

Morphological Advancements through Sidechain Engineering for Organic Photovoltaic Applications

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Abstract

Organic photovoltaics (OPV) materials are an established class of light-harvesting, solution-processable organic semiconductors. These materials have attracted substantial interest from the scientific and commercial communities due to their potential for a low-energy, high-volume form of production, applicability to a multitude of market niches and the facile tuneability of their light-harvesting capabilities to match the desired portion of the solar spectrum. Recent research efforts over the last decade have seen both small molecular and polymeric OPV materials reach power-conversion efficiencies on the order of 10-15%, which represents an efficiency milestone that suggests the commercialization of this technology is likely within the near future.

In order to hasten this eventuality, some of the barriers to commercialization that need to be overcome include a) achieving even higher efficiencies for OPV devices in order to further drive down cost-to-power ratios, and b) establishing longer device stabilities, so that these high light-harvesting efficiencies are consistently maintained over as long a lifetime as possible. One of the key areas of OPV development that can address both these problems is the morphological optimization of the light-harvesting, or *active* layer. Unlike silicon photovoltaic devices, OPV active layers are a metastable blend of at least two semiconducting materials (a p-type, or *donor*, and an n-type or *acceptor*) in roughly equal proportions, and as a result the molecular structures of these semiconductors can heavily influence film morphology, which, due to the nature of OPV light-harvesting processes, heavily influences device efficiency. As such, a significant amount of effort in the OPV field has gone into establishing a predictive structure-morphology paradigm to extrapolate forwards from a molecular structure to envisage what bulk materials property it might possess in an active-layer blend. Unfortunately, this is decidedly non-trivial and in the absence of such a paradigm the OPV field largely advances through systematic structure-property studies. The work in this thesis utilizes these studies to gain an insight into several high-performing classes of p-type materials, where structural changes are made primarily through sidechain engineering as these represent a facile method to control film morphologies while minimizing the change to the fundamental molecular energy levels.

In the first study, a high-performance small-molecular material from the literature, **BTR**, was examined as it had been itself designed through the application of multiple sidechain engineering techniques to another precursor material from the literature, resulting in significantly improved performances. As such, it was unclear as to exactly which technique was most relevant in **BTR's** success. The work in this study therefore focused on the close examination of one of these techniques, and as a result two analogues of **BTR** were designed and synthesized with differing sidechain lengths. OPV devices incorporating these analogues and PC₇₁BM fullerenes as the acceptor were assembled, and it was found that lengthened octyl sidechains (relative to **BTR's** hexyl sidechains) had a significantly detrimental impact upon performance, whereas the shorter butyl sidechains resulted in relatively similar performances. Through the use of grazing-incidence

wide-angle X-ray scattering (GIWAXS) studies to examine the film morphology it was revealed that there was a correlation between longer sidechains and an increasing degree of film crystallinity, with this suspected to be from increased interdigitation from strengthened Van der Waals forces. It is known that films with a high degree of crystallization can hinder charge extraction processes, and so this study concluded that sidechain length was indeed important to the OPV performance of **BTR**-type materials, with hexyl-length sidechains likely the optimal size to confer the highest performance.

It was subsequently theorized that the degree of π -overlap of the benzodithiophene cores of **BTR**-type molecules could be influenced by the steric bulk of the 2D conjugated moieties attached to these cores, with an increased overlap resulting in an enhanced charge-transport network. This resulted in the second study of this thesis, where the installation of varying sidechains resulted in the design of four new **BTR**-type analogues. While a lack of single-crystal structures meant that this hypothesis could not be conclusively confirmed, upon GIWAXS analysis of the films another relationship was observed. A correlation was found between device performance and the orientation of the π -stacked cores with respect to the device substrate, which has been previously demonstrated in the literature to significantly influence device performance. Intriguingly, a more detailed analysis of these films using depth-dependant GIWAXS studies to probe their vertical composition revealed that the **BTR** analogues with higher solubilities in the deposition solvent resulted in films with a distribution of π -stacking orientations as a function of depth, whereas analogues with lower solubilities uniformly resulted in 'edge on' orientations which are known to hinder charge harvesting. While further work is needed to prove causation from correlation, this study provides evidence for the possibility that sidechain-conferred solubilities and their impact upon film formation can affect molecular orientation in the bulk.

One of the key sidechain engineering techniques that had resulted in the high performances of **BTR** was the repositioning of its alkyl sidechains away from the benzodithiophene core, thus reducing the surrounding steric bulk to allow for enhanced π - π stacking. It was hypothesized that this sidechain engineering could confer the same performance improvements when introduced on other high-performing molecules to enhance their efficiencies even further. This led to the third study of this thesis, where a series of twelve oligothiophene-based p-type small molecular materials was synthesized with regioregular, outwards-facing sidechains, in contrast to the commonly-used inwards-facing sidechains found on similar molecules in the literature. It was found that these modifications may have instead enhanced crystallinity to a detrimental level, with GIWAXS scattering patterns found to possess complexities not often observed for organic semiconductors. The lower performances exhibited by these materials relative to their counterparts in the literature with inwards-facing sidechains are believed to be due to relatively lower responses to film annealing treatments because of these increased crystallinities. Oligothiophene analogues with longer sidechains from this study were however found to exhibit slightly higher efficiencies, with the extra lengths potentially conferring an increased responsiveness to the annealing process. These results then suggest that

an optimal sidechain length may exist for these oligothiophene materials that balances enhanced π -stacking with annealing responsiveness.

Departing from the structure-property studies of previous chapters, the fourth study in this thesis instead addresses the issue of morphological stability. Block copolymers are comprised of covalently bound donor and acceptor homopolymers which ideally self-assemble into thermodynamically-favoured lamellar domains. These physically limit the extent of phase-separation possible, thereby enhancing long-term stability. In order to ensure self-assembly however, the two homopolymer blocks should ideally be as chemically distinct as possible and so here a hydrophilic p-type homopolymer and a hydrophobic n-type homopolymer are designed and synthesized so as to achieve an amphiphilic block copolymer. While this block copolymer was itself not assembled in this study, efforts were instead put into developing a synthetic strategy that would allow for the exclusive synthesis of a diblock copolymer through fine end-group control. This would reduce the polymeric impurities believed to currently limit the OPV efficiencies of block copolymer materials. This strategy was carried out through the synthesis of an asymmetrically-functionalized isoindigo n-type monomer, which was shown to grant end-group control upon Suzuki polymerization. This strategy represents a new monomer design which could theoretically be applied across multiple molecular substrates to afford more efficient polymerizations.

Declaration of Authorship

This is to certify that:

1. This thesis comprises my original work towards my PhD except where indicated at the preface,
2. Due acknowledgement has been given in the text to all other materials used,
3. This thesis is less than 100,000 words in length, exclusive of tables, graphs, bibliographies and appendices.

Calvin Jun Hao Lee, 2019

Preface

The candidate acknowledges the assistance of the following individuals towards the completion of the work described within this thesis:

- Prof. Jonathan M. White (School of Chemistry, The University of Melbourne) collected and solved the crystal structures of compounds described in this thesis,
- Dr. Jegadesan Subbiah (School of Chemistry, University of Melbourne) performed all the AFM measurements and assembled the devices and recorded their performances for all materials described in this thesis,
- A/Prof. Christopher McNeill advised on the co-interpretation of the GIWAXS scattering patterns and data,
- Dr. Valerie Mitchell assisted in the co-collection and co-interpretation of the GIWAXS scattering patterns and data.

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To Bethany, thank you for being there for me. It takes a very special person to put up with someone mid-way through a PhD (and about to leave for a foreign country).

And last but not least, thanks to my parents and extended family, who always believed in me. More than anyone else, this would not have been possible without you.

List of Publications and Conference Presentations

Several publications and presentations were produced by the work in this thesis during the term of the PhD candidature. Unless stated otherwise the total contribution from the PhD candidate does not exceed 50% but as supporting content to the overall work.

Journal papers

Calvin J. Lee, Valerie D. Mitchell, Jonathan White, Xuechen Jiao, Christopher R. McNeill, Jegadesan Subbiah and David J. Jones. Solubilizing core modifications on high-performing benzodithiophene-based molecular semiconductors and their influences on film nanostructure and photovoltaic performance. *J. Mater. Chem. A*. 2019; 7:6312-6326

Paul B. Geraghty, **Calvin J. Lee**, Jegadesan Subbiah, Wallace W. H. Wong, James L. Banal, Mohammed A. Jameel, Trevor A. Smith and David J. Jones. High performance p-type molecular electron donors for OPV applications via alkylthiophene catenation chromophore extension. *Beilstein J. Org. Chem.* 2016; 12: 2298-2314

Conference presentations

2nd Asia-Pacific Solar Research Conference. Brisbane, Australia - 2015. Poster title: Novel Synthetic Pathway for 2D Molecular Benzodithiophene Organic Semiconductors

3rd Asia-Pacific Solar Research Conference, Canberra, Australia – 2016. Poster title: Polarized Optical Microscopy on High-Performing Molecular Organic Semiconductors.

14th European Conference on Molecular Electronics. Dresden, Germany – 2017. Poster title: Towards 10% Efficiency – A Study of Benzodithiophene Analogues as High-performing Molecular Materials for Organic Photovoltaics

47th World Polymer Congress MACRO 18. Cairns, Australia – 2018. Poster title: Solar-harvesting Block Copolymers: Designing an Asymmetrically Functionalized Monomer for Exclusive Di-block Formation

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Abbreviations

2-EH	2-Ethylhexyl
5T	Pentathiophene
6T	Hexthiophene
A	Acceptor
AFM	Atomic force microscopy
AM	Air-mass
BCP	Block copolymer
B₂pin₂	Bis(pinacolato)diboron
BDT	benzo[1,2-b:4,5-b']dithiophene
BHJ	Bulk heterojunction
BTR	Benzodithiophene terthiophene rhodanine
CCL	Crystallite coherence length
CHR	2-(3-hexyl-4-oxothiazolidin-2-ylidene)malononitrile
CT	Charge transfer
D	Donor
DFT	Density functional theory
DPP	Diketopyrrolopyrrole
EA	Electron affinity
E_g	HOMO-LUMO energy gap
ETL	Electron-transporting layer
eV	Electron volt
FF	Fill factor
GIWAXS	Grazing-incidence wide-angle X-ray scattering
HOMO	Highest occupied molecular orbital
HR	n-Hexyl rhodanine
HTL	Hole-transporting layer

I-P	In-plane
IP	Ionization potential
IR	Infra-red
J_{sc}	short-circuit current density
LUMO	Lowest unoccupied molecular orbital
MN	Malononitrile
NFA	Non-fullerene acceptor
nm	Nanometer
OFET	Organic field-effect transistor
OOP	Out-of-plane
OPV	Organic photovoltaic
OSC	Organic Solar Cell
PC₇₁BM	Phenyl-C[71]-butyric acid methyl ester
PCE	Power-conversion efficiency
PV	Photovoltaic
SM	Small-molecular
SVA	Solvent vapor annealing
TA	Thermal annealing
TE	Thioester
TEM	Transmission electron microscopy
TIPS	Triisopropylsilyl
UV-vis	Ultraviolet-visible
V_{oc}	open-circuit voltage
XRD	X-ray diffraction

Chapter 1

Introduction

1.1 The need for solar power

When one considers that the estimated annual financial burden of global fossil fuel use exceeds \$5.3 trillion dollars,^[1] or that the energy sector currently accounts for around 40% of annual greenhouse gas emissions to the atmosphere,^[2] it becomes abundantly clear that a larger shift to renewable sources for energy generation needs to occur rapidly. Renewable energy currently accounts for a minority of global electricity generation at just over a 24% portion, the bulk of which is made up of hydroelectricity sources (~18%).^[3] Despite this relatively small number, from an economic standpoint alone change is likely inevitable with renewables contributing to more than 50% of electricity-generating capabilities in 2017.^[3] Developments in photovoltaic (PV) technologies and manufacturing capabilities are responsible for a significant proportion of this due to the rapidly dropping prices involved in the PV industry – since its debut in 1954, silicon PV costs have decreased from over USD\$2780/watt to USD\$0.30/watt today.^[4] Indeed, in Australia for residential silicon PV systems, ‘grid parity’ – that is, the point where the cost of electricity generated from solar panels is equal to or less than that of electricity purchased from the power grid- was reached in 2012 due to ever-decreasing solar manufacturing costs.^[5] ‘Swanson’s law’, a PV counterpart to the well-known ‘Moore’s law’ regarding computing power, highlights the growth of the industry and observes that the price of solar PV modules halve every 10 years.^[6]

1.2 A place for organic photovoltaics

Due to a recent sharp decline in prices, coupled with the inertia of 60 years of commercial development, it is little surprise that the vast majority of commercially-available photovoltaic devices are typically silicon-based, and often referred to as *inorganic* solar cells. Organic photovoltaics (OPV) technologies are a relative newcomer to the power-generating sector, both in terms of research efforts and commercialization, with the first organic solar cell (OSC) device featuring noteworthy (>1%) efficiencies only recently developed in 1986.^[7] Characterized by light-harvesting ‘active layers’ comprised of organic semiconducting compounds, OPV devices are perhaps best valued from a commercial perspective for their ability to undergo solution processing.^[8] The organic nature of the semiconducting materials facilitates dissolution in organic solvents which then allows a roll-to-roll printing process on flexible, lightweight substrates – a process analogous to printing ink on newspaper rolls, and a capability that silicon PV technologies lack.^[9] As a result of this OPVs

have rapidly become a subject of great interest and show great potential to becoming a disruptive technology.^[10] In the 30 years since their debut, laboratory efficiencies of organic solar cells have since exceeded 15%,^[11] with recent developments in the field enabling a realistic prediction of around 20%. The number of scientific publications over the last 20 years, as determined by searching by the keyword ‘organic solar cell’ on the Institute for Scientific Information’s Web of Science, serves as a good metric to illustrate the increasing interest in these technologies (Figure 1-1).

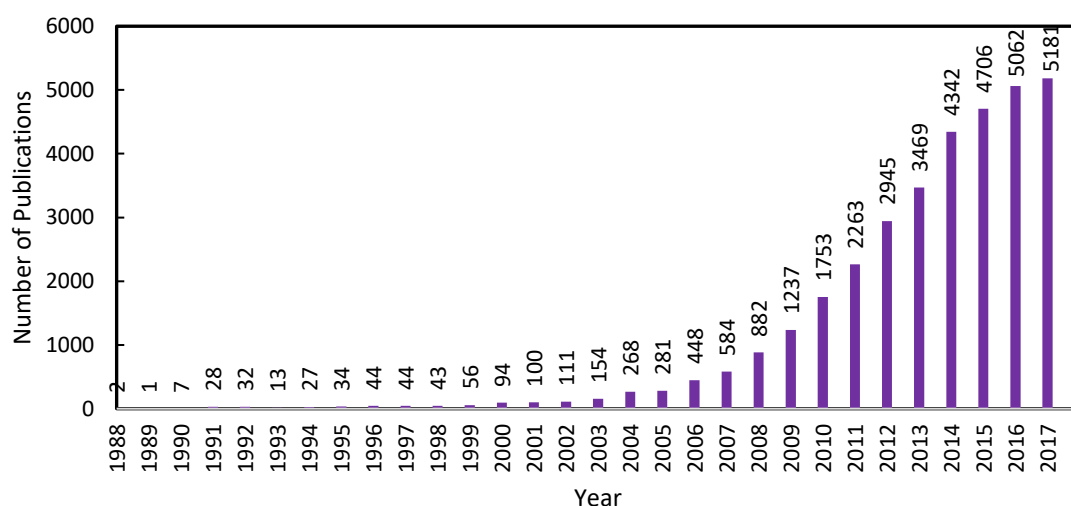


Figure 1-1: Number of publications involving ‘organic solar cells’ in the last twenty years

There are, however, several fundamental barriers that stand in the way of OPVs matching or exceeding inorganic PV in terms of utility-scale power generation, including lower device efficiencies and long-term stability issues.^[12] One must realize however, that the selling point of OPVs is not the overturning of existing sectors, but the potential for the plethora of niche market applications solely suitable to OPV devices and their unique properties. Point-of-use devices, for example, can take advantage of the potential for low-energy production to utilize low-cost solar cells for applications that do not require high efficiencies. Such applications include ‘smart’ sensors on high-volume short-lifetime items like food packaging or disposable safety equipment, which would also reduce solar cell longevity requirements.^[13] The flexible nature of OPV substrates, combined with the lightweight and semi-transparent properties of the thin-film active layer, allows OPV devices to be applied to curved surfaces for both the building-integrated and automotive vehicular PV markets.^[14] Interestingly enough, OPV devices have also been explored for applications in outer space, where their lightweight nature resulted in them outperforming their inorganic counterparts due to the high watt-per-kilo ratio (~ 10 kW/kg).^[15] Recently, a number of OSCs were brought to the edge of space to assess their viability for extra-terrestrial applications, a test which ‘open[ed] a new paradigm for solar electricity in space, from satellites to orbital and planetary space stations’.^[16]

1.3 The fundamentals of organic photovoltaics

A discussion on the fundamental mechanisms behind solar photovoltaics begins inevitably with the sun. The earth is bathed in over 89,000 terawatts of energy at any given second, an amount which could theoretically meet annual global energy demands in the space of one hour.^[17] The broad range of wavelengths within the electromagnetic spectrum emitted by the sun is attenuated by our atmosphere, and as such the amount of solar radiation experienced at a given point is defined by the air-mass (AM) coefficient. AM 0, for example, describes the solar spectrum as experienced outside of the atmosphere, while AM 1.5 describes the solar spectrum as experienced at sea level at a solar zenith angle of 48.2° -corresponding to the approximate latitudes of North America- and is currently used as the standard for solar cell testing.^[18] As seen in Figure 1-2, most of the solar spectrum that is available for use lies within the 300-900 nm wavelength range.

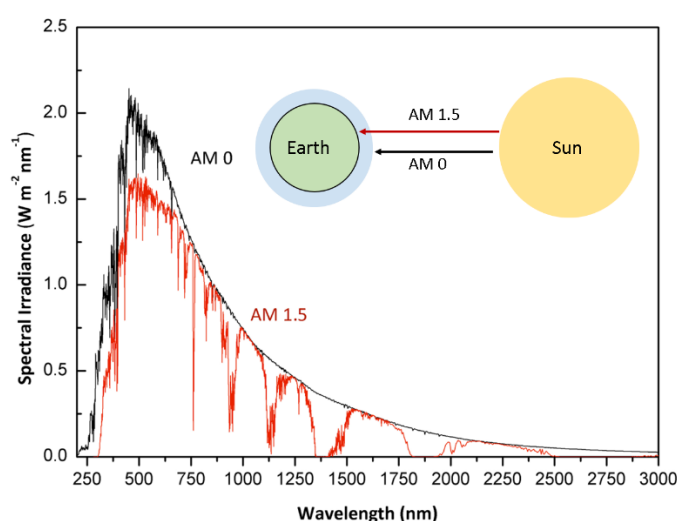


Figure 1-1: Solar irradiance spectrum at various points of the atmosphere.^[19]

All photovoltaic technologies harness the energies from incident photons and converts this to electricity. In its most basic incarnation, a photovoltaic device utilizes a light-harvesting active layer comprised of semiconducting materials connected through electrodes to an external circuit. These semiconducting materials are classified as either electron-rich p-type materials, or electron-poor n-type materials. Organic semiconductors are photophysically distinct from their inorganic counterparts and will be focused on exclusively in this chapter. These semiconductors are defined by their ability to conduct an electrical current through the movement of negative electrons and positive holes as free charge carriers. These properties are typically conferred by an extended conjugation system -that is, alternating single and double covalent bonds- that form π and π^* molecular orbitals through the participation of atomic p-orbitals in a given semiconducting material, and it is through the overlap of these π/π^* -orbitals that free charge carriers can delocalize. This hybridization forms discrete molecular energy levels, and the two of most interest to OPV operations are the highest occupied molecular orbital (HOMO), containing the most weakly held electrons, and the lowest unoccupied molecular orbital (LUMO), which is the next-highest energy orbital. The difference between the HOMO and LUMO is known as the HOMO-LUMO energy gap (E_g) and represents the minimum amount of

energy required to excite an electron from the HOMO to the LUMO. To put this in context, photons with wavelengths of 300 and 900 nm -representing the extremes of the visible spectrum- correspond to photon energies of 4.13 and 1.38 eV, respectively, and typical semiconductors for OPV devices are designed with E_g s between 1 to 2 eV to harvest as much of this spectrum as possible.^[20]

Active layers for OPV devices typically consist of a blend of two or more different semiconducting materials and are required to be a mix of p-type (or electron donor, D) and n-type (or electron acceptor, A) semiconductors. This mix of materials with different electron affinities is required as in OPV devices, absorption of photons do not generate free charges directly, but rather produces a coulombically- bound, neutrally-charged electron-hole pair termed an 'exciton' which does not allow the generation of a photocurrent.^[21] This exciton has a relatively strong binding energy of 0.1 to 1 eV,^[22] and requires an equally large energy offset between the LUMOs of the donor and acceptor materials to break the coulomb attraction (although recent semiconductor blends have shown exciton separation from negligible driving energies).^[23] This separation then leads to the preferential separation of the free electron and hole into the acceptor and donor, respectively.^[24] As such, this process requires a large interface between the donor and acceptor semiconductors termed the 'DA junction' in order to facilitate charge separation.

Figure 1-3 describes the charge generation mechanism in an OPV active layer in more detail. As explained above, absorption of photons (1) that meet the minimum E_g requirement by either the donor or acceptor then generate excitons that, upon diffusion (2) to the DA junction, are transferred through an intermediate charge-transfer state (3) to form a complex where the bound charges are located on different semiconductors.^[25] Depending on the absorbing material this separation can take the form of electron transfer from the excited donor to the acceptor (*channel I transfer*) or hole transfer from the excited acceptor to the donor (*channel II transfer*).^[26] Following charge separation, charge migration (4) occurs where the free charges percolate through the respective semiconducting layers to be collected (5) by the device electrodes to enter the external circuit, thus generating an electrical current.

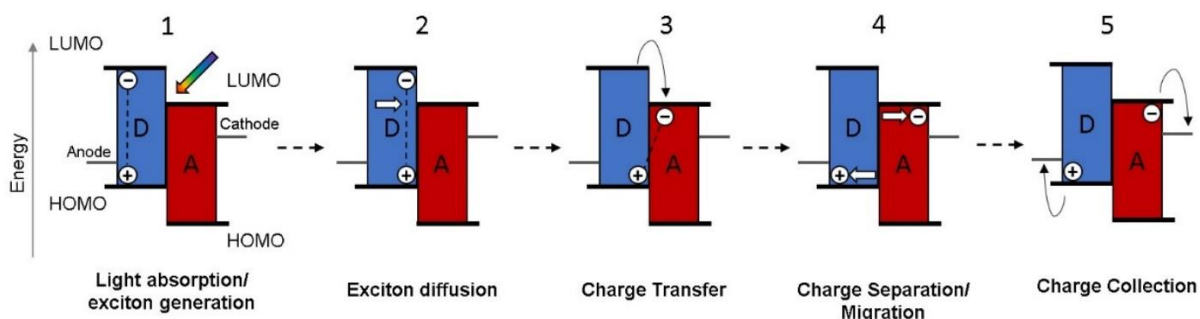


Figure 1-2: Schematic of charge generation mechanism in an OPV active layer through a channel I electron transfer

1.4 Organic photovoltaic devices

Laboratory OPV device architecture at its simplest consists of two electrodes of different work functions - with at least one of these optically-transparent to allow for light transmission- sandwiching the device active layer, on a flexible or rigid substrate. In practice, interfacial layers in between the active layer and the electrodes are commonly utilized to facilitate directional charge extraction, with different interlayer materials specializing as hole-transporting layers (HTL) and electron-transporting layers (ETL),^[27] or to improve the surface contact between the inorganic electrodes and organic semiconductors.^[28] This results in OPV device architecture resembling a multilayer stack in one of two configurations (Figure 1-4) – *conventional*, in which electrons are collected at the top electrode, and *inverted*, in which the polarity of the electrodes are reversed, with electrons collected at the bottom. Though the former is more common in the literature, several issues with this architecture have been found, including the increased susceptibility of the low work function materials typically used as the exposed cathodes to oxidation, leading to solar cell degradation. Inverted architectures, in which the less-susceptible high work function anodes are exposed have been found to be more stable,^[29] but are typically less efficient than standard architectures.^[30]

In addition to the ‘single-junction’ architectures described so far, where a single p-n junction active layer is utilized, multijunction or ‘tandem’ solar cells have been developed which incorporate multiple vertically-stacked light-harvesting layers as individual ‘sub-cells’. These stacked active layers allow for multiple types of complementary semiconducting blends to be used, and therefore can capture more of the incident solar spectrum. Though these can potentially exceed the theoretical efficiency limits of single-junction devices (with the currently best performing tandem device exhibiting efficiencies above 17%),^[31] these architectures are more technically complex to fabricate, and as such have higher price-to-performance ratios than conventional single-junction cells.^[32] All OPV devices fabricated in this work utilize single-junction designs, and tandem cells will not be discussed further. Nevertheless, whichever device architecture is utilized, the energy levels of each layer must be carefully considered to ensure efficient charge transport.

