does not exhibit particularly high or low mobility, its morphology appears to conform to the amorphous nodular structure observed in many other polymer films and spectroscopic measurements reproduce aspects common to many conjugated materials from the characteristic double peak its absorption spectrum to its similar primary Raman modes. Even its Urbach energy is comparable to previously published values for P3HT^[96].

Perhaps unsurprisingly, C-T is the most similar of the copolymers to the homopolymer. This holds true across all characterisation methods. The two materials have charge carrier mobilities that are similar to materials like spin-coated regioregular P3HT.

C-DPPDT has, by quite a considerable margin, the highest charge carrier mobility observed in the series. This is attributed to its push-pull structure, shared with C-BT, but without that material's density of trap states observed via absorption spectroscopy. In addition, many of the expected

features of high mobility polymers are present, including low energetic disorder, a well-ordered microstructure - albeit a slightly unusual one - and well-defined spectra indicative of a high degree of uniformity amongst the individual polymer chains within a film.

In spite of sharing many of the same properties as C-DPPDT, C-BT exhibited a remarkably low charge carrier mobility, which is attributed to the torsion between the different comonomer units indicated by both Raman spectra and by the results of quantum chemical simulation. This torsion is expected to disrupt intermolecular packing, reducing the transfer integrals between adjacent molecules and charge carrier mobility in turn.

Quantum chemical simulations suggest that this low performance is a result of torsion in the material's conjugated backbone. Preliminary analysis suggests that there is a torsional angle of approximately 30° between copolymer units, considerably more than the calculated values for the other copolymers, which appear to be relatively planar.

A similar situation appears to be the cause of the low charge carrier mobility in C-TPD, which has torsional angles of approximately 50° between monomer units in the simulated structure, although in this case the electrical performance is not at odds with the results of other characterisation as it is in C-BT: its activation energy, Urbach energy and various spectroscopic indicators of disorder all tending higher than the other copolymers in the series.

As a series, these materials emphasise the crucial importance of low torsional disorder. In spite of its low energetic disorder and promising absorption spectrum, C-BT has one of the lowest charge carrier mobilities of the entire series, it appears purely due to the aforementioned torsion. This stands in stark contrast to PDDTB, C-T and C-TT which share fairly unremarkable markers for disorder but have relatively planar simulated structures and much higher charge carrier mobilities.

Various possible avenues for future research into these materials present themselves. Firstly, while electrical characterisation of C-TT was hindered due to the aggregate deposits in its films, the material nonetheless exhibited a relatively high charge carrier mobility and the same microterrace structure observed in PBTtT. Refining film fabrication for this material, whether by finding a good solvent or fine tuning the zone-casting procedure, may reap dividends. This is particularly likely for its poor device stability, but enhancements to charge carrier mobility are also possible.

Secondly, while the extracted mobilities from C-BT are extremely low, the fact that the material possesses many of the indicators one would normally associate with high mobility materials, save for the aforementioned backbone torsion, suggest that investigating methods to reduce torsion in the material may be fruitful. Fluorination, as detailed in the previous chapter, could be one option, including a small moiety to space the BT group from the DTTB group could be another.

A third possibility would be to investigate C-DPPDT to determine whether its performance could be further optimised. As the highest mobility copolymer in the series this is perhaps the most obvious avenue to explore, and there are a variety of possible approaches to doing so. While the zone-casting procedure was optimised in order to produce thin films from these materials, post-fabrication steps beyond thermal annealing have not been explored, substrate functionalisation is another possibility and electrode choice has not been explored to optimise charge injection.

Chapter 6

Conclusion

In closing, I will offer some final remarks on the various materials characterised and the methods developed in the course of this thesis, in addition to offering some suggestions for future work based upon these results.

Zone-casting

In order to produce well-ordered films from most of the materials discussed in this thesis, a zone-casting procedure was optimised for each material group. Compared to spin coating this approach produced films that were considerably more uniform with corresponding improvements in charge carrier mobility, on the order of a tenfold increase.

In particular, it allowed for significantly more control over solution temperature and film formation speed, which was critical to processing the fluorinated polyalkylthiophenes and various PDTTB copolymers. While somewhat slower and more complex than other thin film fabrication techniques, this ability to adapt to more stringent processing requirements makes it a potentially valuable tool when working with low-solubility materials or when attempting to access alternative microstructures for a given material.

While the possibility was not explored in depth in this thesis, zone-casting could be trialed in a wider variety of materials as a route to improving charge carrier mobility by accessing otherwise unobtainable microstructures. Due to the higher degree of control provided by this approach there should not be major obstacles to such work, merely optimising the zone-casting parameters described in Chapter 3 for different material solutions should be sufficient.

In addition to the prospect of improved performance, zone-casting avoids the problems that spin coating encounters as substrate sizes increase and it becomes increasingly difficult to maintain a constant rotation speed^[196,197]. Since a frequently cited possibility for organic semiconductors is the production of large area devices, the potential to scale to larger scales is relevant to future applications. A secondary advantage when compared to spin coating is the better efficiency of zone-casting in terms of material usage: while during spin coating a large percentage of solution is lost, in contrast to zone-casting where the majority of solute is deposited as the solvent evaporates.