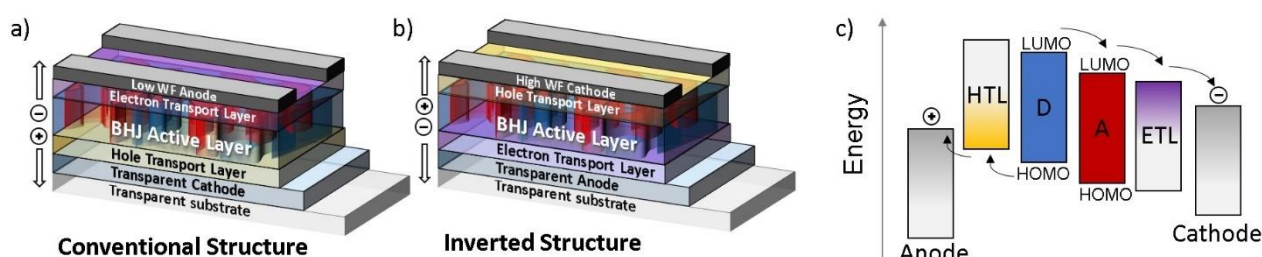


Figure 1-3: OPV device structures following a) conventional architecture, and b) inverted architecture, while c) depicts a general energy level diagram showing electron and hole transport in a device with a conventional structure

Though one of the key selling points for OPV devices is their ability to be printed on flexible substrates in a roll-to-roll process, in practice, this represents an extra degree of complexity that laboratory devices

concerned with the active-layer efficiencies avoid, and instead typically utilize glass substrates and spin-coating as a facile technique for creating uniform thin films of precise thicknesses.

1.4.1 Organic photovoltaic device performance metrics

OPV devices are assessed by several key performance metrics – the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF) and the power-conversion efficiency (PCE). The J_{sc} refers to the photocurrent obtained at short circuit conditions when there is no potential difference between the two electrodes as proportional to the total illuminated area and represents the maximum current attainable by the OPV device. The J_{sc} is affected by the efficiencies of the charge generation and collection processes of the OPV device for the entire incident solar spectrum (that is, all the mechanisms described in Figure 1-3). Methods to improve the J_{sc} include decreasing the size of the absorbing material's HOMO-LUMO energy gap,^[33] as this determines the how much of the incident spectrum is able to be utilized, interlayer modifications to increase charge extraction by the electrodes,^[34] and active-layer morphological engineering to maximize charge harvesting.^[35] The V_{oc} refers to the voltage attained under open circuit conditions when there is no current flow and represents the maximum attainable potential difference of the OPV device. In direct opposition to the J_{sc} , the V_{oc} is linearly related to the E_g between the HOMO of the donor and the LUMO of the acceptor material,^[36] and as such typical strategies to increase V_{oc} values through lowering donor HOMO energy levels also tend to decrease J_{sc} values, unless the acceptor LUMO level is also concurrently lowered. The FF represents a ratio at the maximum power point (MPP) of the realistically achieved performance against the theoretical maximum attainable (see figure below) for an OPV device, and can be represented as the following equation:

$$FF = \frac{V_{max}J_{max}}{V_{oc}J_{sc}} \quad \text{Equation 1.1}$$

where V_{max} and J_{max} represent the voltage and current, respectively, at the MPP of the OPV device, as opposed to the V_{oc} and J_{sc} which give the maximum *theoretical* power generated.^[37] The FF is a measure of the efficiency of the charge collection process for an OPV device, and as such increasing charge mobilities and decreasing resistances -again, commonly through optimized active-layer morphologies- are strategies for increasing FF values.^[37-38] All of these factors come together to determine the overall power-conversion efficiency (PCE) of an OPV device, as given through the equation:

$$PCE = \frac{P_{max}}{P_{in}} = FF \times \frac{V_{oc}J_{sc}}{P_{in}} \quad \text{Equation 1.2}$$

which describes the PCE as a ratio of the total power output of the OV device (P_{max}) against the total amount of incident energy P_{in} – that is, what percentage of an incident photon's energy is converted to electrical energy at the MPP. These are typically plotted on a J-V curve (Figure 1-5) on which the relationship between these four values can be seen. For context, an analysis of state-of-the-art OPV devices with high (>10%) PCEs

indicate that these generally possess V_{OC} , J_{SC} and FF values of 0.88-0.95 V, 15-16 mA cm^{-2} and 70-75%, respectively.^[39]

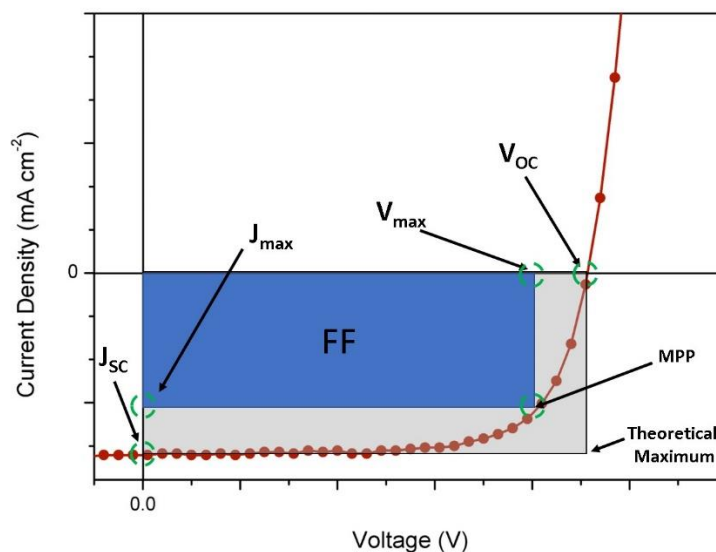


Figure 1-4: Current-Voltage (J-V) curves for a typical photovoltaic device under illuminated conditions. The blue area represents the maximum power able to be generated, and the grey area represents the maximum theoretical power.

1.5 Active layer morphology

OPV active layer morphologies are heavily influenced by the requirements of the charge generation mechanisms. It was established that to harvest a high proportion of the incident light, active layer film thicknesses had to match the 100-200 nm optical absorption pass lengths of the absorbing semiconductors.^[40] Early OPV devices utilized a planar heterojunction architecture, where the donor and acceptor semiconducting materials were layered sequentially on top of each other.^[7] However, as excitons are typically only able to diffuse distances of 10 nm before decaying to the ground state,^[41] bilayer devices - which were generally around 100 nm thick- suffered from low efficiencies in part due to exciton harvesting only being possible within diffusion distances of the DA junction, thus squandering a large fraction of generated excitons.^[42] As such, in order to both maximize the DA interfacial surface area for efficient exciton harvesting, while still maintaining a relatively thick active layer, bulk heterojunction (BHJ) architecture was developed, in which the active layer is comprised of heavily mixed donor and acceptor molecules which partially phase-separate into aggregated domains. An ideal BHJ morphology (Figure 1-6a) involves a interpenetrating network of crystalline domains along with a small degree of amorphous intermixing.^[43] These domains are ideally between 10 – 20 nm in size – small enough to be within excitonic diffusion lengths, but large enough to minimize bimolecular free charge recombination.^[44] In addition, this network should also present a continuous pathway for the free charges to percolate to their respective electrodes.

However, control over nanophase separation remains difficult, primarily due to the fact that the morphologies created from traditional active-layer deposition methods are kinetically frozen and will eventually degrade to a thermodynamically-stable state with this exacerbated in some cases from the heat

generated from solar cell operating conditions.^[45] This degradation typically results in larger domain sizes of the semiconducting materials as they phase-separate, resulting in inefficient charge harvesting.^[46] This remains one of the primary barriers to long-term stability for OPV devices. The most prevalent solutions to this problem rely on controllably driving the active layers towards states with optimal morphologies for light-harvesting processes, involving either post-processing annealing methods or the introduction of additives, which a) have to be optimized for different materials and b) can be challenging to reproduce.^[47] Another possibility involves covalently linking the two semiconducting materials to prevent macroscale phase separation, and will be explored further in Chapter 5.

Another important morphological consideration is the molecular orientation of the semiconductors with respect to the device substrate. With the exception of certain isotropic fullerene materials -discussed further in section 1.7.1- most organic semiconductors possess anisotropic charge mobilities, with intermolecular charge delocalization thought to occur primarily through the π - π stacking direction perpendicular to the plane of the conjugated backbone. As such, molecular orientation can strongly influence OPV device performance through its effect on charge transport. As vertically-stacked OPV devices dictate that efficiency is improved with an increasing degree of vertical charge transport, this means that an optimized molecular orientation is one where the plane of the conjugated backbone is parallel to the device substrate, known in the literature as a ‘face-on’ molecular orientation.^[48] The alternative to this is an ‘edge-on’ orientation, where the aryl plane is perpendicular to the substrate and where vertical charge transport is typically minimized due to non-conductive sidechains preventing the π -face overlap (Figure 1-6b). This molecular orientation is instead ideal for organic field-effect transistors device structure due to their need for horizontal charge transfer.^[49] Determining the orientation of molecules in OPV films will be covered in section 1.6. Fine orientational control of organic semiconducting materials is a non-trivial and non-intuitive process,^[50] with semiconducting materials possessing otherwise favourable chemical or electronic properties often exhibiting low device efficiencies due to a lack of this control. Typical methods to achieve orientational control include altering surface energies of adjacent layers,^[51] changing film-deposition processing conditions,^[52] and careful consideration of molecular design.^[53] The effectiveness of these methods often vary from semiconductor to semiconductor, however, and as such a solution has to be tailored to each new material.

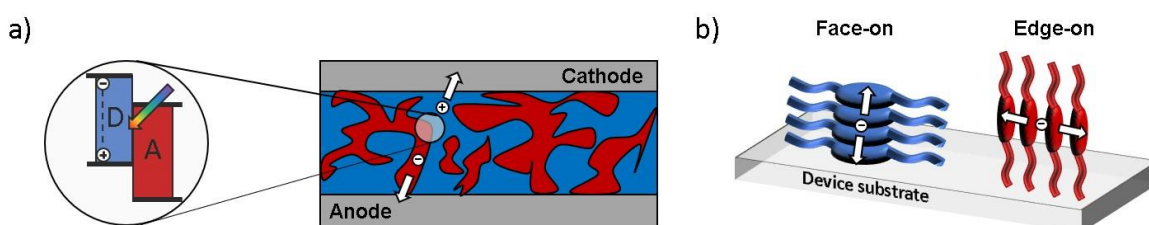


Figure 1-5: Schematic of a) a typical bulk heterojunction morphology for organic photovoltaic device active layer showing free charges percolating to the electrodes, and b) possible molecular orientations with respect to the device substrate, with charges delocalizing along the most efficient intermolecular axis

1.5.1 Sidechain engineering design strategies for morphological control

The focus of this thesis, however, is on morphological improvements through molecular design and so this discussion will be limited only to techniques utilizing this strategy with a specific focus on sidechain engineering. This is of crucial importance to morphological considerations as solubilizing sidechains affect not only the processability of these materials, but also the nanoscale structure through the degree of both alkyl lamellar and π - π intermolecular interactions.^[20] This in turn can have far-reaching implications on semiconductor self-assembly into ordered domains, affecting both the crystalline domain size and the overall orientation of the molecules within them.^[54] Presented here is a discussion of sidechain engineering techniques relevant to the studies in this thesis and their impact on OPV active-layer morphology.

1.5.1.1 Linear alkyl sidechains

One of the most common forms of sidechain engineering studies involve varying the lengths of simple sp^3 linear alkyl sidechains, with an early study in 1992 showing the effects of these variations on poly(3-alkylthiophene) (P3AT) PV performance. C_8 -, C_{10} - and C_{12} -length sidechains were utilized, with a relationship between the number of carbon units and charge transport quickly apparent.^[55] It was concluded that longer sidechain lengths disrupted the intermolecular interactions of adjacent chains, increasing interchain distances and decreasing intermolecular charge transfer, however no evidence was provided to substantiate this theory. As access to techniques for characterizing thin-film morphologies became more widespread, in-depth visualizations of these films as a function of molecular structure were able to be conducted. In 2007, P3AT materials with alkyl sidechain unit lengths of 4, 6, 8, 10 and 12 were studied, utilizing atomic force microscopy (AFM) and X-ray diffraction (XRD) to elucidate the morphological effects of the sidechain engineering.^[56] It was found that up to a point polymers with longer sidechains were generally afforded higher levels of flexibility and increased solubilities, allowing higher orders of crystallinity to be reached due to faster equilibration in the thin-film. Longer sidechains also increased phase separation from the introduced fullerene n-type materials after thermal annealing, due to the larger lamellar spacing allowing more freedom of movement for the fullerenes to aggregate together, thereby increasing crystallinity for both P3AT and fullerene domains. It was also quickly established that for the P3AT substrate, hexyl sidechains provided an optimal balance between intermixing and crystallization of the nanoscale domains, with charge generation decreasing dramatically for longer sidechain polymers. These findings were expanded on in 2009 with another study on P3ATs, this time with butyl (**P3BT**), pentyl (**P3PT**) and hexyl (**P3HT**) sidechain lengths.^[57] Transmission electron microscopy (TEM) was utilized to show that polymers with shorter sidechain lengths resulted in an interlocked morphology when blended with PC₆₁BM, conferring long-term stabilities. Limited fullerene diffusion resulting in a *lack* of crystallinity in **P3BT** however, severely limited electron charge transport, further highlighting the need to establish an optimal intermixing/crystallinity balance.

A further two studies show that this optimal point is found at very different alkyl length regions across different molecular substrates – a study involving thiazolothiazole-thiophene copolymers utilizing hexyl

(**PTzQT-6**), dodecyl (**PTzQT-12**) or tetradecyl (**PTzQT-14**) sidechains were shown through grazing-incidence wide-angle X-ray scattering (GIWAXS, to be covered further in section 1.6) and charge transport studies to possess a relationship between increasing sidechain lengths and an increased degree of crystal structure and charge mobilities (with a sixfold mobility increase from C₆ to C₁₄).^[58] In contrast to the prevailing theory at the time, also of note was that strong lamellar ordering and charge mobilities were observed even though the polymer sidechains were specifically arranged in a non-regioregular fashion in a deliberate attempt to suppress sidechain interdigitation. In contrast to this poly(hexathiophene-alt-bithiazole) polymers with shorter octyl sidechains (**PHTBTz-C8**) through GIWAXS studies show increased crystalline ordering relative to the same polymer with dodecyl sidechains (**PHTBTz-C12**) in both the lamellar and π -stacking planes.^[59] This was attributed to steric hindrance from the longer alkyl sidechains impeding π - π stacking, resulting in a threefold increase in charge mobilities for **PHTBTz-C8**.

Linear sidechains have also found a use in ‘thermal precursor’ approaches to thin-film formation, where soluble precursor compounds are deposited onto the film substrate by solution processing methods, then converted into the target material through in-situ reactions. A series of diketopyrrolopyrrole (DPP)-linked tetrabenzoporphyrin small molecules with varied alkyl sidechain lengths on the DPP unit (**C_n-DPP-BP**, where *n* represents 2, 4, 6, 8 or 10 carbons) were studied, where it was found that the length of the alkyl chains greatly affected the OPV performance.^[60] The precursor tetrabenzoporphyrin moieties all feature four dimethylethano bridges as thermally removable solubilizing units, requiring an annealing temperature of 200 °C. Molecules with larger sidechains tended to possess great diffusion lengths during the thermal conversion process, resulting in significant aggregation into crystallized domains. As a result of this, the shorter sidechain materials were found to possess finer intermixing with the fullerene acceptor which resulted in more efficient charge separation rates. This in turn meant that, with the exception of the **C2-DPP-BP** which possessed insufficient solubilities to form measurable thin-films, shorter sidechains resulted in higher J_{SC} values and higher efficiencies, with PCEs of 5.0% and 0.90% recorded for the **C4-DPP-BP** and **C10-DPP-BP**, respectively. Interestingly, a relationship was also established between crystallite orientations and the alkyl chain lengths through GIWAXS studies. In blend films, **C4-DPP-BP** and **C6-DPP-BP** demonstrated a face-on orientation, whereas **C8-DPP-BP** and **C10-DPP-BP** resulted in isotropically oriented molecules. It was hypothesized that this was due to the changing aspect ratio of the molecules, where the longer sidechains formed a ‘squarer’ molecule which conferred a higher degree of edge-on orientation. In this manner it was suggested that extending the long molecular axis could improve face-on orientation.

1.5.1.2 Branched alkyl sidechains

Considering the undesired overcrystallization that can be conferred by long linear sidechains, increased solubilities can instead be attained using branched alkyl moieties. Studies have shown that a greater number of carbons are required in linear sidechains to match the solubilities conferred by shorter-length branched sidechains – for example, 2-ethylhexyl (2-EH) branched sidechains imparted the same solubilities as linear

tetradecyl sidechains.^[61] These branched chains can also have a significant impact on molecular self-assembly in the thin films - in a series of poly(benzodithiophene-thieno-[3,4-c]pyrrole-4,6-dione) (PBDTTPD) polymers, the replacement of a tetradecyl alkoxy sidechain (**PBDTTPD(C14/C8)**) with a branched 2-EH alkoxy (**PBDTTPD(2EH/C8)**) sidechain resulted in a PCE increase from 4.1% to 7.5%.^[62] This increase was attributed, as determined through GIWAXS studies, to a preferential face-on orientation for **PBDTTPD(2EH/C8)**, relative to the isotropic orientation observed for **PBDTTPD(C14/C8)**. However as always, moderation seems to be key - another study on the same polymer examined the effects of utilizing branched 2-EH sidechains not only on the benzodithiophene (BDT) core but also on the pyrrole moieties (**P1**), which was found to result in low PCEs due to a disruption of π -stacking, presumably from the large steric volume of the branched sidechain.^[63] In contrast to this, replacement with a linear octyl sidechain (**P3**) was found to decrease the π -stacking distance from 0.38 nm to 0.36 nm, with this resulting in an almost doubled PCE from 3.5% to 6.8%.

The larger steric volumes of these branched sidechains can however be harnessed for the selective improvement of specific performance metrics – the replacement of hexyl sidechains with 2-EH sidechains into the terthiophene unit of a terthiophene-isoindigo copolymer (**P[T3(2EH)-il]**) resulted an increased V_{oc} from 0.69 V to 0.88V. This increase was attributed to a higher ionization potential and lowered HOMO level in **P[T3(2EH)-il]**, presumably through the reduced contribution from the electron-withdrawing isoindigo moiety.^[64] The use of the branched sidechain also conferred a higher solubility in the o-dichlorobenzene deposition solvent relative to the linear sidechain-functionalized analogue polymers **P[T3(R)-il]**, where *R* corresponds to hexyl, octyl, decyl or dodecyl lengths), which the authors theorized lead to the formation of a face-on crystallite orientation exclusive to **P[T3(2EH)-il]**, as determined through GIWAXS studies. The influences of material solubility on crystallite orientation during the thin-film formation process will be covered further in Chapter 3. It is worth mentioning however that this increased solubility was achieved through a large torsional twist in the conjugated backbone and a corresponding π -stacking distance increase from 0.37 nm in **P[T3(6)-il]** to 0.42 nm in **P[T3(2EH)-il]**. This also resulted in the loss of high-order crystallinity and came at the cost of lower OFET charge mobilities and a severely reduced OPV device efficiency of 0.3%, relative to the 5.1% seen **P[T3(6)-il]**. After observing large domains in AFM studies, the authors postulated that this poor performance was mainly due to a large degree of phase separation from the fullerene acceptors which offset the beneficial face-on orientation, with the relatively large polymer π -stacking distance enabling the growth of fullerene aggregates. In contrast, the shorter π -distances seen from polymers with linear sidechains were theorized to form p-type fibrillar networks that limited this aggregation.

1.5.1.3 Sidechain positioning

Sidechain placement on the conjugated backbone can be as crucial to film morphology and device efficiency as the actual sidechain composition itself. Sterically demanding conformations caused by suboptimal sidechain placement can result in a significant loss of backbone planarity and reduce π -stacking interactions, the effects of which have already been discussed in previous sections. Regioregularity in most polymeric

systems has been shown to be crucial, with even minor (5-15%) variations causing disproportionate differences (10- to 100-fold decreases) in OFET and OPV efficiencies,^[65] while for a series of oligothiophene substrates, the placement of alkyl sidechains in the terminal α,ω positions resulted in significantly blueshifted absorption onsets of ~ 50 nm relative to oligothiophenes with sidechains on the β and β' positions.^[66] A study of regioregularity on P3HT polymers have shown significant morphological impacts, with larger crystalline domains seen for analogues with higher degree of regioregularity.^[67] Two polymers (**HT94** and **HT98**) of 94% and 98% head-to-tail (HT) regioregularity, respectively, were compared, with an order of magnitude decrease observed for hole mobilities between the polymers of higher and lower regioregularity. This was hypothesized to be due to the longer conjugation lengths of **HT98** which were determined through its larger nanofibrillar width of 200-250 Å (relative to **HT94**'s width of 100-150 Å) from AFM imaging, and thus reducing the number of charge-hindering grain boundaries. As expected, GIWAXS studies also revealed a higher degree of lamellar crystallinity for **HT98**. Interestingly enough, another study on P3HT polymers of 81% and 96% regioregularity have shown that the former tended towards edge-on crystallites and the latter towards face-on crystallites.^[68] This phenomenon was unable to be explained by the authors, however.

Sidechain positioning has also been shown to be able to significantly tune electronic and self-assembly properties even on molecular substrates with much lower sidechain densities than regularly-substituted molecules like P3HT. A quarterthiophene/DPP copolymer series was designed with linear dodecyl sidechains anchored on the flanking thiophenes either in tail-to-tail (TT) configuration (**DPP4Ta**), where the sidechains pointed *towards* the DPP core, or a head-to-head (HH) configuration (**DPP4Tb**), where they pointed *away* from the DPP core.^[69] It was found that a HH configuration resulted in significantly increased blueshifted thin-film absorption profiles, indicating disruption of the conjugated backbone. DFT studies revealed that this was due to the steric clash between the adjacent alkylated thiophenes in the HH configuration resulting in significantly increased dihedral angles between the repeating units, whereas in the TT configuration these alkyl chains were pointed away from adjacent units and therefore able to maintain increased backbone planarity. AFM imaging also revealed that the TT configurations resulted in smoother films and it was proposed that the smaller steric volume allowed greater intermixing with fullerene acceptors in thin-film blends, explaining the higher device efficiencies of the TT polymers relative to the HH polymers. The same study with respect to sidechain positioning was conducted on isomers of a small molecular substrate, comprised also of a DPP core and flanked by bithiophene arms. Hexyl sidechains were appended on either the 3- (**DPP2T-3**), 4- (**DPP2T-4**), or 5-positions (**DPP2T-5**) of the terminal thiophenes.^[70] Through UV-Vis absorption studies it was shown that **DPP2T-4** and **DPP2T-3** exhibited *H*-type (cofacial stacking) and *J*-type (slipped stacking) aggregation behaviour, respectively, while **DPP2T-5** possessed properties from both types of aggregates. Electron diffraction measurements also showed an increased crystallinity for **DPP2T-4** and **-5**, suggesting that the inwards-facing nature of the **DPP2T-3** sidechains disrupted intermolecular interactions to some extent. GIWAXS studies also revealed that all three molecules possessed a face-on orientation, but

unlike the other two isomers, the scattering pattern for **DPP2T-4** changed significantly upon addition of the fullerene acceptor, indicating more interdigitation between the two materials. **DPP2T-4** also exhibited the highest OPV performance recorded out of the three isomers after thermal annealing of 3.3%, suggesting a beneficial impact of its outwards-facing alkyl sidechains on molecular packing.

Another factor to consider in addition to the *position* of sidechains on the conjugated backbone is that sidechain *density*. A series of random terpolymers were designed with a varying ratio of branched 2-EH and 2-butyloctyl (2-BO) alkylthio-functionalized BDT cores, along with an electron-deficient BDT dione moiety.^[71] It was found that polymers which featured a high degree of sterically large branched sidechains (i.e. **PB10**, which contained exclusively 2-BO-functionalized BDT cores) tended to possess low degrees of crystalline order, and those that featured sterically smaller sidechains (i.e. **PB01**, which contained exclusively 2-EH-functionalized BDT cores) possessed high degrees of crystallinity, while the polymer **PB55** that featured an equal ratio of the two sidechains showed intermediate values. Two other terpolymers containing a 3:7 and 7:3 ratio of 2-EH:2-BO cores were also synthesized, and it was found that OPV device performance increased from 8.9% with the introduction of larger 2-BO sidechains, peaked at **PB55** at an impressive 10.1% PCE, then decreased with a higher amount of the smaller 2-EH sidechains to 8.6%. The authors drew a link between the performance of **PB55** and its higher degree of face-on crystallites relative to its counterparts but were unable to account for the orientation observed. Nevertheless, this study is indicative of the effects of subtle sidechain engineering on device morphology and efficiencies.

1.5.1.4 Heteroatom-containing sidechains

Though alkyl sidechains generally do not *directly* impact the optoelectronic properties of organic semiconducting materials, the addition of heteroatoms into these sidechains can result in a greater contribution to molecular energy levels. Electron-donating heteroatoms like oxygen or sulfur are generally utilized through alkoxy or alkylthio sidechains. As these heteroatoms are directly appended to the conjugated backbone, the increased electron donation generally results in deeper HOMO levels and absorption redshifts. Only a handful of studies in the literature, however, have analyzed the morphological impacts of these heteroatom substitutions. One such study examined the effect of this substitution on OPV stability, where different sidechains were appended to a bithienyl-BDT core in a small-molecular substrate.^[72] Branched 2-EH sidechains were linked to the bithienyl moiety through either a simple carbon (**BDTT-TR**), sulfur (**BDTT-S-TR**) or oxygen (**BDTT-O-TR**) spacer. It was found that **BDTT-S-TR** possessed a higher PCE of 9.2% relative to the other analogues, due in part to higher charge carrier mobilities and attributed by the author to a higher degree of crystallinity. This correlated with the results from both AFM and energy filtered transmission electron microscopy (EFTEM). In addition, all three molecules were found to degrade over time due to increasing phase-separation leading to a more aggregated state, however **BDTT-S-TR** proved to possess the most stable morphology due to its more moderate morphological deterioration at higher temperatures, again due to its higher crystallinity.

1.5.1.5 Conjugated sidechains

Conjugated moieties appended to the conjugated backbone have recently been utilized as 2D ‘sidechain’ elements that extend conjugation and charge delocalization across multiple axes. This generally has the result of red-shifting the absorption of the molecule, as well as lowering HOMO energy levels, thus enhancing hole mobilities and ultimately improving OPV performances.^[73] Various studies across multiple substrates have shown that these conjugated sidechains also play important roles in affecting the thin-film morphologies. One such example was a comparison of copolymers comprised of BDT and thienothiophene (TT) units, where either an alkylated furan (**PBDTTT-EFF**), thiophene (**PBDTTT-EFT**) or selenophene (**PBDTTT-EFS**) was utilized as a conjugated sidechain on the BDT core.^[73b] DFT calculations showed that these different moieties resulted in a large variation of the dihedral angles between the conjugated sidechains and the conjugated backbone, with the furan analogue possessing a dihedral angle of 34°, and the thiophene and selenophene analogues both resulting in an angles of 60°. DFT-calculated HOMO levels of the three materials also show a marked difference between the furan analogue and the thiophene/selenophene analogues, indicating that the large 60° dihedral angle effectively disrupts conjugation with the backbone. An analysis of the π -stacking distances as determined from GIWAXS studies show that because of this, the furan analogue is much more closely spaced than the other two materials. Despite this, it also possesses the lowest OPV device efficiency of 5.3%, compared to the 9.0% seen for the thiophene-containing analogue. The large aggregates of **PBDTT-EFF** upon the addition of PC₇₁BM seen in AFM studies on the order of hundreds of nanometres are suggested by the authors to be the cause, resulting in high rates of bimolecular recombination. This highlights the importance of appropriate dihedral angles between conjugated sidechains and the conjugated backbone for the morphological properties of OPV materials. The degree of this offset would also of course affect molecular energy levels, due to the changing degree of electron donation.

The degree of conjugation these sidechains can also have an impact on thermal stability, as seen through a study conducted on a series of copolymers with BDT and benzothiadiazole units. Three different 2D sidechains of increasing conjugation lengths were utilized (branched alkoxy, **P1**, branched thienyl, **P2**, and branched thienothieryl, **P3**), and it was found that **P3** as the polymer with the longest degree of conjugation possessed the highest efficiency of 6.6%, as well as the highest thermal stability, maintaining an efficiency of 5.6% after exposure to 130 °C for 96 hours. The two polymers with lower degrees of conjugation, **P1** and **P2**, exhibited efficiency decreases of 93% and 70%, respectively. It was hypothesized that this stability originated from the increased co-planarity of **P3**, which would have resulted in increased crystallinity through a higher degree of π - π interactions. The authors further went on to suggest that the long fibrils seen from **P3** through TEM could ‘lock’ the PC₇₁BM fullerenes in place, thus hindering their mobilities during thermal annealing.

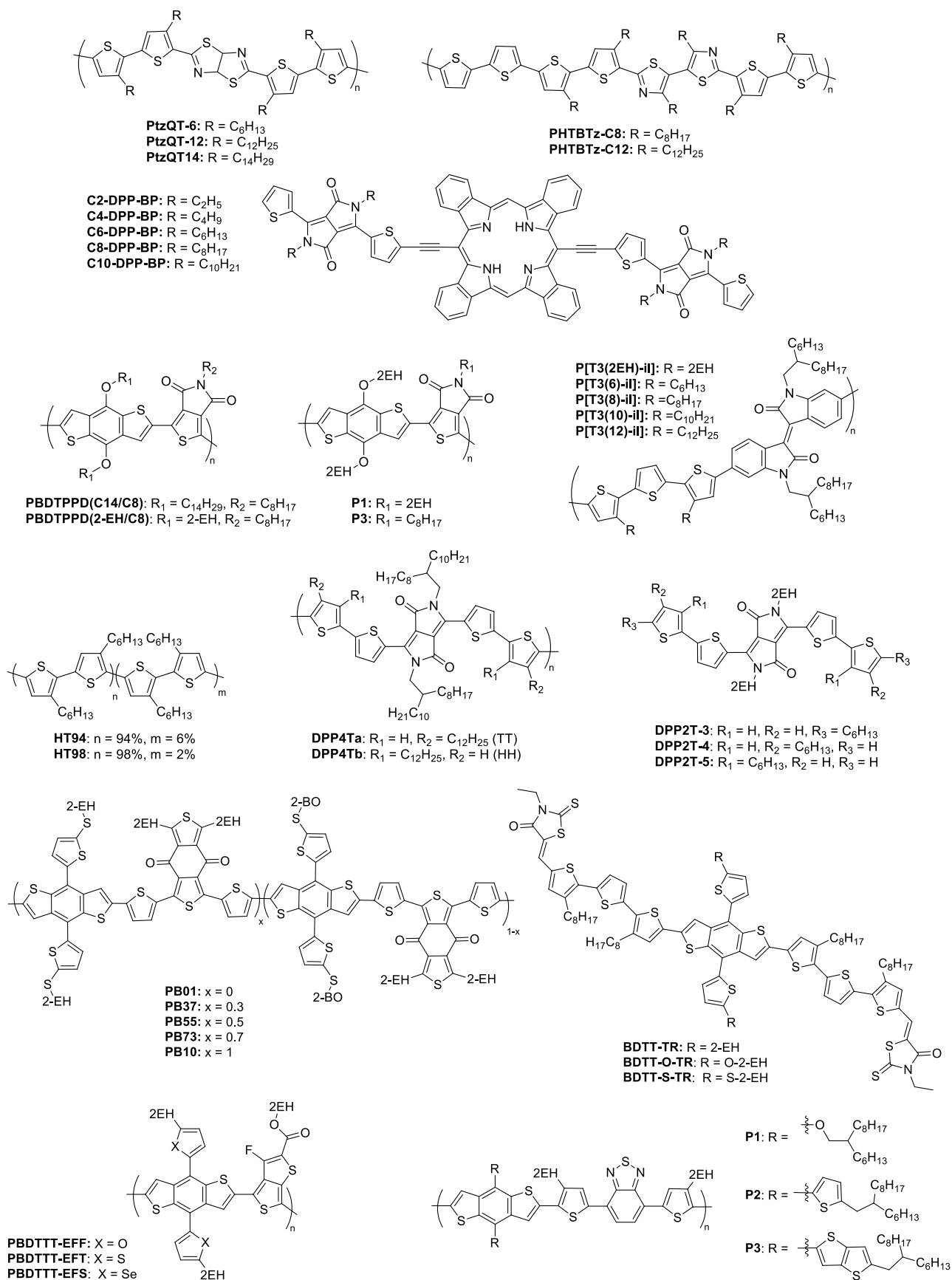


Figure 1-6: Chemical structures of the molecular substrates described in the text upon which sidechain engineering was performed resulting in alterations to OPV device performance and thin-film morphology

1.6 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS measurements are a vital method for the qualitative and quantitative probing of active-layer morphologies in OPV devices, with the usefulness of this technique demonstrated by its incorporation in the majority of the morphological studies in section 1.5. As similar analyses will be performed in chapters 2-4 of this thesis to understand the impacts of sidechain engineering on the studied molecular substrates, it seems prudent to include a discussion on the theory and interpretation of GIWAXS measurements.

Organic materials in OPV thin films are typically paracrystalline, lacking the long-range ordering indicative of true crystallinity, but possessing a higher degree of lattice regularity than completely amorphous materials. The simplest unit of the repeating pattern is termed the *unit cell* in crystallographic parlance and can be comprised of individual or groups of atoms, molecules or ions. The repetition of these features in organic films give rise to repeating patterns of electron density, and it is through the interference -and partial deflection- of these electrons with the electromagnetic waves of an X-ray beam that allows X-ray scattering studies to take place. Scattering occurs when the spacing between repeating elements are comparable to the wavelength of radiation – as X-rays possess wavelengths on the order of 10^{-10} m these are ideal for measuring atomic and intermolecular distances in OPV films. The pattern of varying intensity that results is called the scattering pattern. Due to the low degree of crystalline order, these X-rays are generally synchrotron-sourced to achieve a high signal-to-noise ratio.^[74]

To understand how a scattering pattern is produced it is beneficial to first consider a crystallite as a series of repeating planes in a lattice, separated by a distance of d (Figure 1-8). Under these specular reflections conditions, when an X-ray beam strikes a lattice point with incident angle θ , it is reflected at the same angle. A parallel incident beam that strikes a lattice point at distance d below the first point would have to first travel additional path lengths of AB and then BC upon reflection, compared to the first beam. The net path length difference of the two rays is then given as $AB + BC = 2d \sin \theta$. Although most glancing angles will result in deconstructive interference between reflections, when this path length difference is equal to a positive integer multiple n of the X-ray wavelength, i.e. when $AB + BC = n\lambda$, then the reflections will interfere constructively and be of a detectable intensity when the incident angle satisfies Bragg's law, i.e. when

$$n\lambda = 2d \sin \theta \quad \text{Equation 1.3}$$

This means that the more reflecting planes that a crystallite possesses, i.e. the more crystalline that it is, then the more reflections produced when struck by an X-ray beam. Reflections that arise from regularly spaced planes where $n = 2, 3, \dots$ are termed 2nd-order or 3rd-order reflections, and so forth.

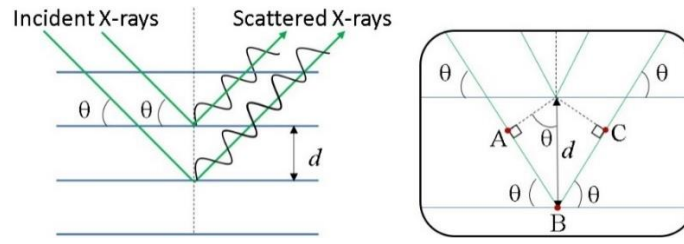


Figure 1-7: Simple model of a crystallite as stacks of reflecting lattice planes separated by distance d , showing X-rays reflections with constructive interference after satisfying conditions for Bragg's law

In practice OPV samples typically reflect X-rays as nonspecular diffuse scattering due to the presence of surface roughness on the film, and thus the incident angle θ , or α_i , will not equal the exit angle α_f . The scattering pattern that arises is formed from the distribution of electron density in lattice $\rho(\mathbf{r})$ of the sample probed by the beam, where $\mathbf{r} = (r_1, r_2, r_3)$. This scattering pattern is recorded by a detector as a 2D image, which collects all scattering as pixel coordinates $(2\theta, \varphi)$ where 2θ represents a scattering angle from the sample frame of reference (where the incident and exit angles are combined) and φ represents the azimuthal scattering angle (Figure 1-9). These coordinates can inform on momentum transfer $\vec{q}$, which is the difference between the incident and final X-ray vectors ($\vec{k}_i$ and $\vec{k}_f$ respectively, each with lengths of $\frac{2\pi}{\lambda}$) and therefore is defined as $\vec{q} = \vec{k}_i - \vec{k}_f$. By applying a 3D Fourier transformation to this scattering pattern, this momentum transfer $\vec{q}$ can be converted into a scattering vector with a length of $\frac{4\pi \sin \theta}{\lambda}$ on a theoretical 'reciprocal space' lattice $\rho(\mathbf{s})$ where $\mathbf{s} = (s_1, s_2, s_3)$, thereby mapping $(2\theta, \varphi)$ to reciprocal space. As both $\vec{k}_i$ and $\vec{k}_f$ possess the same lengths then $\vec{q}$ can be considered as belonging on the surface of a sphere with radius $\frac{2\pi}{\lambda}$ (known as the Ewald Sphere) centred on the realspace lattice of the sample.^[75] The sphere can be considered as a geometrical representation of the scattering equation, so where the reciprocal lattice points intersect with the surface of the sphere are the points where Bragg's law is satisfied thus resulting in scattering on the detector. In this manner the scattering pattern on a detector gives rise to specific features in reciprocal space upon Fourier transformation, which itself corresponds to specific repeat spacings in the realspace crystal lattice, and which can ultimately inform on the nanoscale structures in the film. This repeat spacing d , known as the lattice spacing, can be expressed in terms of the length of $\vec{q}$ through equation 1.3 and is given as

$$d = \frac{2\pi}{q} \quad \text{Equation 1.4}$$

thus allowing d to be determined through the position of the Bragg peaks on the scattering pattern. For the analysis of samples with micron-scale thicknesses typical of OPV films, standard transmission geometries for X-ray experiments where the sample is orientated normal to the incident X-ray beam are of limited use, as the relatively insignificant volume of material results in a proportionately insignificant scattering intensity. The thickness of the film substrate on which the organic film is cast is also comparatively much larger, and as such will tend to dominate the scattering signal. To resolve this issue a grazing incidence angle α_i , typically a few tenths of a degree, is utilized, changing the scattering experiment from a transmission to a reflection

geometry, and thus transmitting the X-ray beam through a larger volume of the film (i.e. a length of $t/\sin \theta$, where t is the depth of the film).^[76] This technique is termed grazing-incidence X-ray scattering (GIXS, Figure 1-9), and depending on the detector distance from the sample can be further classified as small-angle X-ray scattering (GISAXS) or GIWAXS experiments. As decreasing the detector distance allows a larger angular range accessible, the former is typically used to probe features at low q -values (and thus of structures of 3-50 nm), while the latter is used to probe features from large q -values (and thus of molecular segments of 0.2-5 nm), and as such the two techniques can provide complementary information.^[77] Only GIWAXS studies are utilized in this thesis, however, and the discussion henceforth will be limited to this technique.

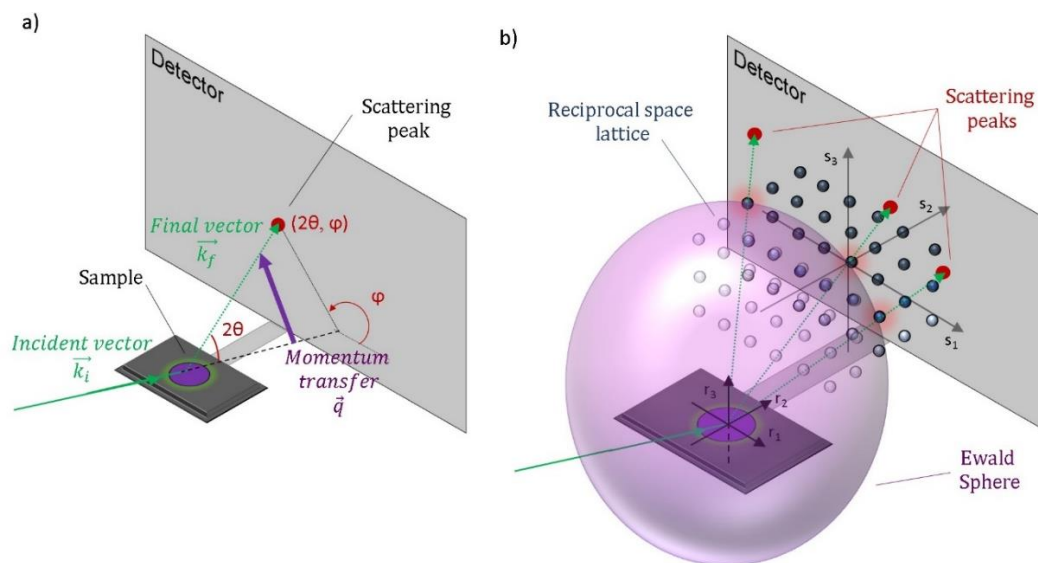


Figure 1-8: Schematic of a GIXS experiment depicting a) the relationship between the incident/ final vector of a single instance of X-ray scattering and the momentum transfer $\vec{q}$, as well as pixel coordinates expressed as scattering angle 2θ and azimuthal angle ϕ , and b) the Ewald Sphere centred on the sample lattice defined in real-space coordinates $\vec{r} = (r_1, r_2, r_3)$ and the Fourier-transformed reciprocal space lattice with coordinates $\vec{s} = (s_1, s_2, s_3)$. Here multiple points (outlined in red) on the reciprocal lattice satisfy Bragg conditions for X-ray scattering and so intersect the Ewald Sphere, resulting in experimentally-observed scattering peaks.

The nature of the GIWAXS experimental geometry also allows measurements to be obtained of crystallite orientation in the sample with respect to the plane of the device substrate. These experiments typically also use an 2D area detector to allow the analysis of the sample in both the in-plane and out-of-plane axes simultaneously.^[78] Crystallite orientations, as well as their degree of crystallinity, dictates the nature of the GIWAXS scattering patterns observed. Highly crystalline films tend to produce well-defined Bragg peaks on the detector, which will appear in the vertical (q_z) axis if the reflecting planes are oriented out-of-plane to the substrate (Figure 1-10a), or in the horizontal (q_{xy}) axis if the reflecting planes are parallel to the substrate (Figure 1-10b). If crystallites are bimodal or have multiple reflecting planes which distinctly possess both orientations, then sharp peaks will be seen in both axes (Figure 1-10c), with the peak width increasing proportionately to an increasing amount of orientational isotropy (Figure 1-10d) culminating in Debye-Scherrer-like rings for fully isotropic materials (Figure 1.10e). Though usually not observed for most OPV materials, those with higher degrees of crystallinity can possess diagonally tilted reflecting planes resulting

in distinct off-axis peaks (Figure 1.10f). The peak width of any scattering reflection is determined by the size of the crystallite in the perpendicular direction to the responsible reflecting planes, and in this manner the degree of crystallinity of any peak can be given through the Scherrer equation:^[75]

$$CCL = 2 \frac{\pi \kappa}{FWHM} \quad \text{Equation 1.5}$$

where the CCL is the crystallite coherence length describing the size of the crystallite (or more accurately, the size of the crystallite giving rise to coherent scattering), κ is the crystallite shape factor,^[79] and the FWHM is the full width at half-maximum calculated for the peak. It can be seen that as crystallite sizes increase towards infinity, peak sizes shrink towards infinitely small points.

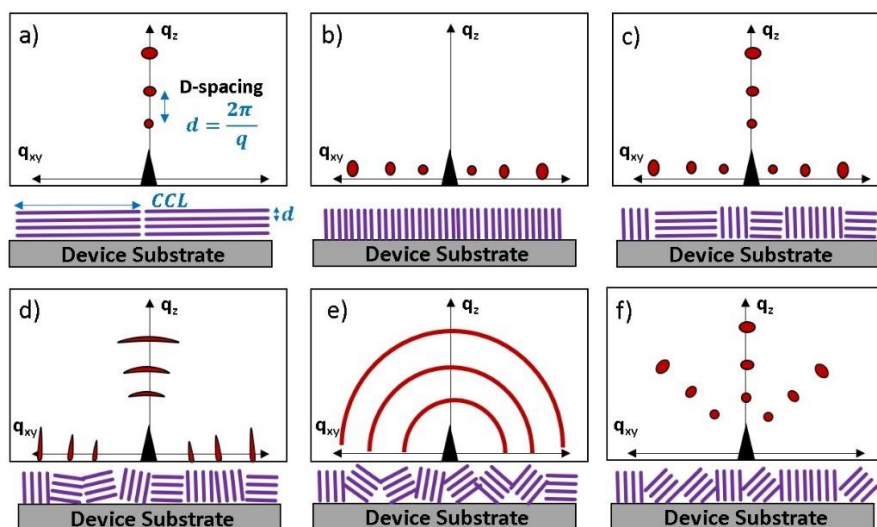


Figure 1-9: Typical GIWAXS scattering patterns from crystallites (purple segments) with specific orientations with respect to the device substrate, in the vertical (q_z) and horizontal (q_{xy}) axes. The black cone represents a beamstop that prevents the specularly reflected beam from damaging the detector.

A crystallographic unit cell possesses three lattice parameters (a, b, c), with Miller indices in the form (h, k, l) describing the planes arising from the unit cell lattice. For OPV materials, the (100), (010) and (001) indices are typically associated with specific types of molecular packing (Figure 1-11). The (100) plane is the direction along which alkyl lamellar packing occurs, and due to strong Van-der-Waal interactions between sidechains for most molecular substrates, higher-order reflections are usually observed. The (001) plane is assigned to spacings along the long axis of the conjugated backbone, however reflections are usually not observed for larger molecules due to a low degree of order. The (010) plane is the direction along which π -stacking occurs between conjugated backbones and is usually around 0.35-0.38 nm for most organic semiconducting small molecular materials.^[80] The π -stacking planes are usually orientated in a parallel or perpendicular manner to the device substrate, giving rise to the ‘face-on’ or ‘edge-on’ orientations described in section 1.5.^[81] The degree of crystallite orientation can be quantified by integrating the intensity of a Bragg peak at a given q value – typically the (100) reflection is utilized - across a 90° sector between the q_{xy} and q_z axes as a function of the azimuthal angle ϕ . This degree of orientation is known as the Hermans’ orientation parameter S :^[82]

$$S = \frac{1}{2} \left(3 \frac{\int_0^{\frac{\pi}{2}} I(\varphi) \cos^2(\varphi) \sin(\varphi) d\varphi}{\int_0^{\frac{\pi}{2}} I(\varphi) \sin(\varphi) d\varphi} - 1 \right) \quad \text{Equation 1.6}$$

If determined from the (100) reflection, a value of $S = 0$ would mean a completely isotropic orientation, and a value of $S = -0.5$ and $S = 1$ would mean a perfectly face-on orientated and edge-on orientated crystallite, respectively.^[83] A GIWAXS pattern is observed in Figure 1-11c, where Bragg peaks from both 1st-to-3rd order (h00) alkyl lamellar reflections can be seen in the vertical q_z axis as well as a (010) π -stacking reflection in the q_{xy} axis, and are characteristic of an edge-on orientation. As the Ewald Sphere cannot account for reflections directly on the q_z axis except for directly above the beamstop, this region is typically overlaid with a mask and not considered for analysis. Figure 1-11d depicts the corresponding linecut of the scattering pattern.

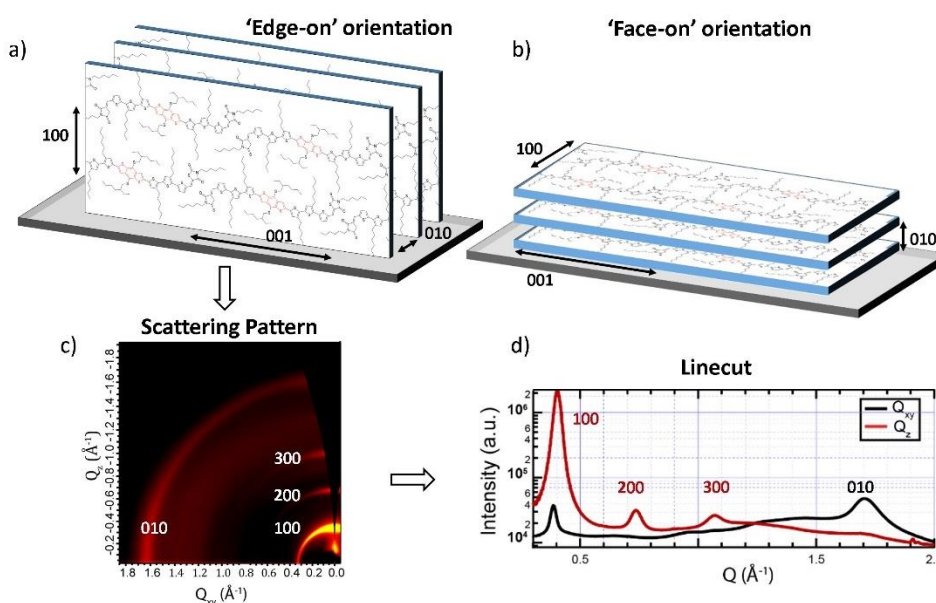


Figure 1-10: Common packing motifs typical for molecular structures studied in this thesis with assigned Miller indices in the form (h,k,l) for a) an edge-on orientation, b) a face-on orientation, and with the corresponding c) GIWAXS scattering pattern for the edge-on orientated material, and d) linecut of peak intensity along the q_{xy} and q_z axes

1.7 Active Layer Materials

As this work focuses on active-layer morphological improvements through molecular design, a brief discussion of important structural elements and design trends utilized for OPV semiconducting materials is in order. Semiconducting materials for OPV applications tend to be mainly classified along two characteristics: function and molecular weight, with the former being divided into n-type acceptor and p-type donor materials, and the latter into small-molecular and polymeric materials.