Fluorinated Polyalkylthiophenes

Based on the work discussed in Chapter 4, it appears that fluorination of sites on the conjugated backbone is a generally applicable method for increasing charge carrier mobility via reduction in backbone torsion and corresponding improvement in conjugation length. By far the best performance among the fluorinated materials was attained in F-P3OT, with F-P3HT approaching similar values. The materials with branched side-chains performed relatively poorly, though previous research has produced similar findings^[170], supporting the conclusion that branched side-chains interfere with the ability to form an ordered, tightly packed structure, at least in the absence of larger side chain spacing.

Aside from the relative mobilities of the fluorinated materials, a novel approach was also developed to produce quantitative predictions of conjugation length using absorption spectra. The relative simplicity of such measurements makes this approach a potentially valuable tool for performing rapid, straightforward characterisation of thin films.

This produced values indicative of fully chain-extended structures in F-P3OT and F-P3HT, with the expected reduced values in their non-fluorinated counterparts, but produced unphysically large values when applied to F-P3EHT.

A weakness of the existing model is that while it produces reasonable values in materials with relatively strong H-aggregate character, J-aggregate materials and the intermediate H-J aggregates seem to be outside of its scope for the time being, producing unphysically large conjugation lengths. It bears mentioning however that an attempted expansion of the model to a more general framework drawing on the work of DeJong *et al.* to allow accommodation of variable Huang-Rhys factors^[154] seemed to produce promising results in the PDTTB series, and might merit further investigation with the goal of arriving at a powerful, general method for gauging conjugation length from a set of relatively simple spectroscopic techniques.

PDTTB Copolymers

Characterisation of the PDTTB copolymer series was conducted using approaches similar to the F-P3AT study. These materials exhibited a broad range of charge carrier mobilities, with the C-DPPDT exceeding $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while C-TPD and C-BT produced values on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Due to the impact of poor solubility on film formation in C-TT and C-BT (see 5.2), establishing conclusive relationships between charge carrier

mobility and material properties was quite difficult. However, some general statements can be made.

C-T was extremely similar in terms of physical properties and electrical performance to the homopolymer, with both exhibiting mobilities comparable to materials like P3HT. The similarity between the two can be attributed to the small size of the thiophene copolymer unit relative to the others.

By contrast, in spite of including the second smallest copolymer moiety, C-TT had some of the worst electrical performance of the entire copolymer series. This fabrication process for this material, in conjunction with C-TPD, remained unoptimised even at the end of the project due to lack of a good solvent for either of them, resulting in considerable difficulty in producing uniform thin films. Nevertheless, certain areas of the C-TT films formed highly ordered microterrace structures similar to materials such as PBTTT^[2], suggesting that its performance could be significantly improved if a good solvent was found and film fabrication optimised.

C-TPD and C-BT, while not suffering from the same issues that hampered C-TT, did not perform well either, with both of their mobilities on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

In the case of the C-BT, preliminary quantum chemical modelling suggest this is due to significant torsion between the DTTB and BT moieties, which greatly hinders intramolecular charge transport, despite the donor-acceptor-donor structure produced by including the BT moiety.

The poor electrical transport in C-TPD seems to result from 2 factors: torsion between copolymer units and high side chain density interfering with close molecular packing. While the other copolymer moieties either lack alkyl side chains or (in the case of C-DPPDT) have considerably lower side chain density, C-TPD is a relatively compact moiety with a side chain, resulting in a side chain density greater than regioregular

P3HT^[107]. This increased density has the potential to disrupt backbone conjugation due to interaction between the various side chains. In the specific case of C-TPD, there is a degree of tension between the side chains and the coulombic interactions between the oxygen atoms in the TPD moiety and the sulfur atoms on the adjacent thiophenes^[35].

As noted above, by far the best performance among the copolymers was found in C-DPPDT, which exhibited mobility values over $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, on par with some of the highest measured in polymer materials to date. This is attributed to the materials planar backbone, coupled with its donor-acceptor-donor electronic structure. Combined with existing work on materials incorporating similar moieties^[96,110], this reinforces the value of fused planar moieties in the synthesis of high-performance polymeric semiconductors.

As with the fluorinated alkylthiophenes, recurring themes are the importance of precise control during film fabrication, the vital role of low disorder and the sometimes dramatic effects of relatively small structural changes at the molecular level.

Further Work

Based on the results in chapter 4, it appears that fluorination, and perhaps by extension hydrogen-like bonding generally, is another potential candidate for enforcing backbone planarity in polymer semiconductors. This could be used in conjunction with the inclusion of fused planar moieties as the substitution is made off the conjugated backbone, but the same independence from the backbone means it can potentially be used in a broad range of materials, provided they possess a suitable combination of potential fluorination sites and moieties with partial positive charge like the sulfur heteroatom in the thiophene group.

Closing Remarks

In closing, this thesis illustrates the complex interplay of factors that influence charge transport in organic semiconductors, from moiety selection to device fabrication.

Alongside other recent work it reinforces the conclusion that high crystallinity in itself is insufficient to guarantee high charge carrier mobility, but that in fact such materials must also have viable charge transport pathways between crystalline grains if they exist. Moreover, several materials with apparently amorphous microstructures have exhibited even higher mobilities.

The marked contrast between the performance of F-P3EHT and the other fluorinated materials discussed in chapter 4 and between the copolymers discussed in chapter 5, emphasises the impact of side chain packing on charge transport: an otherwise planar backbone can have its conjugation disrupted by side chain effects, and a reduction in molecular packing density can be a significant hindrance to charge transport between conjugated segments.

These results contribute to the growing understanding of the relationships between charge transport, optoelectronic properties and microstructure and underline the need for continued research to study this diverse and complex family of materials.

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