1.7.1 N-type semiconductors

Though the work in this thesis focuses primarily on p-type semiconductor material development, it is worth briefly discussing the development and merits of n-type semiconductors. For more than half the existing lifespan of the OPV research field, these have been primarily limited to fullerene-based acceptors (FAs, see Figure 1-12), with the vast majority of active-layer material development performed on electron-rich donor

materials.^[84] FAs are generally based on modified C₆₀ and C₇₀ fullerenes,^[85] with C₆₀ itself -the first FA to be studied- attracting attention due to its capacity for accepting up to 6 electrons from photoinduced charge transfer processes, as well as the isotropic nature of its charge-transporting properties. Further development lead to the more soluble methanofullerene [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and the asymmetric [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), which led to significantly improved PCEs.^[86] FAs have established themselves as suitable ‘workhorse’ electron acceptors, contributing to PCEs of >11%,^[87] due in part to their 3D character, high electron charge mobilities, LUMO energy level compatibilities with high-performing donor materials, and entrenchment into the existing OPV paradigm from years of optimization.^[23] These materials however, do possess numerous drawbacks, including high material costs, limited variability of their energy levels and weak absorption in the visible spectrum.^[88] Despite this, fullerenes are still the most widely-used acceptor materials in OPV research and industry.^[86]

Recently non-fullerene acceptors (NFAs) have risen to prominence for their ability to address these shortcomings.^[23] Though the first reported BHJ OPV device utilized a perylene-based NFA,^[7] it is only in the last few years that they have again become a major focus of research efforts, with PCEs rising from 6% to over 15% since 2015.^[89] The rapid development of these NFA materials can be attributed to the fact that the wide range of design strategies and synthetic methods that lead to the development of high-performing donor materials were found to be equally as applicable to acceptor design.^[84] Organic semiconductor p-type material research has provided chemists with an extensive library of structural moieties spanning a wide spectrum of electron affinities to draw on. This was combined with the use of the push-pull molecular architecture, first applied to p-type squaraine polymers,^[90] where selective combination of covalently-linked electron-rich and electron-poor moieties can tune HOMO/LUMO energy levels through hybridization.^[91] This tunability of n-type materials thus allowed optimal pairings with donor materials to both a) facilitate charge harvesting through favourable energy cascades with minimal energy losses, and b) maximize solar harvesting through strong absorbances in regions complementary to that of paired donor materials, which tend towards the higher wavelengths. Indeed, an OPV device with the highest-recorded tandem device PCE to date (15.0%) utilizes an NFA with an absorbance in the near-infrared.^[11] NFAs also tend towards higher solubilities in a wider range of solvents than fullerenes, as they are more easily functionalized with long or branched alkyl chains. This has led to high-performance NFAs that are able to be solution-processed from ‘green’ solvents such as tetrahydrofuran and isopropanol, which increases their viability to industrial translation.^[92]

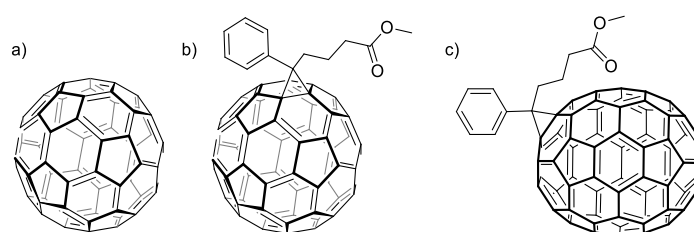


Figure 1-11: Chemical structures of the fullerene-based electron acceptors a) C₆₀, b) PC₆₁BM and c) PC₇₁BM

A review of NFAs in the literature has led to the identification of common structural elements, including strong electronegative moieties (i.e. carbonyls, imines, fluorines and cyano groups) to improve the electron-accepting abilities of the n-type semiconductor, and high planarity to facilitate electron delocalization. Push-pull type NFAs can be traced back to a cyano-functionalized poly(p-phenylenevinylene) (PPV), which proved the inspiration for the design of electron acceptors with strongly electronegative moieties.^[93] This strategy has since evolved into the incorporation of electron-poor moieties commonly used as components of push-pull p-type semiconductors -such as isoindigos, benzothiadiazoles and DPPs- as key structural elements of n-type semiconductors.^[94] Careful selection of these moieties, which each possess unique energy levels, can lead to highly tailored acceptor materials. Also worth mentioning are the indacenodithienothiophene (IDTT) based NFAs, which are multiple fused-ring small molecules functionalized with out-of-plane alkyl sidechains and electron-withdrawing end-capping groups. In 2015, an IDTT-based NFA termed **ITIC** was designed and upon incorporation with various donor materials resulted in PCEs of >9%.^[95]

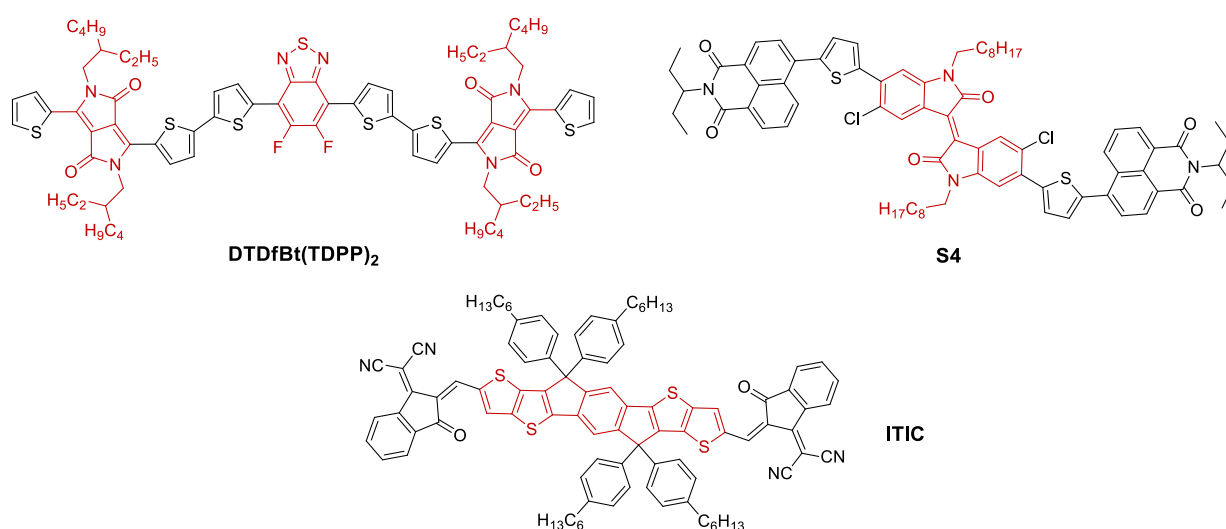


Figure 1-12: Chemical structures of typical non-fullerene acceptors, namely the DPP/benzothiadiazole-based DTDfBt(TDPP)₂,^[94a] isoindigo-based S4 and ITIC (with the core electron-poor moieties highlighted in red)^[95]

1.7.2 P-type semiconductors – Polymers

PPV polymers were one of the first classes of widely-used donor materials for OPV research, with efficiencies of up to 3.3%.^[96] PPV materials were instrumental for the early studies that lead to current understandings of OPV fundamentals, such as the origin of the open-circuit voltage,^[97] active-layer morphologies^[98] and charge carrier mobilities.^[99] These materials however suffered from a large E_g , limited absorbance of the solar spectrum and relatively low charge mobilities, which limited the maximum PCE possible. As such, around the turn of the millennium PPV-type donors were supplanted by another material.

If fullerenes can be described as the workhorse electron acceptor materials, then regioregular poly(3-hexylthiophene-2,5-diyl) (**P3HT**) would be their p-type, electron donor counterpart. In the decade following the first P3HT:PC₆₁BM OPV device, reported in 2002,^[100] it attained great prominence for its -at the time- excellent electronic properties, amenability to solution processing and long-term stability.^[101] These

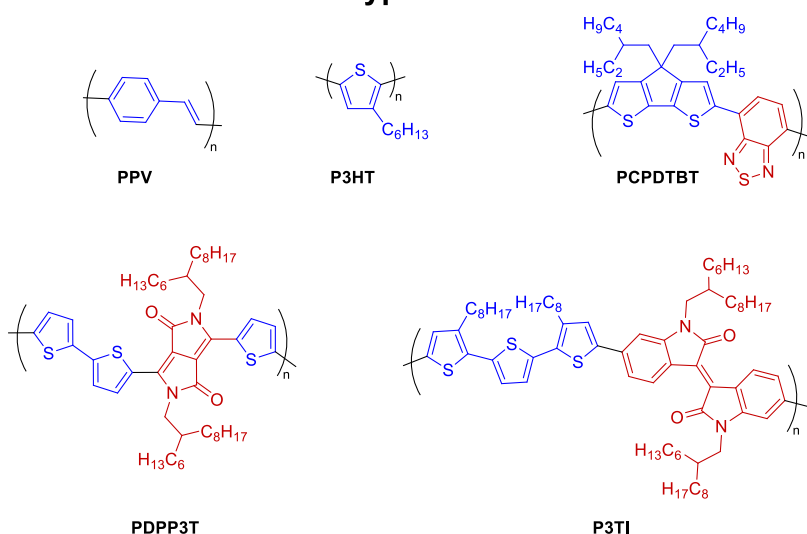
favourable electronic properties are partly due to the introduction of the sulfur heteroatom into a five-membered ring system, resulting in an increased electron density in its conjugated ring. As a ubiquitous model system for OPV materials, an exhaustive amount of optimization was performed on this donor/acceptor mix,^[102] which ultimately achieved a PCE of 7.5% from a single-junction cell.^[103] This however seems to represent an efficiency limit for **P3HT** devices, and compared to recently-developed materials it possesses a limited absorbance of 350-650 nm. This corresponds to a HOMO-LUMO energy gap of around 2 eV, which comprises harvesting of just 46% of the available spectrum.

Further development became focused on expanding the light-harvesting range of p-type materials, primarily through lowering the E_g via HOMO/LUMO energy tuning to achieve optimal energy gaps of 1.5-2 eV.^[20] First reported in the early 90s in the form of a polythiophene with electron-poor pyridine moieties resulting in a redshifted absorbance,^[104] the previously-discussed push-pull molecular architecture entered into the focus of OPV research due to this need for low energy gap materials, and was initially mainly utilized in polymeric systems due to the relative ease of alternating copolymer synthesis. This generally involved copolymerizing electron-rich and electron-poor monomers to form the conjugated polymer backbone through transition metal-catalysed cross-couplings such as Suzuki-Miyaura, Stille or Kumada-type polymerizations.^[91] One of the earliest such polymers, **PCPDTBT** was developed in 2007 and consisted of alternating fused thiophenes as the electron-rich component and benzothiadiazole as the electron-poor component, which resulted in an exceedingly broad absorption spectrum of up to 900 nm.^[105] The infrared-harvesting capabilities of this polymer saw PCEs eventually exceeding 5.5%, representing a significant milestone at the time. This trend continued, with many of the electron-deficient moieties previously discussed in section 1.7.1 debuting around this time. The first DPP-based polymer was reported in 2009 and was synthesized via the copolymerization of a thiophene-flanked DPP unit along with a bis-borylated thiophene comonomer in a Suzuki polycondensation to form **PDPP3T**. The combination of the electron-deficient fused-ring DPP and the electron-rich, highly planar terthiophene units resulted in a polymer with a low E_g of 1.31 eV, extending the absorption of the material up to 930 nm and featuring impressive charge mobilities for the time in the $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ range, resulting ultimately in a PCE of 4.7%.^[106] In 2011, the introduction of an alkylated terthiophene moiety to an electron-deficient isoindigo core -in this case through a bis-stannylated thiophene comonomer- resulted in a polymer, **P3TI**, that saw a doubling of the PCE value to 6.3% compared to a isoindigo/monothiophene copolymer. This was attributed to the dialkylated terthiophene, due to the improved film morphology from its solubilizing alkyl chains and lower E_g of 1.5 eV from the increased electron-donating ability of two extra thiophene units.^[107] It is worth mentioning that the higher performance of **P3TI** (6.3%) to the identical polymer **P[T3(C8)-il]** (5.2%) discussed in section 1.5.1 is likely due to the use of diiodooctane (DIO) as a solvent additive to optimize the active-layer morphology.

In 2014 one of the first single-junction OPV devices exhibiting a PCE of >10% was reported, which utilized the BDT based polymer **PTB7-Th**.^[108] The BDT unit was first used in the synthesis of OPV devices in 2008 as an

electron-rich building block, and gained popularity for its highly planar, fused-heterocyclic nature leading to high hole mobilities, as well as its easily-functionalizable nature leading to high tunabilities of molecular energy levels. Early syntheses of BDT-based materials quickly demonstrated facile functionalization of the 4- and 6-positions on the fused thiophene rings with various organometallic moieties thus facilitating cross-coupling reactions. Initial functionalization of the 4- and 8-positions on the benzene ring introduced dialkoxy sidechains resulting in a range of polymers,^[109] amongst which was **PTB7** (PCE = 7.4%), the precursor to the previously discussed **PTB7-Th** polymer. The PCE improvement from **PTB7** to **PTB7-Th** came about from the replacement of the alkoxy sidechains with alkylated thiophenes, thereby creating the coplanar structure previously discussed in section 1.5.1.5. This had the effect of further tuning of molecular energy levels and broadening the absorption spectrum of these molecules, as well as intriguingly increasing charge mobilities through favourable intermolecular interactions leading to enhanced π -surface overlaps. An analysis of high-performing (PCE >8%) BDT-based materials from 2010-2015 show that copolymerization of electron-deficient moieties into push-pull structures resulted in VOCs of 0.8-0.9 V, while favourable intermolecular interactions and high charge mobilities resulted in J_{sc} s of over 12 mA cm⁻².^[110] Further modifications to the 2D structure included examining the effects of substituting other heteroatoms into the 2D-conjugated sidechains -where the sulfur atom was replaced with oxygen or selenium to create furan and selenophene analogues which resulted in decreased and increased dihedral angles, respectively- as well as introducing even more heavily conjugated sidechains -for example, in the form of thienylenevinylene units- to broaden absorption onsets. Currently, the highest PCE (>13%) single-junction polymer solar cell reported, **PBDB-T-SF**,^[111] utilizes a BDT-based polymer which was the product of fluorinating another high PCE (>12%) BDT-based polymer, resulting in lowered HOMO/LUMO energy levels and a correspondingly higher J_{sc} .^[112] **PTB7-Th** -under the name **PCE10**- is also utilized in the highest performing tandem OPV cell to date, exhibiting a PCE over 15% when matched with a non-fullerene acceptor with a complementary absorption.^[11] This demonstrates the immense value of the BDT structural element to OPV research.

P-type donors



BDT-based p-type donors

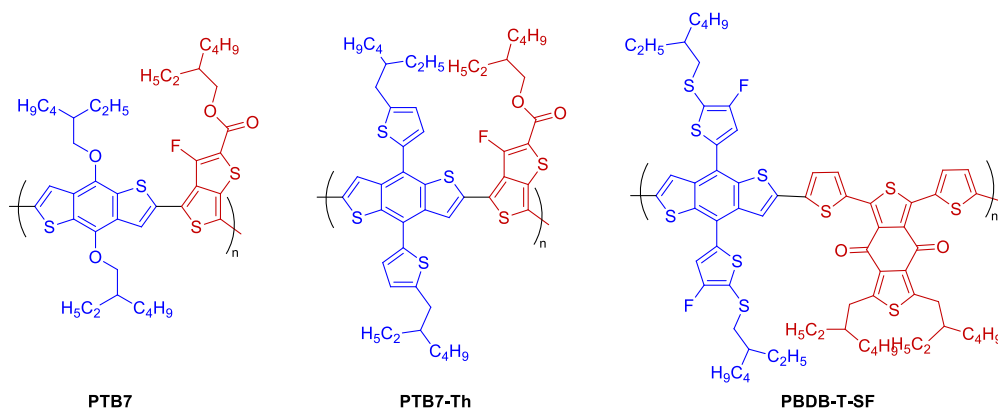


Figure 1-13: Chemical structures of the p-type polymeric donors discussed in the text, segregated into BDT-based and non-BDT-based materials. Electron-rich and electron-deficient moieties are highlighted in blue and red respectively.

1.7.3 P-type semiconductors – Small molecules

Though the earliest solar cells were comprised of small-molecular (SM, molecular weights of < 10,000) materials, conjugated polymers came to dominate the p-type donor field, in part due to the great successes of PPV and P3HT-derivative materials. Although SM systems have generally lagged behind conjugated polymers due to lower key performance metrics as well as difficulties in solution processing, recent developments have narrowed this gap to present SM semiconductors as viable alternatives to polymeric materials with efficiencies of over 13% currently reported from ternary solar cells. SMs are favoured due to several key advantages, including well-defined molecular structures for device reproducibility,^[113] relative ease of purification and intrinsically high charge mobilities. Their smaller structures and a greater tendency towards crystallinity^[114] is what confers these higher mobilities – as well as the initial difficulties in solution processing and device efficiencies, with rapidly formed overcrystallized domains hindering exciton harvesting. One of the earliest studies demonstrating the value of SM materials revealed that these higher charge recombination rates could be suppressed under AM 10 illumination, thus suggesting that SM materials could perform better than their polymeric counterparts under low-light conditions.^[115] Recently, a better understanding of molecular design leading to more efficient chromophore/sidechain pairings have partially resolved these high charge recombination rates, and is one of the primary reasons behind the rise of SMs.

Synthetic considerations tend to result in axi- or centrosymmetric SMs, with the rise of DA architectures meaning these are generally comprised of electron-rich cores flanked or end-capped with electron-deficient moieties and appended with solubilizing sidechains, as opposed to the alternating nature of copolymers. Several different donor or acceptor moieties can also be utilized within the same molecule, giving rise to A-D-A, A-D¹-D²-D¹-A, D¹-A-D²-A-D¹, etc. architectures. The terminal nature of electron-deficient moieties necessitates different structures to those utilized in copolymers, with derivatives of benzodithiazoles, rhodanines and DPPs commonly harnessed.^[114] The symmetrical nature of SMs have also been found to

confer physical properties which have morphological implications – a series of SM materials possessing either symmetrical bithiophene (**TB3t-BT**) or benzodithiophene (**TB3t-BDT**) cores or an asymmetric benzotrithiophene core (**TB3t-BTT**) resulted in stark differences in molecular packing and the formation of crystalline domains as a function of the symmetry and co-planarity imparted by these core moieties.^[116] **TB3t-BTT** exhibited the lowest melting point out of all three analogues while also displaying the highest solubility in most organic solvents, suggesting relatively weaker intermolecular interactions. The authors suggested the cause of this to be its asymmetric nature, with the symmetrical analogues displaying more ordered stacking in the solid state. **TB3t-BDT** was also found to possess a higher melting point and increased crystallinities relative to **TB3t-BT**, attributed to the increased planarity of the fused heterocyclic core. XRD analysis supports this theory, with **TB3t-BTT** found to be more amorphous in nature with less crystal structure and order observed than the other two analogues. As DFT-calculated structures show that **TB3t-BT** possessed a lower degree of co-planarity due to the larger dihedral angles in the bithiophene core (8.53° vs 5.95° for **TB3t-BTT**) this suggests that the asymmetry of the latter has a greater impact upon crystal packing. This was seen to have a significant effect on OPV device performance, with an optimized PCE of 1.6% obtained for **TB3t-BTT** while **TB3t-BDT** exhibited the best efficiency of 4.1%. Interestingly enough **TB3t-BTT** required a greater ratio (4:6 w/w, relative to a 6:4 w/w ratio for the other analogues) of the fullerene acceptor to achieve this optimized efficiency, which the authors attribute to its amorphous nature conferring a greater miscibility with fullerenes, thus requiring a greater fullerene concentration to create pure domains.

The impact of molecular symmetry can also be seen even after single-atom changes to the chemical structure of substrates. A series of molecules with dithienosilole cores and flanked by electron-deficient thiadiazolopyridines were synthesized, with only the position of the pyridine nitrogens varying between analogues (proximal/proximal – **P1**, distal/distal – **P2**, proximal/distal – **P3**). Symmetrical molecules were found to possess the highest OPV efficiencies (**PT1**, 7.0%, **PT2**, 5.6%), which the authors attributed to a higher degree of order and self-assembly of the thin-film from increased dipole-dipole interactions. In contrast, the asymmetric analogue **PT3** exhibited a lower PCE of 3.2%.^[117]

The nature of the symmetry itself has been found to affect OPV performance – a study involving oligothiophene substrates observed an odd-even effect on OPV performance with respect to the number of thiophene units in the conjugated backbone.^[118] Odd- or even-numbers conferred axi- or centrosymmetry, respectively, and it was found that the axisymmetric analogues possessed larger dipole moments upon excitation, which the authors suggested were the cause for the higher J_{sc} s observed. Well-developed, ideally-sized (<20 nm widths) crystalline fibrils for efficient exciton harvesting were also observed for the odd-numbered oligothiophene, as opposed to the larger (~40 nm) fibrils observed for the even-numbered analogues, strongly suggesting that the axisymmetric nature of the structures also played a significant role in determining film morphology. These structures, and other p-type SMs based on oligothiophene cores (distinct from materials which utilize oligothiophenes as flanking moieties) will be discussed further in

Chapter 4. It is worth mentioning that though there is a comparative lack of fully asymmetric materials in the literature, this by no means suggests that symmetry is a requirement for high-performance OPV materials and is likely due to synthetic difficulty in synthesizing these molecules. A series of D-A-A' molecules consisting of a thienoacene donor and benzothiadiazole-malononitrile acceptor were synthesized, differing on the pyrrole alkyl substituent, with one analogue (**iBuBTDC**) resulting in over 9.3% PCE.^[11] Single-crystal structures revealed that these possessed a π -stacked dimer packing structure which itself possessed centrosymmetry, thereby conferring the degree of crystallinity required for long-range π -stacked networks.

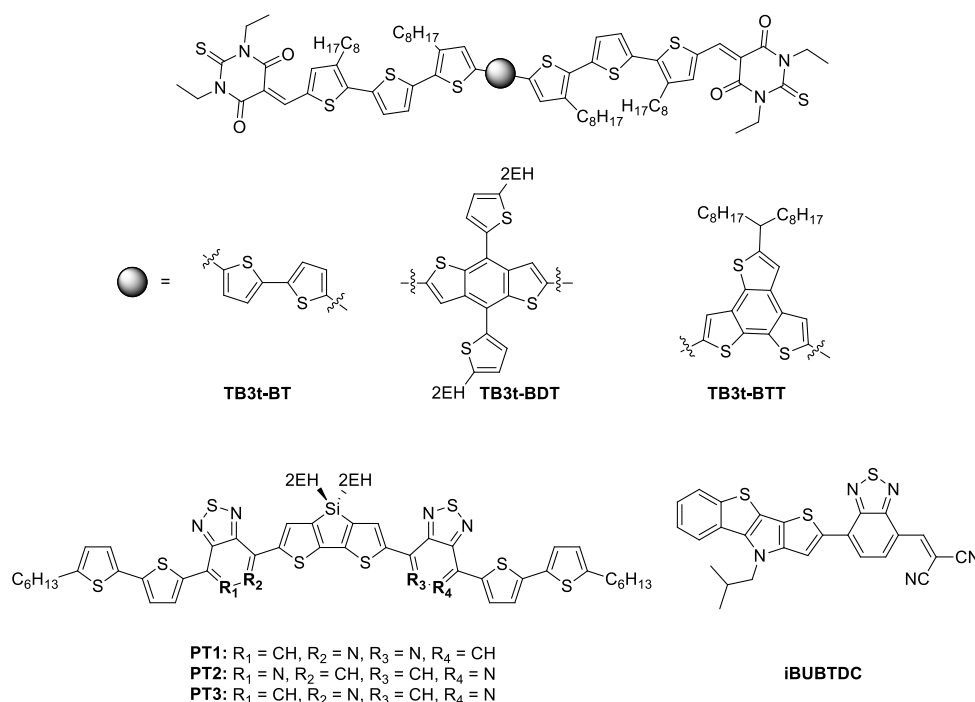


Figure 1-14: Chemical structures of the p-type small molecules discussed in the text with respect to their symmetry or asymmetry.

As a structural element that will be studied in-depth in this thesis, the electron-rich BDT moiety previously discussed in section 1.7.2 for its incorporation in polymers, also deserves to be examined for its use in the literature in small-molecular substrates. Its value to the SM-OPV field is arguably even greater than to the polymer field- of the seven SMs currently reported in the literature with PCEs of >11% from binary active layer blends, five of these contain BDT cores (Figure 1-16). **SM1** consists of a BDT core flanked by alkylated terthiophenes and end-capped by cyano (CN) ester electron-deficient units. It was blended with **IDIC**, a low E_g ITIC-based n-type SM with an absorption complementary to that of the higher E_g BDT-based material, with this resulting in a PCE of 10.1% after thermal annealing.^[39b] The lower-lying HOMO and strong absorbance of **SM1** was attributed to the cyano functional group on the ester end-cap, with **SM2**, an analogue without CN-functionality possessing a much lower performance at 5.3% PCE. This stronger absorbance manifested as a ~40 nm redshift for **SM1**, with this allowing better spectral coverage when considered with the n-type material of 200-800 nm. The redshifted absorption onset also partially accounts for the difference in V_{oc} values observed for **SM1** (0.91 V) and **SM2** (0.77 V) from the lower HOMO values. **SM2** also possesses a much

lower J_{SC} of 10.8 mA cm⁻² relative to **SM1**'s 15.18 mA cm⁻², which the authors attributed to a number of reasons – 1) optimally sized 20 nm domains as determined by photoinduced force microscopy, 2) higher hole charge mobilities, and 3) balanced electron/hole mobilities, with these all traced to the relatively higher crystallinities induced by the CN moiety.

Two other BDT-based SMs with A¹-D¹-A²-D²-A²-D¹-A¹ structures, where A¹ is n-ethylrhodanine, A² are naphthothiadiazole units and D¹ are alkylated terthiophenes also resulted in high device efficiencies of 10% (**BDTTNTTR**) and 11.5% (**BDTSTNTTR**) after SVA with CS₂.^[39d] Here the two analogues differ on the nature of the 2D conjugated sidechain substituent on the BDT cores, with a 3-alkylthiophene for the former and a 3-alkylthio-thiophene for the latter. The high performances observed for these molecules are credited partially to the HOMO-lowering (~5.3 eV), crystallinity-inducing naphthothiadiazole units, while the improvement of **BDTSTNTTR** over its counterpart is presented as due to the sulfur atom insertion into the conjugated sidechain. The authors here claim this insertion allowed 1) the branch point of the alkyl sidechain to be moved further away from the molecular backbone, thus reducing steric hindrance, 2) the facilitation of S-S interactions to improve intermolecular packing, and 3) a decreased HOMO level due to the greater π -electron accepting capabilities of the divalent sulfur and its empty 3d-orbital. Indeed, higher crystallinities, larger hole mobilities and lower HOMO levels are observed relative to **BDTTNTTR**, with a broad absorbance of 300-800 nm and outstanding J_{SC} of 16.21 mA cm⁻² observed.

The last two BDT-based materials to be discussed also achieve their high performance through optimized morphologies, in this case through fluorination of the conjugated backbone. 2D-conjugated BDT cores were flanked by 2-(thiophen-2-yl)thienothiophene π -bridges and end-capped with either monofluorinated indanediones (**BTID-1F**, 10.4%) or difluorinated indanediones (**BTID-2F**, 11.3%).^[39c] The use of the thienothiophene moieties were also considered both for an increased aromaticity for higher VOCs (0.93-0.95 V), as well as to provide a gradient of decreasing electron density along the conjugated backbone for increased intramolecular hole transport. From UV-Vis absorption studies of thin-films, increasing fluorination was found to correspondingly increase dense and ordered π -stacking which manifested as redshifted absorbances and more vibronic structure in the spectra. Increased fluorination was also attributed with a formation of vertical phase separation between p- and n-type semiconducting materials -as determined through X-ray photoelectron spectroscopy- through the preferential concentration of the lower free-energy hole-transporting donors at the air/film interface, resulting in a beneficial morphology for inverted devices.

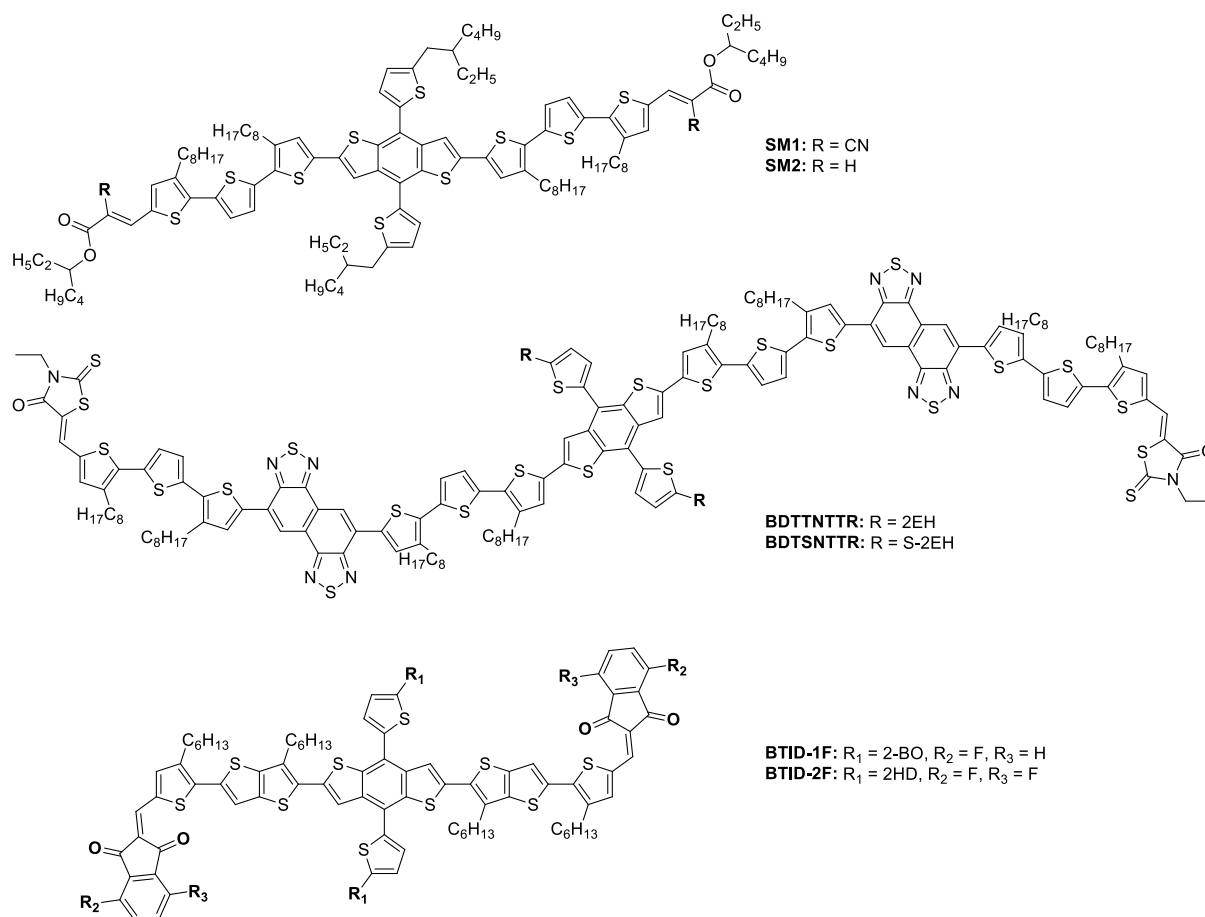


Figure 1-15: Chemical structures of high-performance BDT-based p-type small molecules discussed in the text

1.8 Outline and objectives of this thesis

Clearly there is a demonstrated need to improve OPV device efficiency, performance and commercial viability. Despite several decades' worth of OPV research, a universal understanding of techniques to improve the nanoscale morphology of the light-harvesting active layer remains out of reach. This is primarily due to the extreme morphological variance observed between different active layer molecular materials, as morphology-influencing factors like molecular structure, solubility and crystallinity are all heavily substrate-dependant. As the literature contains a vast number of reported substrates it is obviously impractical to optimize each one and so an efficient approach suggests targeting OPV active-layer semiconducting materials already known to possess properties leading to high-performing devices and gaining as in-depth an understanding as possible about their structure-property relationships with respect to OPV morphology.

This thesis focuses on gaining this understanding and subsequent morphological control through the study of a wide array of analogues, synthesized from the application of rational design strategies to a few high-performance molecular substrates. As nonconjugated alkyl sidechains represent one of the few structural elements that can have large impacts on morphology-influencing properties while maintaining the fundamental nature of these substrates, the studies contained within this thesis focus on sidechain engineering techniques as a core concept of these design strategies. This work has led to the synthesis of

twenty different target materials spanning four categories of substrates of significant importance to the literature. OPV devices have been fabricated for the majority of these materials, and their thin-film morphology critically examined through a combination of atomic force microscopy (AFM), X-ray scattering and single-crystal X-ray diffraction studies. These results are used to gain a fundamental understanding of optimal molecular design routes for future OPV material development.

This thesis is divided as follows:

Chapter 1: An overview of OPVs is given, with a brief discussion of the underlying photophysics of their operation and the active layer morphological requirements of these processes, as well as a variety of techniques currently used to control this morphology. As GIWAXS measurements constitute a large portion of the studies within this thesis, the theory behind the technique and interpretation of results are also discussed. Examples of relevant active layer molecular substrates are also explored, as are the effects of certain sidechain engineering techniques. A brief outline of the thesis and its objectives are also presented.

Chapter 2: Previously reported in the literature, the high performing molecular p-type material BTR was designed and synthesized through the application of sidechain engineering techniques, and at the time represented one of the highest-performing materials.^[119] As a combination of techniques was applied simultaneously in its design, the exact magnitude of any one of these structural alterations on material performance was therefore unknown. This study presents the results of altering the thiophene π -bridge sidechain lengths of the BTR substrate, and details the synthesis of two analogues and their inclusion into OPV devices. An analysis of nanoscale crystallinity is carried out to rationalize the device performance observed.

Chapter 3: Examination of BTR π -stacking interactions revealed offset benzodithiophene core moieties, with this offset believed to be due to the steric bulk of the thienyl core substituent. In this study BTR analogues with four different core substituents with a range of steric and solubility properties were designed to alter the degree of this offset, ideally leading towards more efficient charge transport. Analysis of OPV devices and their thin-film morphology however instead revealed a relationship between material solubility, thin-film molecular orientation and device performance.

Chapter 4: After the sidechain engineering techniques applied to BTR were shown to significantly improve intermolecular packing and charge transport properties, the application of these techniques to other molecular substrates were considered. Here a series of previously-reported p-type oligothiophenes with pseudo-regiorandom sidechains were structurally altered to increase π - π interactions in the same manner as BTR.^[118] The effects of these sidechain engineering techniques applied were assessed across a range of oligothiophene molecular substrates with variations to both conjugation length and end-group acceptor moieties made. Twelve analogues were synthesized and utilized in OPV devices, which then underwent morphological analysis to assess the viability of this cross-substrate molecular design strategy.

Chapter 5: Block copolymers represent a novel method to control active-layer morphologies and use covalently-bound p- and n-type homopolymers to achieve nanoscale phase-separated domains. The use of block copolymers with amphiphilic properties increases the degree of phase-separation, and in this study sidechain engineering was utilized in the synthesis of two hydrophilic P3HT analogues. A novel synthetic route with fine end-group control was also designed for the synthesis of a hydrophobic n-type isoindigo polymer, utilizing a single monomer with asymmetric functionalities.

Chapter 2

BTR π -bridge sidechain modifications

2.1 Chapter introduction

In 2015 a SM p-type material comprised of a BDT core flanked by hexyl-functionalized terthiophene π -bridges and end-capped with electron-poor n-hexyl rhodanine moieties (**BTR**, Figure 2-1) was reported.^[119] This molecule featured excellent optoelectronic properties, and when utilized in a blend with PC₇₁BM for an OPV device, produced a high J_{sc} of 13.90 mA cm⁻² and FF of 77%. This resulted in a PCE of 9.3%, meaning that even today this remains one of the highest performing SM materials in the literature. As recalled from Section 1.4.1 this FF lies beyond the ‘typical’ range of 70-75% for high-performing OPV materials, suggesting that **BTR** possessed significant charge mobilities. This in turn suggested that **BTR** could be utilized in thicker (<200 nm) active layers to facilitate both device processing and solar harvesting, whereas materials with lower FFs generally require thinner active layers to minimize charge recombination. Hole mobilities derived from space-charge-limited current (SCLC) methods of 1.6×10^{-3} cm²V⁻¹s⁻¹ were obtained, with these well-matched with the electron mobilities recorded. GIWAXS scattering patterns of **BTR** as-cast thin films revealed 3rd-order $h00$ reflections and a 010 π -stacking reflection, *both* of which were located in the vertical q_z axis. This ran contrary to the perpendicular nature of $h00$ to $0k0$ reflections expected from an edge- or face-on orientation. The authors attributed this to the existence of a bimodal orientation in the film, resulting in a 3D π -network facilitating improved charge transport. Single-crystal structures also showed that **BTR** arranges into π -stacked dimers, with relatively low stacking distances of ~ 0.36 nm. Interestingly enough a nematic liquid crystalline (NLC) high-temperature phase was also observed, suggesting that even at these high temperatures of <190°C, **BTR** molecules were aligned enough along the long axis of the conjugated backbone to maintain order.

BTR was designed through the application of sidechain engineering to an existing high-performing structure in the literature with an identical chromophore (**SMPV1**, Figure 2-1).^[120] On **BTR** the alkyl sidechains on the terthiophene moieties were all situated exclusively on the 3-positions, with this repositioning performed in an effort to achieve a pseudo head-to-tail regioregularity, ultimately resulting in all sidechains orientated away from the core. It was hypothesized that this would declutter the physical space around the BDT moiety, thus improving π - π stacking for enhanced charge transport. To aid this the lengths of these sidechains were reduced from eight to six carbon units, and to counter this loss of solubility, additional hexyl sidechains were appended to the 2-(2-ethylhexyl)thiophene core substituent. These sidechain engineering efforts ultimately resulted in higher performances, increased charge transport and unique physical properties for **BTR**.

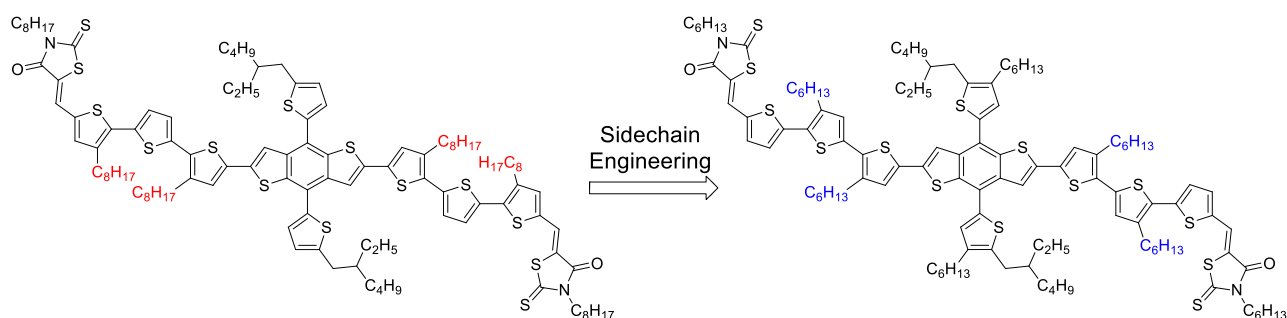


Figure 2-1: Sidechain engineering alterations made to known chromophore SMPV1 (left) resulting in BTR (right)

Though obviously beneficial, these simultaneous sidechain alterations meant that understanding the standalone effects of any one of these changes proved difficult, hindering the development of even higher-performing materials. As such, by carefully designing analogues where these changes could be studied in isolation, structure-property relationships for the BTR substrate could then be established. At the time of this study, a review of the existing literature on sidechain length alterations on other substrates (Section 1.5.1) suggested that a ‘balance point’ existed with respect to sidechain length, which a) conferred sufficient miscibility with PC₇₁BM fullerenes during the thin-film formation process to facilitate the intermixing required for a DA junction for a large interfacial area, but also b) conferred sufficiently crystallinity to allow for optimal π -stacking distances and large domains for efficient charge transport. It had also been shown that insufficient sidechain lengths can induce insufficient solubility in deposition solvents, resulting in a poor film quality with the formation of aggregates and pinholes, however this length obviously changes across substrate types.

Further uncertainty on this subject arose from the relatively novel design of the molecules, as at that time few SM BDT-type molecules had been reported in the literature,^[121] and of these none were designed with the ‘regioregular’ sidechain orientation found on the **BTR** π -bridges, thus providing little in way of comparison. In addition, while BDT cores in polymeric substrates had been extensively studied, including sidechain length optimizations, the vast majority of these studies were conducted on sidechains appended to the 2D thienyl core substituent (Section 1.5.4). In between this and the fundamental differences of the A-D-A architecture of **BTR**, the existing literature could not heavily be relied on to establish where the optimal solubility/crystallization ‘balance point’ length could be found (if it had not been already), or indeed whether it would be most strongly affected by sidechains appended to the core substituent or π -bridges.

As such, in this chapter the first goal of the research was to ascertain the impact of oligothiophene π -bridge alkyl sidechain lengths on the intermolecular packing, active-layer morphology and ultimately, the device performance for the BTR substrate. To do so two novel analogues of **BTR** were designed where the sidechain length from the original hexyl sidechains were systemically varied, manifesting as shorter butyl-substituted and longer octyl-substituted π -bridges on molecules termed **BT₄R** and **BT₈R**, respectively (Figure 2-2). It was reasoned that these lengths would suffice to quickly establish a) whether any fundamental structure-property relationships existed at all, and b) the nature of this relationship and whether it could be used to further optimize the BTR substrate. Alkyl lengths directly adjacent to the original six-carbon sidechains (i.e.

pentyl and heptyl sidechains) were decided against as studies had previously shown that odd-numbered sidechains adversely affected OPV performance relative to their even-numbered counterparts due to intermolecular packing disruptions, however this odd-even effect is still poorly understood.^[122]

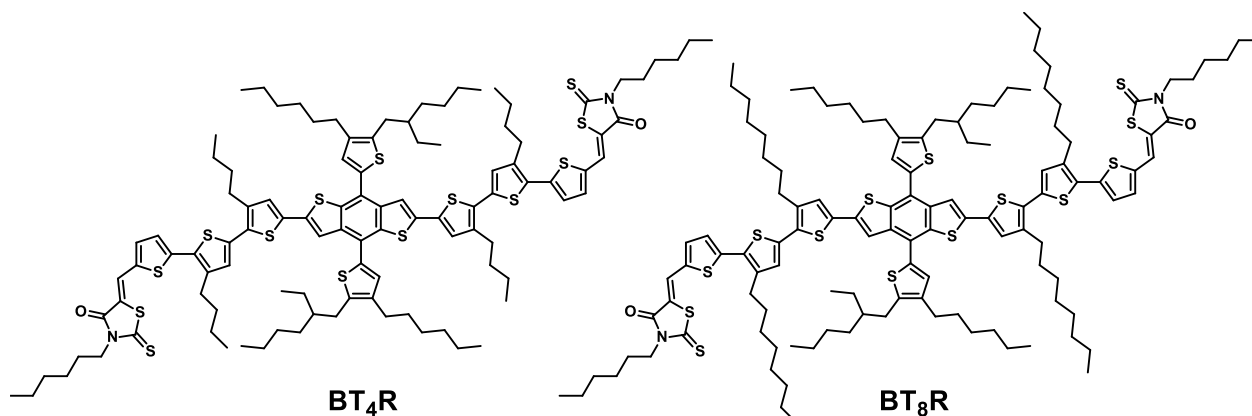


Figure 2-2: Chemical structures of the BT_xR series with alkyl sidechains extended for visual clarity.

The second goal of this chapter was to establish a synthetic protocol designed for a modular assembly of **BTR** and BTR analogues. As a large number of different analogues was likely required in order to establish structure-property relationships, it was realized that a modular synthetic approach would allow these analogues to be relatively rapidly assembled, especially if the individual components could be synthesized a) with orthogonal functional groups and b) in bulk quantities for scale-up procedures. This would allow for components which were found to confer optimal properties to be rapidly integrated together, thus expediting the rate and quantity at which subsequent-generation, improved analogues could be synthesized. Figure 2-3 depicts the reduction of **BTR** into its core, modular components. Furthermore, as it was hoped that the high-performance analogues would eventually be harnessed for commercial enterprises, this synthetic protocol was also designed with an eye towards industrial relevancy, thereby invalidating the previous synthetic route utilized for **BTR** which involved toxic organotin reagents.

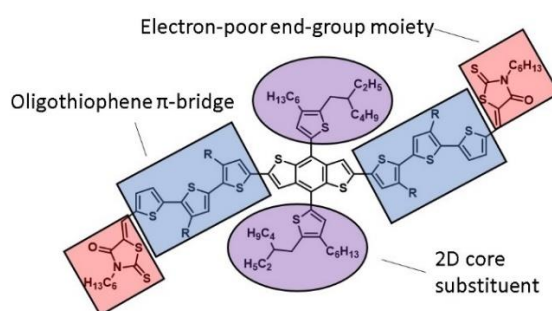


Figure 2-3: Breakdown of the BTR molecule substrate into its core components.

This chapter shows the implementation of this modular synthetic protocol, with a specific focus on the assembly of the oligothiophene π -bridge through catenation of an asymmetrically functionalized 3-alkylthiophene key intermediate. This led to the synthesis of the two target BTR analogues, **BT₄R** and **BT₈R**, in multigram quantities. Extensive physical and spectroscopic characterization of these compounds were

carried out, after which they were utilized to fabricate OPV devices in a blend with PC₇₁BM as an n-type semiconductor. Both materials exhibited optimized performances after SVA with THF, with **BT₄R** possessing a high PCE of ~9%, comparable to that of **BTR**. **BT₈R** however exhibited much lower efficiencies of ~5%. GIWAXS analysis of the device films revealed that the longer alkyl sidechain lengths from **BT₈R** were the cause of this behaviour, resulting in an unfavourable active-layer morphology and thus confirming that oligothiophene π -bridge lengths were indeed critical to the performance of BTR analogues. It was also shown that the hexyl-length sidechains on these π -bridges are optimal for BTR substrates, resulting in the desired crystallization/solubility balance point.

2.2 Contribution from the candidate

The candidate was responsible for the synthesis, purification, and full characterization of all molecules described in this study leading to the **BT₄R** and **BT₈R** analogues, except where noted in this paragraph. UV-Vis spectroscopy, POM studies, and the in-depth GIWAXS studies on **BTR** were also carried out by the candidate, while its initial synthesis, purification and all other material characterization were performed by Dr. Paul Geraghty. Professor Jonathan White was responsible for obtaining the single-crystal structures discussed in this chapter, and Dr. Jegadesan Subbiah was responsible for OPV device fabrication and characterization. Sample preparation, data collection/processing and interpretation of the GIWAXS measurements was performed by the candidate, with Dr. Valerie Mitchell, Dr. Xuechen Jiao and Prof. Chris McNeill providing feedback on the interpretations of this data.

Elements from this work – thermogravimetric analysis, differential scanning calorimetry, polarized optical microscopy, UV-Vis spectroscopy, cyclic voltammetry, photoelectron spectroscopy in air and OPV device data- was also published in the following peer-reviewed article with contributions from other colleagues.

Geraghty P.B., Lee C., Subbiah J., Wong W.W.H., Banal J.L., Jameel M.A., Smith T.A., Jones D.J. High performance p-type molecular electron donors for OPV applications via alkylthiophene catenation chromophore extension. *Beilstein Journal of Organic Chemistry* 2016, 12:2298-2314. DOI:10.3762/bjoc.12.223.

The PhD candidate is only claiming credit for work described in this chapter and not the entire contents of the publication.

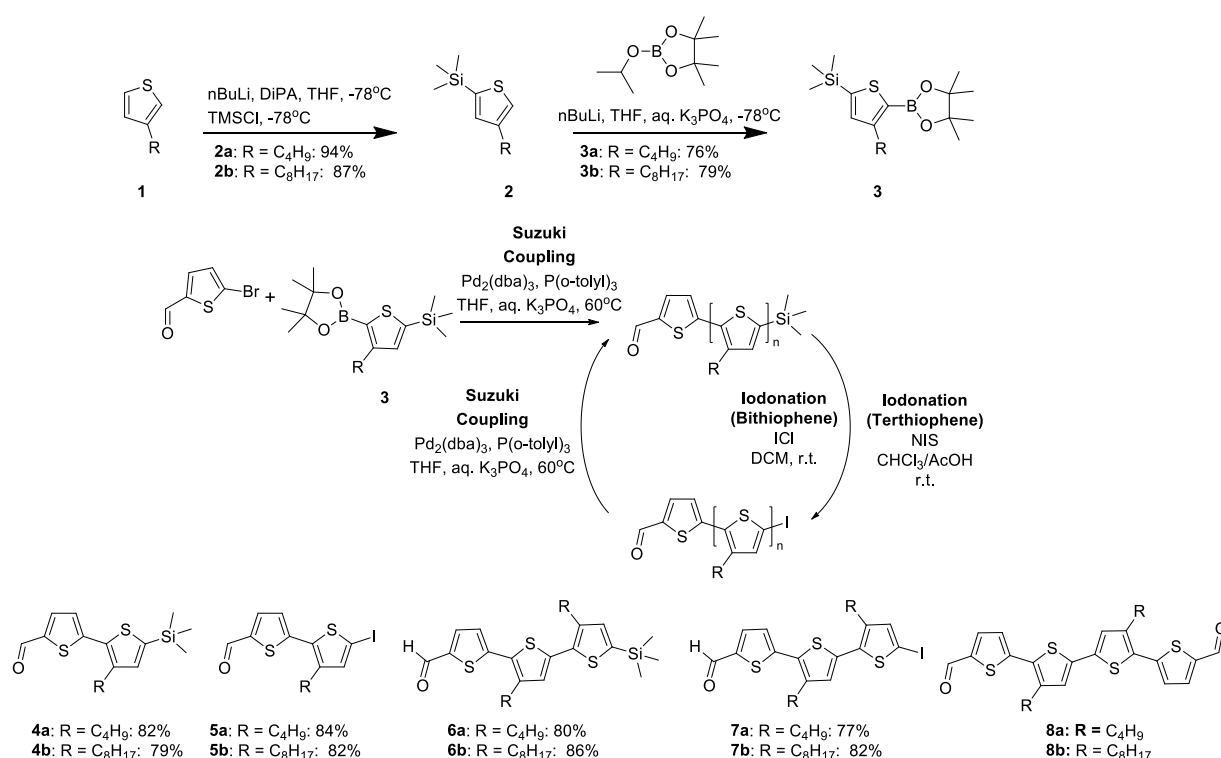
2.3 BT_xR synthesis

2.3.1 Oligothiophene π -bridge

For this study, the synthesis of the oligothiophene π -bridge utilized a modified version of a previously published route for the synthesis of **BTR**.^[119, 123] Much like in the work of Sun et al, in this study a 3-alkylated thiophene key intermediate was also utilized to build up the oligothiophene moiety, one aryl unit at a time, through iterative Suzuki couplings (Scheme 2.1). The modified synthesis in this study starts with the requisite commercially available 3-alkylthiophene, **1a** or **1b**, where **a** denotes a butyl sidechain and **b** denotes an octyl sidechain. Unlike the previous publication, the key intermediate here features a trimethylsilyl protecting group, both as a 'masked' halide to protect against diborylation in the subsequent step and to facilitate purification for scale-up efforts. To do so, **1a** or **1b** were deprotonated via 1.1 eq. of lithium diisopropylamide (LDA) formed in situ from the reaction of *n*-butyllithium (*n*-BuLi) with diisopropylamine (DiPA), with the sterically large LDA base inducing a high selectivity deprotonation at the C5 carbon. Following this the lithiated intermediate was quenched with trimethylsilyl chloride to form the silyl-protected thiophenes **2a** and **2b**, which could be easily purified via distillation to remove the lighter 3-alkylthiophene in relatively high yields of 80-90%. Once accomplished, with the addition of 1.1 eq of *n*-BuLi **2a/2b** were deprotonated, this time at the C2 position, and quenched the lithiated intermediate with excess 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Again, unreacted starting material was able to be distilled off, resulting in the borylated thiophenes **3a/3b**. These asymmetrically functionalized thiophenes operated as the key intermediates that were utilized for iterative Suzuki coupling reactions to build up the oligothiophene bridges, with the synthetic method described so far able to produce this key intermediate on a mole scale with about a 70-80% yield. A boronic acid pinacol ester (Bpin) functional group was chosen for incorporation for its stability at high temperatures,^[124] thus facilitating purification via distillation. Chain extension was then initiated from the commercially available 5-bromo-2-thiophenecarboxaldehyde through a Suzuki-Miyaura cross-coupling with the key intermediate, forming the bithiophenes **4a/4b**. An aldehyde moiety was installed here to provide a reactive functional group for attachment of the end-group acceptors. These silylated bithiophenes were purified via silica column chromatography, resulting in yields of around 80%. Next, the TMS protecting group was converted to a reactive halogen using 1 eq. of iodine monochloride (ICl) in a solution of dichloromethane (DCM) via a halodesilylation of the bithiophene, thus generating the required iodo-bithiophenes **5a/5b** for the subsequent iterative Suzuki couplings. Column chromatography was again used for purification, resulting in yields of around 80%. Successive Suzuki couplings with the key thiophene intermediate and iodination of the growing oligothiophene bridge constituted a simple and efficient iterative method (Scheme 2.1) that has been since shown to successfully synthesize 3-alkylated quarter- and pentathiophenes.^[39a] For the purpose of this study however, this cycle was utilized only once more, first coupling the key intermediates **3a/3b** with the iodinated bithiophenes **5a/5b** respectively, yielding the

silylated terthiophenes **6a/6b** in yields of 80-86%, followed by a final iodination to yield the desired iodinated 3-alkyl terthiophenes, **7a/7b**.

These second iodinations were carried out using *n*-iodosuccinimide (NIS) as a halogen source, as on the terthiophene substrate ICl resulted in acid-catalyzed proto-desilylation of **6a/6b**, resulting in a 10-15% loss in yield. This was theorized to occur through the in-situ formation of HI or HCl, presumably through the presence of water in the reaction. Though this side reaction is also present in the formation of the iodinated bithiophenes, the relative similarities in molecular weight of the halogenated and deprotected terthiophenes, relative to their bithiophene counterparts, rendered the purification of **7a/7b** through column chromatography exceedingly difficult. The use of NIS was found to significantly hinder the formation of the desilylated terthiophenes. Also, of note was the formation of quarterthiophene side products **8a** and **8b** during the synthesis of **6a/6b** through a palladium-catalyzed Ullman-type homocoupling of **5a/5b** in non-trivial quantities. Similar homocouplings involving analogous conditions have been reported, and the formation of these side products were successfully reduced in later reactions via increasing the stoichiometric ratio of the preferentially-reactive borylated thiophene key intermediates relative to the iodinated oligothiophene from 1.1 to 1.3.^[125]

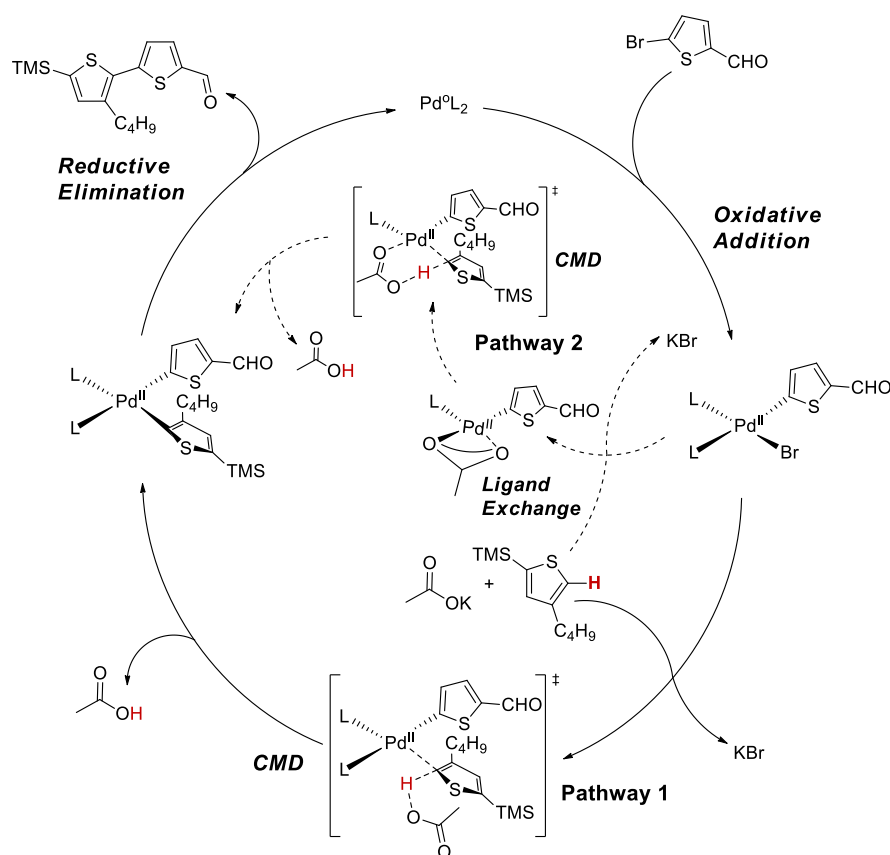


Scheme 2-1: Oligothiophene π -bridge synthetic pathway

2.3.2 Direct arylation cross-coupling

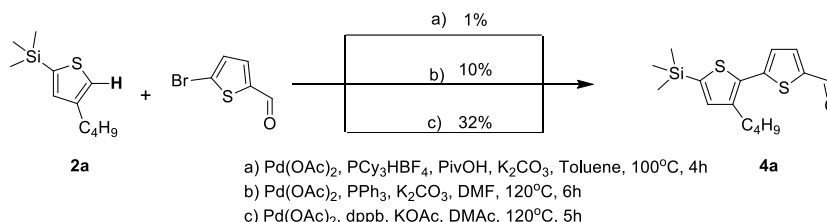
An attempt was made to streamline the oligothiophene synthetic route further, in terms of both the synthetic steps needed and the atom economy of the pathway, via a direct C-H arylation between thiophene precursor **2a** and 5-bromothiophene-2-carbaldehyde for the synthesis of bithiophene **4a**, thus bypassing the need for

borylation and allowing the use of compound **2a/b** as the key intermediates. This involved activating otherwise unreactive C-H bonds by a metal catalyst, to allow carbon-carbon bond formation to an aryl halide. Direct arylation reactions between 3-alkylthiophenes and a variety of halogenated aryl systems have been widely reported, due in part to the facile palladation of the latter and highly selective reactivity of the former, with this selectivity stemming from the sterically hindered C2 positions on the thiophene.^[126] This technique has even allowed the polymerization of P3HT via an asymmetrically functionalized 2-iodo-3-hexylthiophene monomer through a direct heteroarylation polymerization (DHAP), albeit with minor defects from homocoupling and β -branching.^[127] In the literature the mechanism for this reaction, particularly for heterocyclic substrates, is generally held to proceed through a base-assisted concerted metalation-deprotonation (CMD) pathway.^[128] Here the mechanism utilizing the thiophene substrates is shown and an acetate base, which proceeds through one of two catalytic cycles depending on whether a bidentate ligand (**Pathway 1**) or a monodentate ligand (**Pathway 2**) is used. Following oxidative addition, exchange of the halogen ligand to the acetate anion then facilitates the CMD key step: deprotonation of the thiophene substrate while simultaneously forming a carbon-metal bond. In the case of **Pathway 1**, the C-H activation and deprotonation of the thiophene substrate is assisted intermolecularly. Reductive elimination then affords the product.



Scheme 2-2: Catalytic cycle for a direct arylation between thiophene substrates utilizing a palladium species with bidentate ligands (Pathway 1) or monodentate ligands (Pathway 2)

In this study initial direct arylation attempts utilized three different conditions reported in the literature (Scheme 2.3). Schipper reported conditions for a high-yielding direct arylation between the C5-position on a 2-carboxyaldehyde-functionalized thiophene and a phenyl bromide (Scheme 2.3a), however for **2a** this resulted in a low conversion rate of the starting reagents.^[129] This was attributed to the sterically-hindered nature of the C2-position on **2a**. Subsequently, similar reaction conditions to those utilized for a C2 coupling between a similarly hindered thiophene-3-acetic acid and bromobenzene were then attempted (Scheme 2.3b).^[130] Complete conversion of the starting reagents was observed, however desilylation of the bithiophene product and subsequent direct arylation to this side product resulted in low yields.^[126a, 131] Chen et al suggest that this desilylation was caused by the cleavage of the Si-C bond by the electrophilic palladium centre,^[126a] and utilized reaction conditions for the coupling of a 2-(TMS)thiophene to a bromobenzonitrile substrate that was shown to minimize desilylation. High coupling yields in the literature were achieved through the use of a 1,4-bis(diphenylphosphino)butane ligand (dppb) and dimethylacetamide (DMAc) solvent, however it was suggested that the observed yields were a result of efficient coupling as opposed to a tolerance to the silyl moiety, as reactions utilizing the same reagents but with a threefold increase in reaction time resulted in a seven-fold increase of desilylation. For **2a** (Scheme 2.3c), the reported conditions did in fact prove to have a positive influence on product yield with an increase to 32% and the minimization of product desilylation, however the overall conversion rate proved to be low with a substantial portion of unreacted reagents returned. Increased rates of desilylation with longer reaction times were also observed.



Scheme 2-3: Initial optimization of direct arylation reaction conditions

The sterically bulky nature of the hexyl sidechain at the C3 position was suspected to be the cause of the low conversion rates, and further theorized that this bulk was interfering with the reductive elimination of the two thiophene substrates by hindering the close proximity needed for this process. Figure 2-4a depicts the intermediate formed in the catalytic cycle that immediately precedes reductive elimination. It was hypothesized that by utilizing ligands with a bulky or bidentate nature the bite angle θ between the ligands could be widened, and thereby force the two aryl centres into closer proximity. In addition, if these ligands were also electron-deficient, this would hypothetically weaken Pd-C bonds between the catalyst and the thiophene substrates, thus promoting reductive elimination. Operating under this hypothesis a study was conducted to improve the yields for the direct arylation between the thiophenes through optimized catalyst/ligand pairings. Optimized conditions from Scheme 2-3 that resulted in the highest yields were utilized (Figure 2-4b), but paired with a series of commercially available phosphine-based ligands chosen for their sterically bulky or electron-deficient nature (Figure 2-4c). To rapidly screen these ligands for their

performance, high pressure liquid chromatography (HPLC) measurements of the crude material from each reaction was utilized for a quantitative analysis (see Section 2.8 for experimental details).

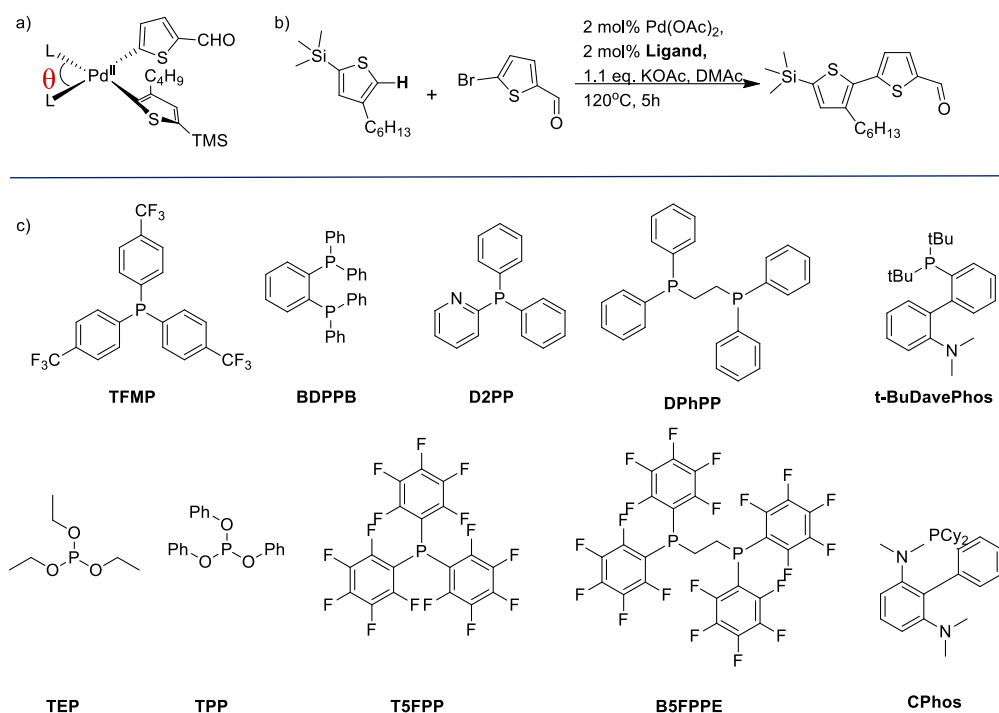


Figure 2-4: a) The intermediate palladium complex formed prior to reductive elimination, b) the reaction conditions utilized for the ligand screening, and c) the chosen ligands.

By assessing the relative quantities of the starting materials, products and by-products, and comparing them to an internal standard, coupling and desilylation yields can be determined, giving the overall gross yield. The results of the ligand screening can be seen in Table 1, with dppb included as a standard. Though many of the ligands resulted in gross yields exceeding that of the standard, it was also found, contrary to the initial hypothesis, that a) the more electron-deficient ligands (**TFMP**, **B5FPPE**, **T5FPP**, etc) tended to produce lower yields, relative to the more electron-rich phosphine ligands and to the dppb standard. Also observed was a non-trivial amount of desilylation upon inclusion of the vast majority of the screened ligands. The hypothesis here was that their increased electron-withdrawing nature in turn increased the electrophilicity of the palladium centre, thus enhancing its ability to cleave C-Si bonds as described previously, although the fact that the greatest amount of desilylation is attributed to the relatively electron-rich **DPhPP** ligand indicates that other factors were also at play. It can also be seen that the bidentate ligands **DPhPP** and **B5FPPE** resulted in poor couplings yields (~27-50%), while another bidentate ligand, **BDPPB**, performed relatively well (~67%), perhaps indicating that the sp² linked phosphines induced a more favourable bite angle than the sp³ linked phosphines. The relatively electron-rich **t-BuDavePhos** proved to be the highest-performing ligand with a coupling yield of 86.1%, an almost 20% increase over the similar ligand **Cphos**. As the key difference were the relatively smaller tert-butyl phosphino-linked moieties on **t-BuDavePhos** (relative to the larger cyclohexane moieties) and lack of a phosphine-adjacent dimethylamino group, it was theorized that these structural features decluttered the physical space around the palladium core, thus facilitating coordination

of the TMS-functionalized thiophenes. In this manner the CMD step, and not the reductive elimination as previously hypothesized, would appear to be the rate limiting step. Though significant yields for this direct arylation were obtained, translation to large-scale reactions still require further optimization.

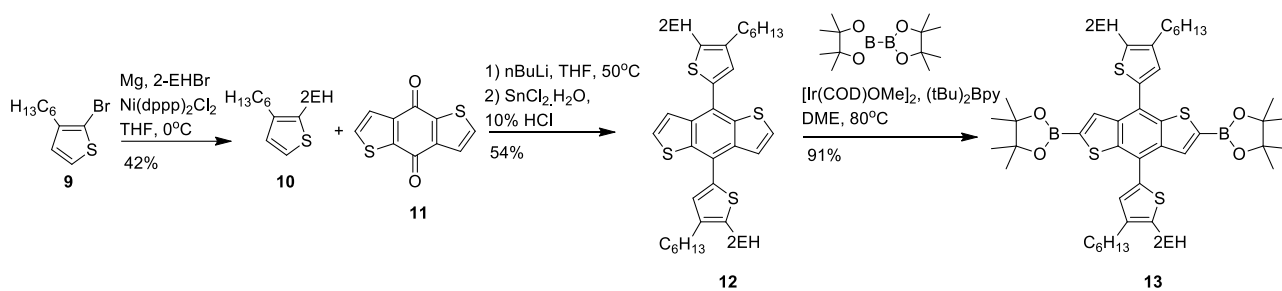
Table 1: Ligand screening results

Ligand	Coupling yield (%)	Desilylation (%)	Gross yield (%)
DPPB*	32.0	0.00	32.0
TFMP	45.1	24.1	21.0
DPhPP	51.1	28.4	22.7
B5FPPE	27.7	0.00	27.7
T5FPP	51.5	14.7	36.8
D2PP	63.1	19.4	43.7
TEP	65.7	20.4	45.3
TPP	71.5	24.6	46.9
CPhos	68.7	18.8	49.9
BDPPB	66.7	16.7	50.0
t-BuDavePhos	86.1	19.9	66.2

**Standard for catalytic screening*

2.3.3 Benzodithiophene core

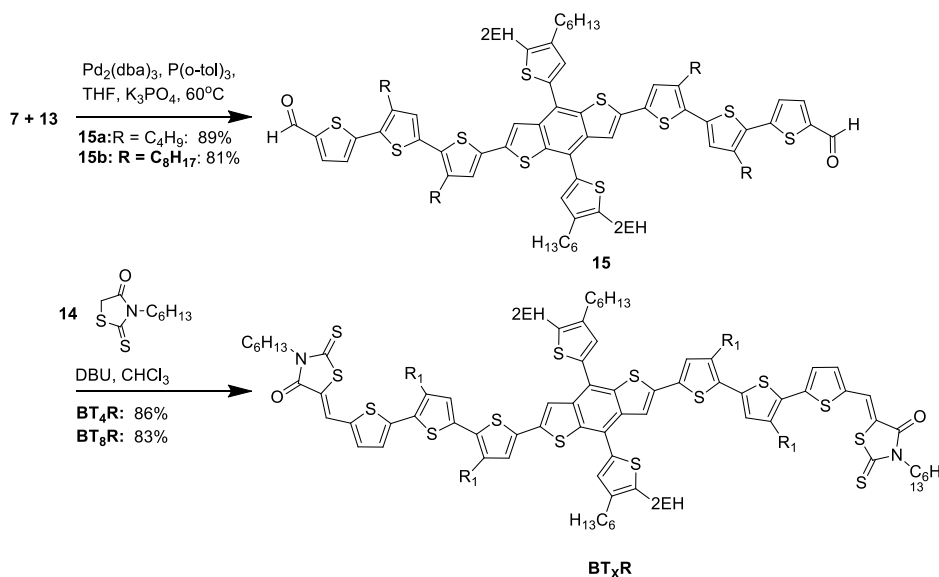
In a previous publication the benzo[1,2-b:4,5-b']dithiophene core utilized in the original synthesis of **BTR** was functionalized with trimethylstannyl moieties at the C2 and C6 positions to allow the attachment of the terthiophene π -bridges via Stille coupling conditions. As the use of toxic organotin compounds in the large-scale pathway was to be avoided, the BDT cores were functionalized with Bpin moieties for Suzuki cross-coupling to the terthiophenes. As seen from Scheme 2.4, the synthesis of the dialkylthienyl-functionalized BDT core itself follows the same pathway utilized in the original publication – first, the commercially available 2-bromo,3-hexylthiophene **9** was coupled to the freshly prepared 2-ethylhexyl magnesium bromide through Kumada coupling conditions, which yielded the target 2,3-dialkylthiophene **10** after purification via distillation in yields of ~40%.^[39a, 119] Following this, the dialkylated thiophene was installed onto the BDT core. **10** was deprotonated at the C5-position via n-BuLi, and then introduced to the BDT dione **11** via a condensation reaction. The addition of tin chloride under acidic conditions allowed the reduction of the central ring to restore benzene aromaticity, affording the dithienyl BDT core **12** after purification by column chromatography with a yield of 54%. In a departure from the original **BTR** publication, the BDT core **12** was then bis-borylated using an iridium-catalyzed C-H activation. Purification of the bis-Bpin-functionalized compound through precipitation in IPA lead to the analytically pure **13** in yields of 85% on a multigram scale.



Scheme 2-4: 2D BDT core synthetic pathway

2.3.4 BTR analogues

The electron-poor end-group acceptor *n*-hexyl rhodanine **14** was synthesized from the commercially available reagent, hexyl amine, utilizing a one-pot microwave reaction described in the literature (Scheme 2-5).^[132] Due to the efficient nature of the microwave reaction, **14** was able to be synthesized on a multi-gram scale, which could be purified via distillation. A simple Suzuki cross-coupling between the 3-alkyl terthiophenes **7a/7b** and the bis-borylated BDT cores **12** yielded the dialdehyde-functionalized penultimate materials **15a** and **15b**. Precipitation in IPA before column chromatography greatly facilitated purification, as this removed the vast majority of the unreacted terthiophene, leaving only a mono-coupled BDT core as the major side product which possessed a much higher r.f. on silica to that of the target product. High yields of 80-90% were able to be achieved. These were then reacted with a five-fold excess of **14** through a base-catalyzed Knoevenagel condensation, previously utilized in the original synthesis of **BTR**.^[119] It was found that increasing the quantity of the base (DBU) to 10 mol% allowed the condensation to proceed with around 90% conversion in 15 minutes, and that shielding the reaction from light prevented the formation of multiple side products. The purification of the final products could be greatly simplified by precipitation in methanol to facilitate removal of unreacted **14**, after which both silica column chromatography and size-exclusion chromatography were used to isolate the analytically pure targets **BT₄R** and **BT₈R** in yields of around 80%.



Scheme 2-5: BT_xR synthetic pathway

2.4 Physical, spectroscopic and electrochemical properties of BT_xR analogues

With the BT_xR analogues synthesized, full characterization of the materials were also performed to assess the impact of sidechain engineering on their properties. Here data collected from both these analogues as well as **BTR** itself as an additional data point is presented to better construct structure-property relationships. The information presented here is in good agreement with the data reported in the previous publication on BT_xR materials.^[39a]

2.4.1 Thermal properties

The thermal stabilities of **BT₄R**, **BTR** and **BT₈R** were assessed via thermogravimetric analysis (TGA, Figure 2-16, Section 2.8.5) and were found to possess good stabilities, with observed 5% weight loss decomposition temperatures at around 390-400°C. Following this, as **BTR** had been found to possess a complex phase transition behaviour with a high-temperature NLC phase, a more in-depth examination of these transitions was also recorded for these analogues using differential scanning calorimetry (DSC, Figure 2-5). These thermograms show that the structural modifications performed had a clear impact upon the degree of attraction between molecules, as per the observed melting point for the materials. **BT₄R** possesses the highest melting point at 207°C, followed by **BTR** at 196°C and **BT₈R** at 158°C, indicating that lengthened alkyl sidechains appear to disrupt intermolecular packing to some degree. The phase behaviour for **BTR** has been previously reported, and again exhibits three phase transitions upon both heating and cooling while both **BT₈R** and **BT₄R** display only a single endothermic and two exothermic transitions. The relative enthalpies of these transitions are also observably different between the analogues, with smaller and broader peaks observed for **BT₈R** which are consistent with decreased intermolecular interactions caused by the increased insulation from the longer alkyl chains.

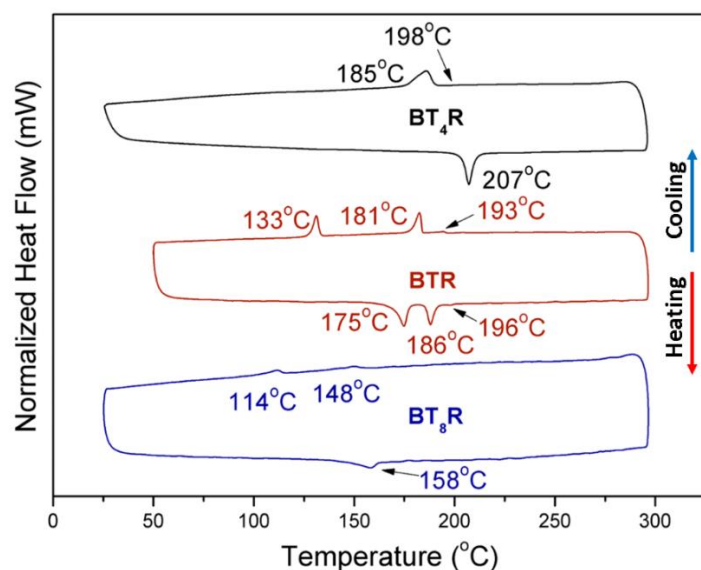


Figure 2-5: DSC thermograms of BT_xR analogues, with samples heated under nitrogen at a rate of 10°C s⁻¹.

Polarized optical microscopy (POM) was utilized to assist the identification of these transitions, with the heating profiles found in Table 5, Section 2.8.6. As previously mentioned **BTR** was found to possess an isotropic-to-nematic crystallization transition at 193°C, seen as a characteristically small, low-enthalpy peak attributed to a high degree of molecular ordering. These nematic liquid crystalline (NLC) phases are believed to be induced by molecules with high orientational order along the long (director) axis of the conjugated backbone but poor positional order along all other axes (see Figure 2-6a). The NLC phase of particular interest due to an implied nanoscale structure capable of facilitating 3D charge transport.^[133] NLC phases can be identified under polarized light by a birefringent Schlieren texture, which consist of dark and light bands converging on a point singularity. These differing intensities are caused by the various distributions of molecular orientation along the director axis phase-shifting the polarization of the transmitted light.^[134] By utilizing POM in conjunction with a heating platform, from the fully isotropic melt observed at 210° an isotropic-to-nematic phase transition was observed upon the cooling of **BT₄R** to 198°C, evolving the characteristic NLC Schlieren texture (Figure 2-6b). Around 190°C nucleates were observed, with this resulting in full crystallization of **BT₄R** by 185°C. A similar NLC phase was not observed for **BT₈R** at either of the exothermic peak temperatures, with nucleation initiating directly from the isotropic melt at around 150°C. No visible changes to the film morphologies were observed below the crystallization temperatures suggesting that the exothermic peaks seen in the DSC thermograms (i.e. for **BT₈R** at 114°C) are perhaps indicative of the subtle crystallization of smaller structural features like the alkyl sidechains. The lack of an NLC phase in **BT₈R** can perhaps be attributed to a smaller aspect (length to width) ratio, as most molecules with NLC phases possess long and rod-like structures,^[133b, 135] and it can be seen from Figure 2-2 that **BT₈R**'s lengthened alkyl sidechains induce a 'squaring' of the molecule relative to the more rectangular **BTR** and **BT₄R**. Here it can be seen that relatively minor sidechain engineering on the BTR substrate can have a significant impact on intermolecular packing.

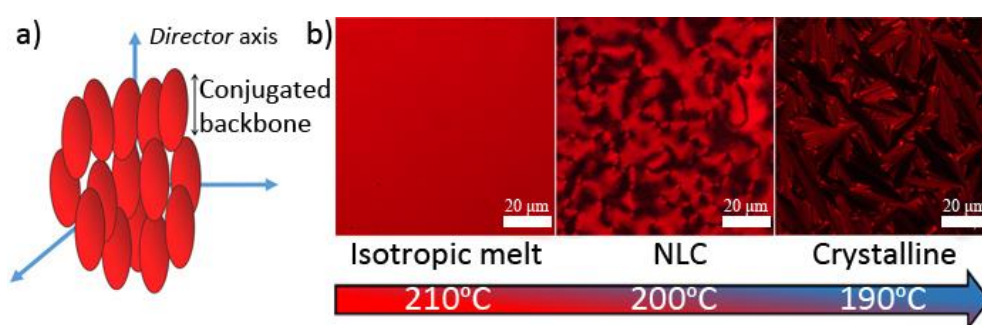


Figure 2-6: a) Semi-aligned nanoscale structure of molecular cores needed for an NLC phase, and b) Images of **BT₄R obtained by POM showing phase transitions upon cooling.**

2.4.2 Spectroscopic and electrochemical properties

The absorption spectra of the BTR analogues and **BTR** itself were measured in both dilute chloroform solution and as thin films cast from chloroform (Figure 2-7), with the relevant data presented in Table 2. As all the materials in this study possessed the same chromophore, unsurprisingly no significant differences were

observed between the absorption spectra of the three molecules in chloroform, with each exhibiting a broad absorption in the 400-650 nm range and peak maxima around 515-520 nm. High molar extinction coefficients (ϵ_{max}) of 8 to $9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ are calculated which was attributed to the partial 2D-conjugated nature of the thienyl-functionalized BDT core. When cast onto thin films, all three compounds exhibited red-shifted absorptions of around 50-70 nm, characteristic of H-aggregate materials, and develop more complicated structures with the evolution of two peaks at ~ 570 - 590 nm and ~ 630 nm. Effects of the sidechain alterations are more apparent here – **BT₈R** is seen to have a relatively less pronounced peak at 630 nm corresponding to a 0-0 energy transition, and is indicative of reduced π - π stacking. Curiously, both BT_xR analogues are also blue-shifted by about 20 nm when compared to **BTR**, and also possess slightly higher absorption onsets. Similar optical HOMO-LUMO energy gaps ($E_{\text{g}}^{\text{opt}}$) were estimated from these onsets and are seen to be around 1.7-1.8 eV.

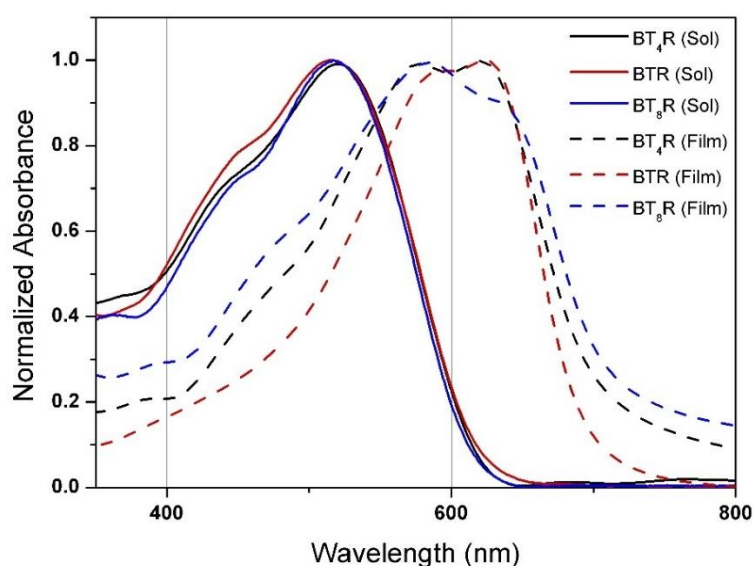


Figure 2-7: UV-Vis absorption spectrum of the BT_xR series in solution (solid line) and as-cast films (dotted lines)

Cyclic voltammetry (CV) studies were used to probe the electrochemical properties of the solid-state BTR analogue materials, (Figure 2-17, Section 2.8.7) with the relevant data summarized in Table 2. All three materials show one reversible oxidation process and one irreversible reduction process within the accessible window. Ionization potentials (IP) and electron affinities (EA) were estimated from the first oxidation and reduction potentials, respectively, from which the electrochemical energy gaps (E_{g}^{CV}) could be calculated. These were found to be virtually identical at 1.97-2.00 eV, suggesting reasonable potential for harvesting of the solar spectrum. The larger electronic vs optical energy gap observed is not unexpected with the ~ 0.2 eV difference due to the additional Coulomb energy needed to overcome the repulsion upon electron injection in the case of CV measurements.^[136] IPs were also directly measured by photoelectron spectroscopy in air (PESA) and give a measure of the HOMO energy levels of the materials, which show similar trends to the IPs obtained from CV measurements but differ by about 0.2 eV. All three HOMO energy levels were found to be relatively low-lying, potentially facilitating high V_{oc} values.

Table 2. Absorption and electronic energy levels of BTR analogues

	Solution $\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M ⁻¹ cm ⁻¹)	Film $\lambda_{\max}$ (nm)	Film λ_{ons} (nm)	Film $E_{\text{g}}^{\text{opt}}$ (eV)	Film $E_{\text{ox}}^{\text{ons}}$ (V)	Film $E_{\text{red}}^{\text{ons}}$ (V)	Film IP (eV)	Film EA (eV)	Film E_{g}^{CV} (eV)	PESA HOMO (eV)
BT ₄ R	520	8.9 x 10 ⁴	570	705	1.75	0.94	-1.04	-5.38	-3.40	1.98	-5.20
BTR	521	9.9 x 10 ⁴	592	698	1.80	0.93	-1.04	-5.37	-3.40	1.97	-5.21
BT ₈ R	516	6.9 x 10 ⁴	568	715	1.73	0.98	-1.02	-5.42	-3.42	2.00	-5.24

2.5 Photovoltaic properties and performance

OPV BHJ devices utilizing the BT_xR series in the active layer were fabricated utilizing a conventional device architecture (ITO /PEDOT:PSS/BT_xR:PC₇₁BM/Ca/Al, Figure 2-8a). The active layer was comprised of a 1:1 (w/w) blend of BT_xR:PC₇₁BM semiconductors and deposited via spin-coating from chloroform to form a ~250 nm thick layer. Here devices were assembled either as as-cast films or films processed with solvent vapor annealing (SVA) using THF with the respective J-V curves shown in Figure 2-8b/c and data reported in Table 3. SVA treatment exposes the active layer film surface to close proximity to an organic solvent, which penetrates the film via passive diffusion and is a well-established method in the literature for increasing the degree of nanoscale order in the active-layer morphology.^[137] Spin-coated films typically result in kinetically-trapped structures, and as such SVA treatments are utilized to drastically lower the glass transition temperature of the materials. This imparts higher molecular mobilities, thus allowing molecules to demix into lower-energy states, and has been shown to result in crystalline domains with greatly increased sizes for **BTR** and other small molecular materials.^[138]

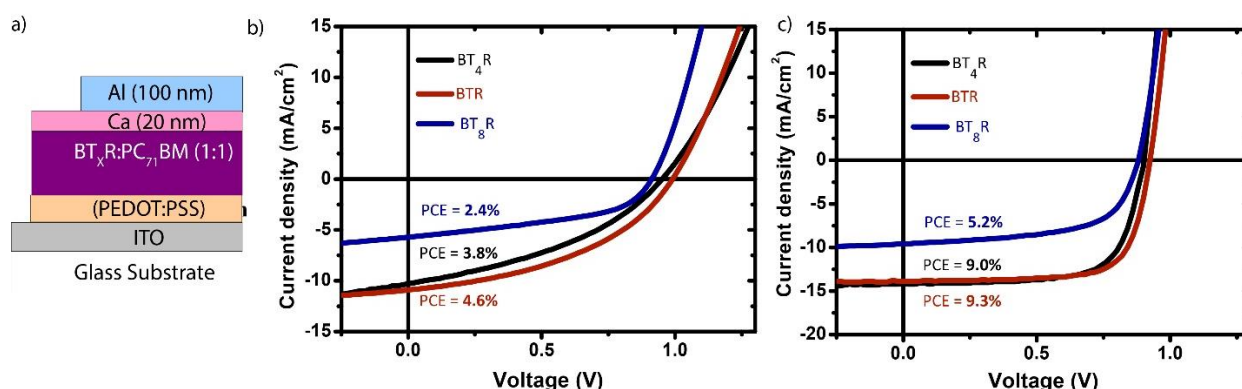


Figure 2-8: Schematic of OPV device architecture, and current-voltage characteristics of BT_xR:PC₇₁BM BHJ solar cell devices b) as-cast and c) after solvent-vapor annealing

In the BT_xR series, the as-cast devices all exhibit high V_{OCs} of above 0.90 V but relatively poor performances hindered by low FFs of <45%. **BT₈R** in particular is seen to have a particularly low J_{SC} of 5.7 mA cm⁻², roughly half that of the other two materials. Upon SVA, these performances are seen to greatly improve, with **BT₄R** in particular possessing a PCE analogous to that of **BTR**. The increased PCEs were attributed to improved FFs and J_{SCs} , presumably due to the increased charge transport from the SVA-induced morphology. Here the

moderately-solubilizing THF is utilized as the solvent for the annealing treatment - Chen and co-workers have found that solvents with greater solubilizing capabilities and high vapor pressures resulted in improved performances for small molecular materials,^[139] however studies by Engmann et al have observed that the use of high-solubilizing solvents like chloroform for the SVA treatment of **BTR** resulted in films with excessive phase separation, adversely affecting performances.^[138] The decreased V_{oc} of the devices after SVA treatment is not unexpected and has been suggested in the literature to be due to increasing intermolecular interactions between the donor and acceptor, with this red-shifting the absorption profile of the active layer and subsequently reducing the optical bandgap.^[140] Xie and coworkers have reported a post-SVA thermal annealing treatment that shows recovery of the V_{oc} to pre-SVA levels, however it is likely that the efficacy of this technique will be highly substrate-dependant.^[140b]

Table 3: Photovoltaic performances of BT_xR : $PC_{71}BM$ BHJ solar cells fabricated under different annealing conditions

Active Layer (1:1 Donor: $PC_{71}BM$)	Annealing Conditions	V_{oc} (V)	J_{sc} ($mA\ cm^{-2}$)	FF (%)	PCE (%)
BT_4R	As-Cast	0.94	10.3	39	3.8
BT_4R	SVA – THF (20 sec)	0.88	14.0	73	9.0
BTR	As-Cast	0.98	10.8	43	4.6*
BTR	SVA – THF (20 sec)	0.92	13.9	72	9.3*
BT_8R	As-Cast	0.92	5.72	45	2.4
BT_8R	SVA – THF (20 sec)	0.88	9.60	62	5.2

From this data it is clear that sidechain engineering efforts have resulted in stark impacts upon the performances of the materials – while **BT_4R** possesses an excellent PCE of 9.0% with an FF of 73% and a J_{sc} of $14.0\ mA\ cm^{-2}$, **BT_8R** has a much lower device performance with a PCE of 5.2%, FF of 62% and a J_{sc} of $9.60\ mA\ cm^{-2}$. As these sidechain modifications were not expected to have significantly impacted the energy levels of the chromophore -a hypothesis supported by the similar UV-vis solution absorption profiles of the BT_xR series- the large decrease for the device performance was then suspected to originate from differences in the active-layer morphology. Visual inspection of the SVA-treated films support this hypothesis, with **BT_8R** films possessing significantly rougher surfaces indicative of a poor film quality (Figure 2-9).

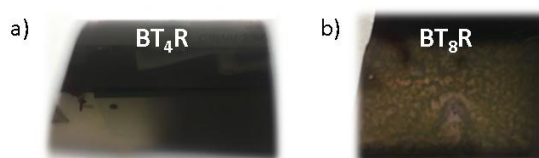


Figure 2-9: Spin-coated, SVA-treated films of a) BT_4R and b) BT_8R showing differences in film quality

2.6 Morphological analysis

2.6.1 X-ray crystallography

To elucidate on the packing of individual crystalline BT_xR molecules in thin films, X-ray quality single crystals were grown for all three materials in the series, with the single crystal structures solved using data from the MX1 beamline at the Australian synchrotron.^[141] These structures are seen in Figures 2-10 (**BT_4R**), 2-11 (**BTR**)

and 2-12 (**BT₈R**), and are presented as a) single molecules, b) separated by alkyl lamellar layers and c) separated by π -stacking distances. All three molecules possess triclinic pinacoidal space groups. As expected, increasing the alkyl sidechain length correspondingly increases the observed distances between alkyl lamellar layers from 18.86 Å to 19.04 Å to 19.26 Å, with a widening of approximately 0.2 Å between lamellar layers per ethyl unit added. As the expected width of this moiety is around 2.5 Å,^[142] an increasing degree of interdigitation between sidechains of the analogues accounts for the surfeit length, and is particularly noticeable in the case of **BT₈R** (Figure 2-12b). Significantly different packing between lamellar layers can also be observed for the three analogues, as highlighted by the calculated angles between the BDT core moieties (highlighted in red). While **BT₄R** appears to slot almost directly between two neighbouring molecules in the adjacent lamellar layer (Figure 2-10b), the cores of adjacent **BTR** molecules are much more strongly associated with an angular offset of just 11.8° (Figure 2-11b). The offset of **BT₈R**'s BDT core moiety falls between these two values, with an intermediate angular offset of 29.1°. It can also be observed that while the terminal rhodanines of **BT₄R** and **BT₈R** are hydrogen-bonded through their carbonyl moieties to the vinylic protons or aromatic of adjacent molecules, **BTR** does not display this same behaviour. Its rhodanine moieties are more offset along the long axis of the conjugated backbone – accounting for the greater interchain separation of 41.8 Å relative to the 36-37 Å separation for **BT₄R** and **BT₈R** – however whether this is a casual effect of the BDT core offset is currently unknown.

Another clearly observable structural difference are the π -stacking motifs of the analogues. As mentioned in Section 2.1, a previous publication revealed that **BTR** packed into coplanar π -stacked dimers, with a ‘brick layer’ packing motif that can also be observed from the **BTR** crystal structures (Figure 2-11c), with intra-dimer and inter-dimer π -stacking distances of 0.36 nm and 0.37 nm, respectively. This motif is known in the literature to confer more effective 2D charge transport, provided that there is sufficient π -overlap.^[143] The pairs of molecules in each dimer is marked out with similarly-coloured arrows. This same dimer-like stacking is not observed for **BT₄R** which possesses a ‘slipped’ stacking motif and exhibits a constant π -stacking distance of 0.35 nm, however a ‘brick layer’ motif is present in **BT₈R** where the intra-dimer and inter-dimer π -stacking distances are 0.36 nm and 0.44 nm, respectively.^[143] In addition, unique to **BT₈R** is an offset along the π -stacking axis (Figure 2-12d) where each dimer (again marked by coloured arrows) exhibits significant transverse displacement relative to its neighbours and is likely linked to possessing alkyl sidechains with orientations normal to the conjugated backbone, as seen in Figure 2-12c. This large π -stacking distance and decreased π -overlap in the crystalline domains of **BT₈R** could partially account for the poor OPV performance, with the low J_{SC} observed attributable to the relatively hindered intermolecular charge delocalization.

Different degrees of torsional strain can also be observed from the dihedral angles between the BDT core and the oligothiophene π -bridges, as well as between the BDT core and the thienyl headgroup moieties. The π -bridge/core strain appears to be primarily affected by the degree of core offset between lamellar layers, presumably due to the steric repulsion of the neighbouring core moieties. However, as the observed V_{OCs} are

relatively similar between the three analogues, it would seem that the distortion along the conjugated backbone does not significantly impact upon the degree of conjugation.

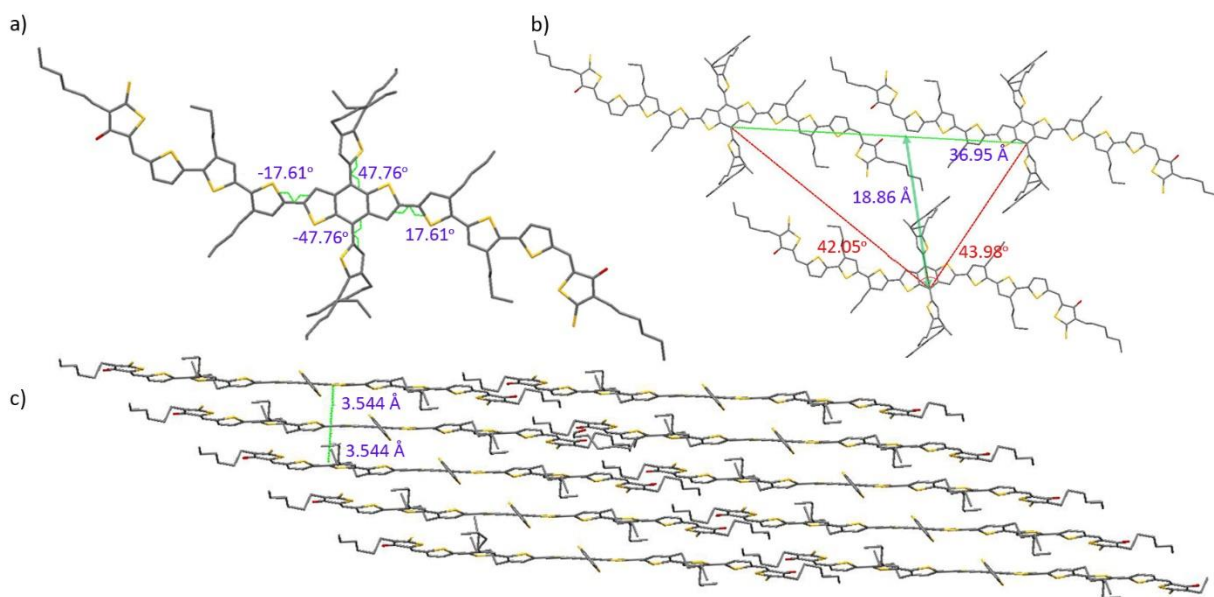


Figure 2-10: Single crystal structures of BT₄R, seen a) as a single unit with dihedral angles labelled, b) as packing across alkyl lamellar layers with the core-core distance (purple) and angles (red) labelled, and c) as a 2-molecule long π -stacked layer with π -stacking widths labelled. Hydrogen atoms and some alkyl chains have been omitted for clarity.

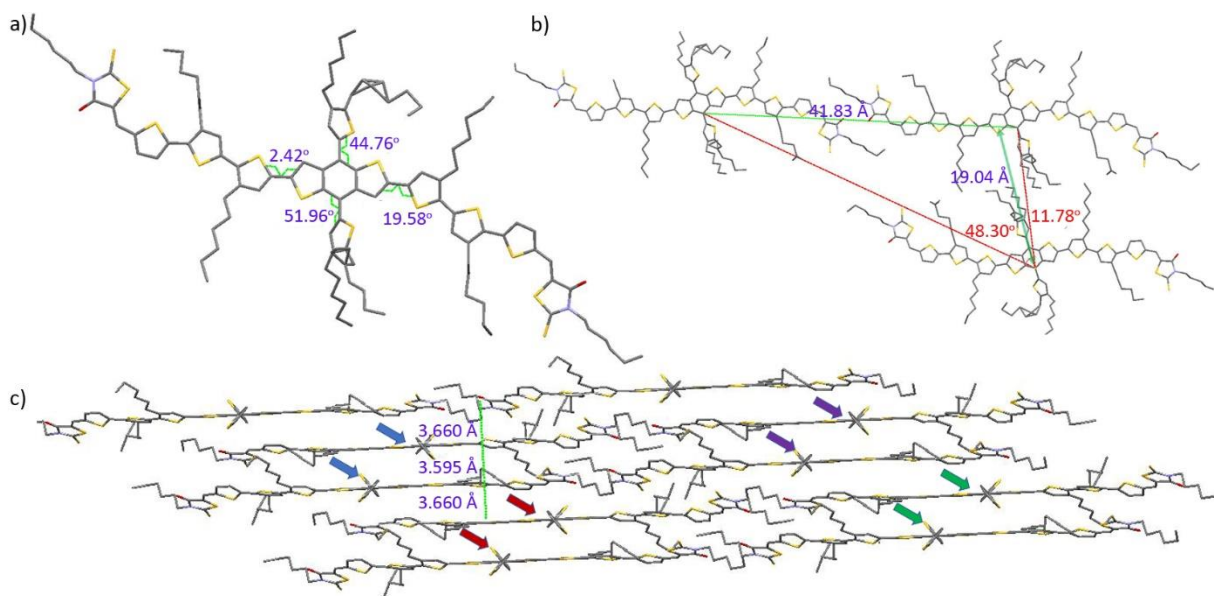


Figure 2-11: Single crystal structures of BTR, seen a) as a single unit with dihedral angles labelled, b) as packing across alkyl lamellar layers with the core-core distance (purple) and angles (red) labelled, and c) as a 2-molecule long π -stacked layer with π -stacking widths labelled and dimer pairs marked by coloured arrows. Hydrogen atoms and some alkyl chains have been omitted for clarity.

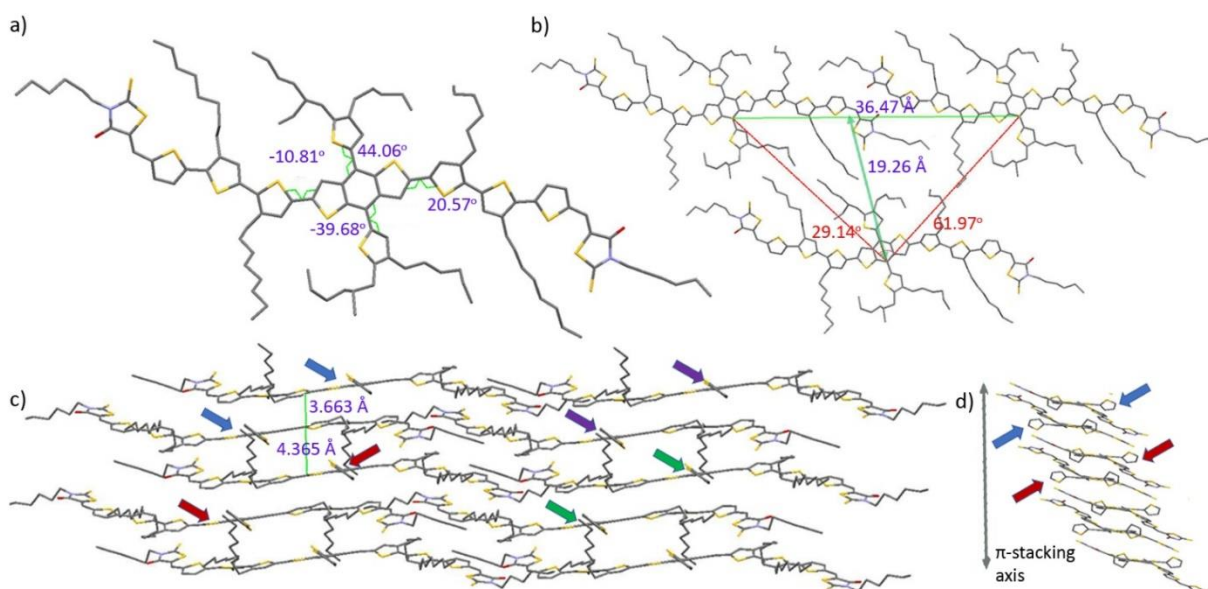


Figure 2-12: Single crystal structures of **BT₈R**, seen a) as a single unit with dihedral angles labelled, b) as packing across alkyl lamellar layers with the core-core distance (purple) and angles (red) labelled, c) as a 2-molecule long π -stacked layer viewed normal to the long axis of the conjugated backbone, with π -stacking widths labelled and dimer pairs marked by coloured arrows and d) a π -stacked layer as viewed along the long axis of the conjugated backbone. Hydrogen atoms and some alkyl chains have been omitted for clarity.

2.6.2 GIWAXS measurements

In light of the varied film morphologies and performance of the OPV devices, GIWAXS measurements were performed on the SAXS/WAXS beamline at the Australian synchrotron to understand the nanoscale structure in the films as a function of molecular structure.^[144] The films for analysis were prepared in an analogous process to the device films – PEDOT:PSS was first spin-coated onto a silicon substrate, annealed, and then spin-coated with either the neat **BT_xR** material or a 1:1 (w/w) **BT_xR**:PC₇₁BM blend, and either left as-cast or solvent-vapor annealed. GIWAXS scattering patterns of the three types of films for **BT₄R**, **BTR** and **BT₈R** can be seen in Figures 2-13, 2-14 and 2-15, respectively, along with the corresponding linecuts of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes. Table 4 summarizes the information extracted from the scattering patterns and includes the (100) and (010) d-spacing as well as the crystallite correlation length along the (100) plane. Due to the peculiarities of the molecular orientations of the **BT_xR** analogues -to be shortly covered- also included are the Hermans' orientation parameter S for both the (100) and (010) reflections to reinforce the conclusions drawn. It should be noted that as these reflections are typically perpendicularly situated on the q_{xy}/q_z axes for a given molecular orientation, when determined from a (010) reflection -counter to the example given in Section 1.6- S values of -0.5, 0 and 1 indicate completely edge-on crystallites, isotropically oriented crystallites and completely face-on crystallites, respectively.

The neat, as-cast film of **BT₄R** (Figure 2-13a) exhibits a scattering pattern with good long-range order in the vertical axis as indicated by the peaks assigned to the first, second and third $h00$ reflections at $q_z = 0.36 \text{ \AA}^{-1}$, $0.72 \text{ \AA}^{-1}$ and $1.08 \text{ \AA}^{-1}$ respectively. This is attributed to strong ordering across alkyl lamellar layers stabilized by sidechain crystallization. A d-spacing of 1.73 nm is obtained from the scattering pattern which is noticeably

different than that of the corresponding lamellar interchain distance of 1.89 nm from the single-crystal derived structure, as expected of the transition from the crystalline material to paracrystalline thin films. The scattering pattern and its linecut show that although the 100 reflection is present in both axes, indicating a certain degree of molecular isotropy with respect to the substrate, the higher-order $h00$ reflections are primarily limited to the vertical axis. This would ordinarily suggest a higher degree of edge-on than face-on crystallite orientation, however in the broad arc assigned to the 010 π -stacking reflection, seen at $q = 1.71 \text{ \AA}^{-1}$, the area of greatest intensity is not in the horizontal axis but the vertical axis. This is curious as for molecular architectures that host alkyl sidechains perpendicularly oriented away from the conjugated backbone, it is expected that the direction of lamellar stacking be normal to that of π -stacking. This same behaviour can be seen for a number of scattering patterns of the BT_xR series, where both the 100 and 010 reflections are simultaneously of greatest intensity in the q_z axis. Though in a previous publication of **BTR** a similar phenomenon was attributed to a bimodal crystallite orientation,^[119] recent results in the literature have suggested instead a ‘rolling log’ molecular orientation, where in the film bulk BT_xR crystallites rotate around the long axis of the conjugated backbone, which itself is parallelly locked in-plane relative to the substrate, thus producing a scattering pattern reminiscent of a 2D powder.^[145] Locking the backbone along the in-plane axis shifts the observed orientation distribution so that the 100 and 010 reflections appear more strongly in the vertical, out-of-plane axis due to the off-specular nature of q_{xy} axis scattering, when realistically these molecules possess a statistically-random, isotropic distribution. The Hermans’ orientation parameter is weighted by the peak intensity as a function of the azimuthal angle by the sinusoidal term $\langle I(\varphi) \sin \varphi \rangle$ and can partially account for this distorted distribution,^[146] outputting values of $S(100) = 0.03$ and $S(010) = -0.07$ consistent with an isotropic distribution for the **BT₄R** neat film.

Upon addition of the fullerene acceptor a characteristic broad, isotropic reflection at $q = 1.31 \text{ \AA}^{-1}$ can be observed and is attributed to amorphous PC_{71}BM . The degree of crystal structure for **BT₄R** is significantly reduced in the blend film with the disappearance of higher-order $h00$ reflections and an increase of the FWHM for both the 100 and 010 peaks (Figure 2-13 c/d), resulting in a corresponding decrease for the calculated CCLs in the 100 plane from 21.3 nm in the neat film to 11.9 nm. The broad nature of the reflections reduces the accuracy of the calculated orientation parameters but suggest that the fullerene addition has not had a significant impact upon crystallite orientation. Upon SVA treatment the degree of crystallinity is improved, with the evolution of overlapping reflections around $q = 0.5 - 0.8 \text{ \AA}^{-1}$ in both axes, one of which was assigned to a 200 alkyl lamellar reflection, and the other attributed to an unidentified reflection with a d-spacing of $1.03 \text{ \AA}^{-1}$. Both $h00$ and 010 reflections are more clearly defined with lower FWHMs, with a corresponding increase of the 100 CCL to 13.4 nm. The 100 d-spacing is seen to increase to 1.89 nm, which is consistent with the alkyl lamellar spacing seen from the single-crystal derived structure, and suggests the SVA treatment has allowed **BT₄R** to shift from a kinetically-trapped intermolecular packing state into a more thermodynamically-favoured one.

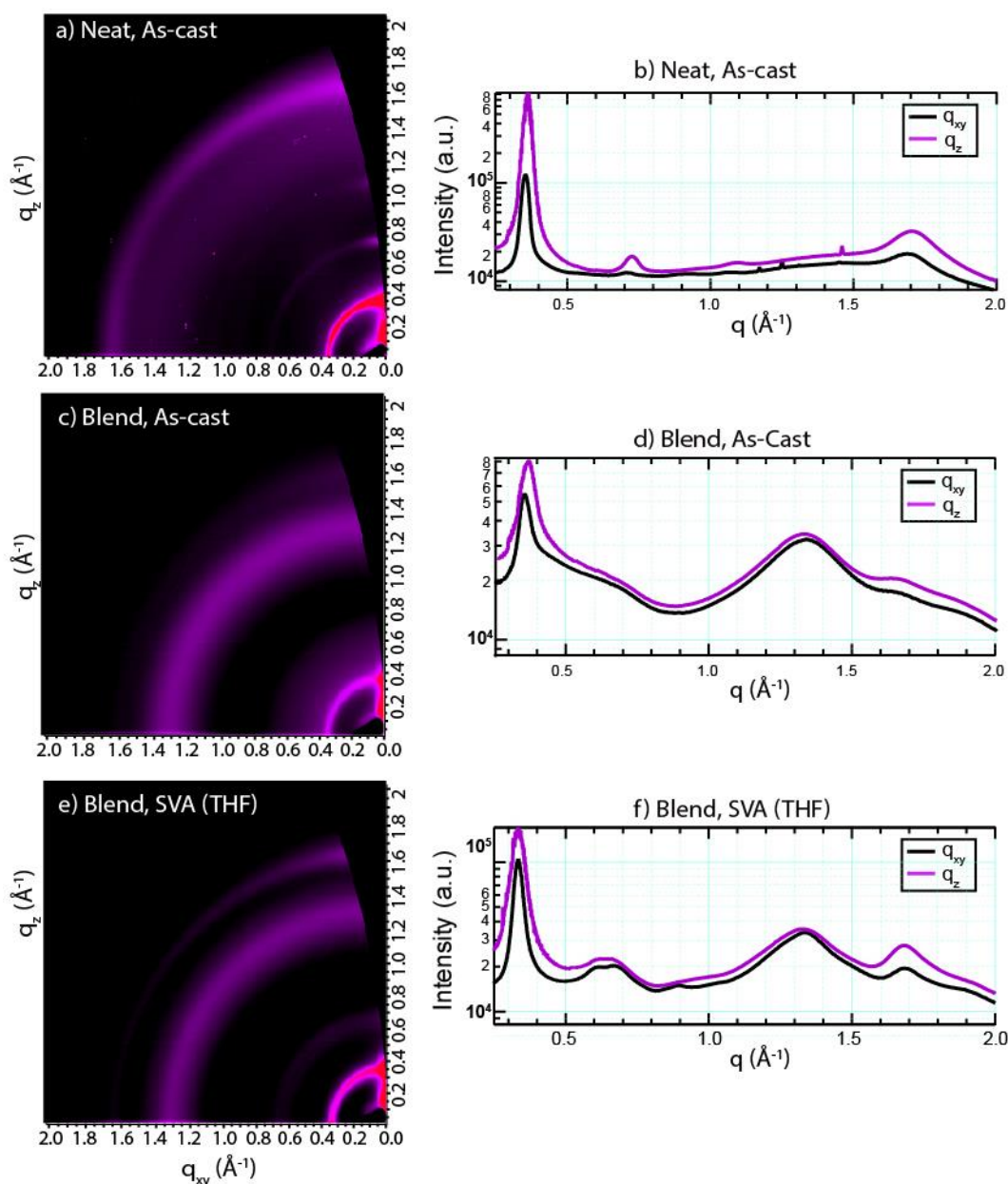


Figure 2-13: BT₄R GIWAXS scattering patterns that are: a) neat, as-cast; c) in a 1:1 fullerene blend, as-cast; e) in a 1:1 blend and SVA-treated; and their respective sector profiles along the Q_{xy} and Q_z axes

In previous work a GIWAXS scattering pattern for as-cast neat BTR films was reported,^[119] which is in good agreement with the scattering pattern obtained for this study (Figure 2-14a). This as-cast film of **BTR** appears to possess a similar nanoscale structure to that of **BT₄R**, with up to 3rd-order $h00$ also observed in the vertical axis -albeit corresponding to a larger d -spacing of 1.88 nm- as well as the ‘rolling log’ orientation. **BTR** however does possess a higher degree of isotropy, with well-defined arcing of the 200 and 300 reflections observed as well as greater relative intensities of all $h00$ peaks in the q_{xy} linecut. The sharper peaks observed also manifest a larger CCL of 29.5 nm for the neat **BTR** film, however like **BT₄R** the crystallite length decreases upon the addition of PC₇₁BM (Figure 2-14c) to 18.7 nm. In keeping with the higher overall relative crystallinity of **BTR** though, slight but observable 200 and 300 peaks can be seen in the linecut of the **BTR** blend film (Figure 2-14d), with a slight decrease of the d -spacing to 1.85 nm. SVA treatment (Figure 2-14 e/f) again

increases the overall crystallinity of the material with a calculated CCL of 22.9 nm, with the peak overlapping the 200 reflection at $q = \sim 0.6 \text{ \AA}^{-1}$ more distinct relative to the one present for **BT₄R**. Thermally annealed films of **BTR** (see Chapter 3) result in a sharper peak and reduced FWHM for this reflection, perhaps suggesting a polymorphic, co-crystallized form of **BTR**.

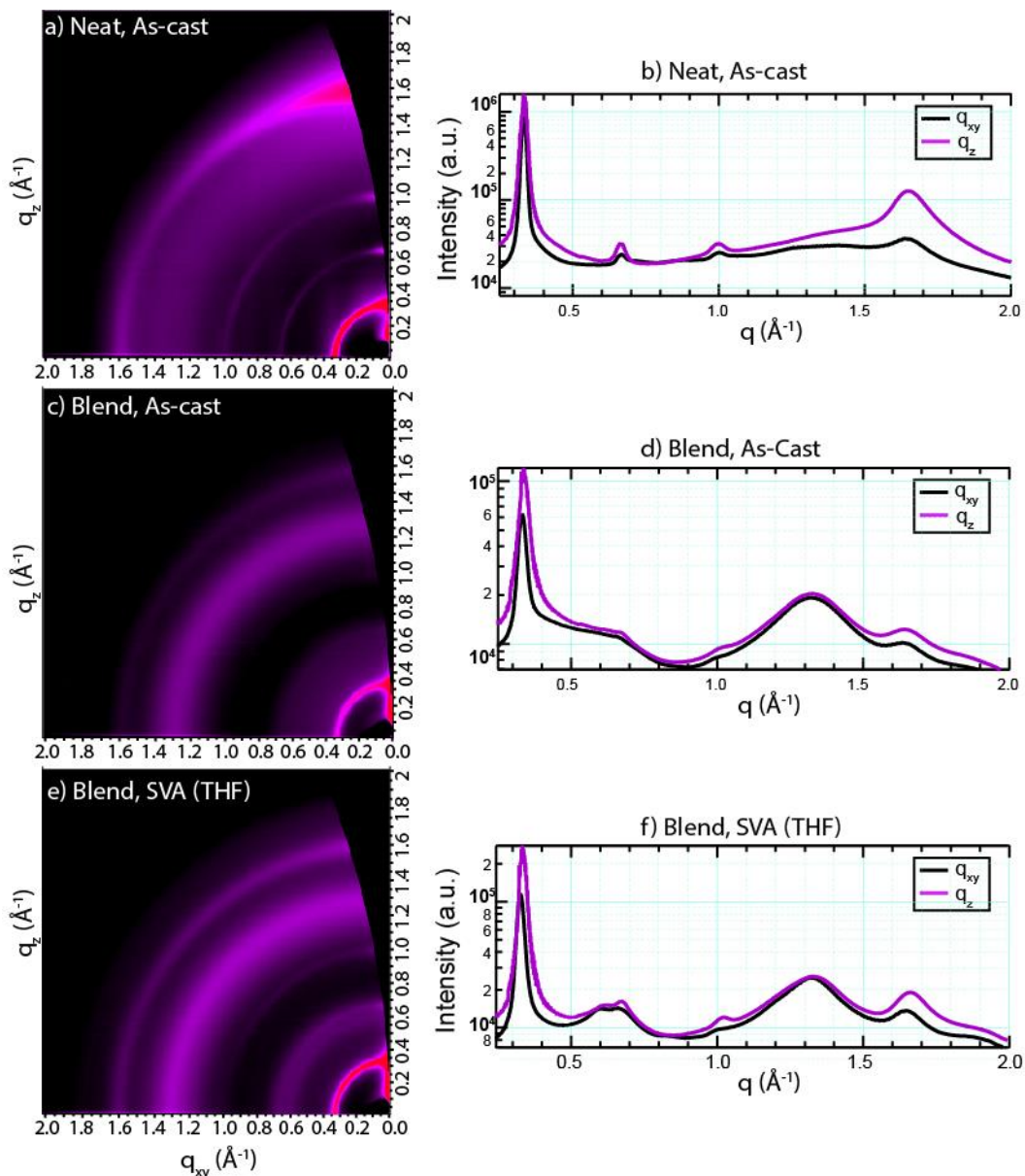


Figure 2-14: BTR GIWAXS scattering patterns that are: a) neat, as-cast; c) in a 1:1 fullerene blend, as-cast; e) in a 1:1 blend and SVA-treated; and their respective sector profiles along the Q_{xy} and Q_z axes

Broadly similar with scattering patterns of the other materials in the **BT_xR** series, the neat as-cast film of **BT₈R** (Figure 2-15 a/b) however exhibits the sharpest $h00$ peaks yet, resulting in a large calculated CCL of 35.8 nm. In keeping with the higher crystallinity of the **BT₈R** is the presence of 1st to 4th-order $h00$ reflections in the q_z axis of the scattering pattern, unique amongst the **BT_xR** series. The 100 d-spacing is again seen to increase with the inclusion of longer sidechains to 2.03 nm. **BT₈R** also responds in a similar manner to the other materials upon the addition of PC₇₁BM and upon SVA is calculated to possess the largest 100 CCL for SVA-treated films at 25.9 nm. Curiously, the calculated 010 d-spacing of 0.38 nm for all three films of **BT₈R** does

not reflect either of the two π -stacking distances observed in the single crystal structure, suggesting that the packing in the thin films may be fundamentally different to that of the crystalline material.

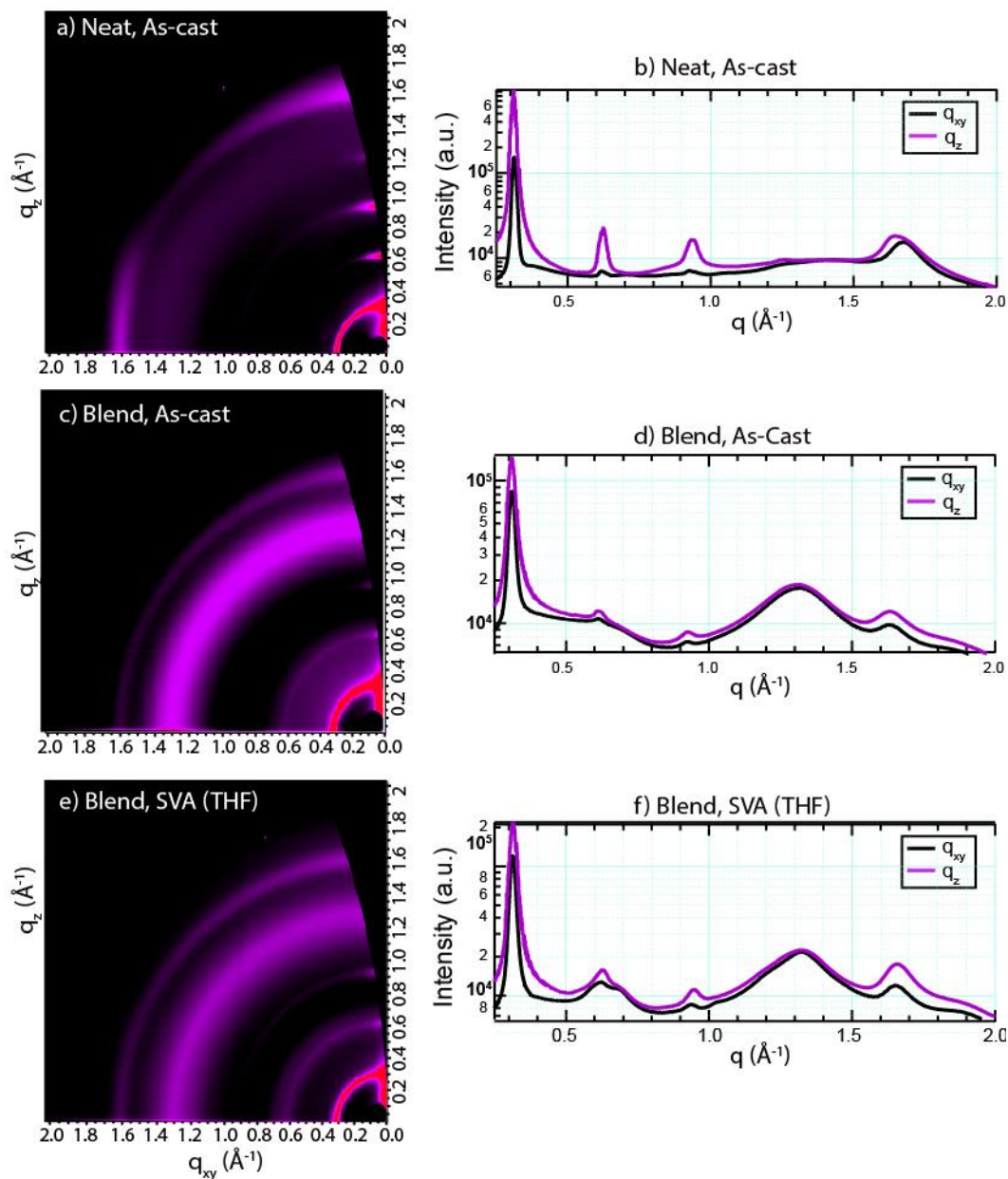


Figure 2-15: BT₈R GIWAXS scattering patterns that are: a) neat, as-cast; c) in a 1:1 fullerene blend, as-cast; e) in a 1:1 blend and SVA-treated; and their respective sector profiles along the Q_{xy} and Q_z axes

From the holistic analysis of the GIWAXS data several trends become apparent which can be utilized to rationalize the device performance observed. In all three molecules in the BT_xR series, upon the addition of the fullerene acceptor and subsequently upon SVA, treatment crystallite size and structure is disrupted in the instance of the former and is increased in the latter. This disruption of crystalline order has been established in the literature to be due to heavy intermixing of PC₇₁BM into the crystalline domains of the donor, and also accounts for the reduced CCLs observed.^[147] The relatively static d-spacings between the neat and blend films for all BT_xR materials and isotropic reflection of PC₇₁BM support the earlier assumption that this intermixing results in the fullerenes generally forming amorphous but distinct phases without any

significant degree of intercalation with the donor molecules, even considering the uniquely offset nature of the inter-lamellar **BTR** cores or the longer sidechains of **BT₈R**. The beneficial effects of SVA treatment on crystallinity and OPV device performance for the BT_xR materials is not unexpected, with the work of Engmann et al having shown through GISAXS studies that optimally-sized crystalline domains for efficient exciton harvesting were formed after SVA treatment with THF.^[138] This was shown to arise from the partial dissolution of **BTR** crystallites formed from the spin-coating process, resulting in the presence of more seed crystals in the solvated amorphous matrix and conferring a relatively high nucleation density. This led to the formation of moderately-sized crystalline phases of around 30 nm for **BTR**, whereas the use of chloroform as a more solubilizing solvent resulted in the dissolution of the majority of crystallites, with nucleation limited to the remaining larger crystals and thus forming much larger domains on the order of around 60 nm, hindering exciton harvesting. The altered sidechain lengths of **BT₄R** and **BT₈R** appear to have had a minimal effect on solubility in THF during the SVA process, as the degree of crystallite size increase remain relatively constant across the BT_xR series, with a uniform 2-4 nm growth from the crystallites present in the as-cast blend films.

(010) d-spacings also remain relatively uniform between all materials in the series at 0.37-0.38 nm, which is curious as single-crystal structures all show varied lengths of 0.35 nm – 0.44 nm for the corresponding π - π stacking distances, even in the as-cast films. As per the aligned 100 and 010 reflections of greatest intensity in the vertical axis, all three materials also possess the randomly-distributed ‘rolling log’ orientation, with the isotropicity of the molecules with respect to the substrate in concordance with most of the orientation parameters calculated for both 100 and 010 reflections. This isotropicity can potentially confer a 3D ‘network’ of π -stacking orientations beneficial for intermolecular charge transport, accounting for the high charge transport observed for **BTR**. Interestingly a high *S* (010) value of 0.68 is calculated for **BT₄R**, suggestive of higher degree of face-on crystallites with respect to the substrate. Although the exact nature of the crystallite orientation is hard to quantify due to the ‘rolling log’ packing, a more face-on orientation for **BT₄R** relative to **BT₈R** would account for the higher OPV device performance seen, offsetting the potential hindrance to charge transport from its smaller CCL.

Lengthening of the alkyl sidechains results in an intuitive increase of the 100 d-spacing with the BDT cores pushed further apart via steric repulsion, with these d-spacings increasing by ~0.15 nm per ethyl unit added. This is an almost tenfold increase over the interchain alkyl lamellar widening observed from single crystal structures but still roughly half of the actual ethyl length, and as such is indicative of a lessened but still extant extent of sidechain interdigitation. This sidechain lengthening can also be seen to manifest an increasing degree of crystallinity of these films, both from the degree of structure apparent within the respective linecuts as well as the calculated CCLs – from amongst the SVA treated films, **BT₈R** possesses an almost doubled CCL of 25.9 nm compared to **BT₄R** at 13.4 nm. This phenomenon has been discussed previously in Section 1.5.1 – longer alkyl sidechains have been observed to induce higher degrees of crystallinity in both

the neat material and in blends with fullerenes, as well as for both small molecular and polymeric substrates. In neat materials longer sidechains have been linked to increased molecular self-assembly due to the amplified van der Waals interactions inducing greater interdigitation between the alkyl chains.^[122b, 148] While the extent of this interdigitation can vary across molecular substrates, this relationship is apparent for the BT_xR series by simple visual examination of the single crystal structures – an occurrence that is aided by the regioregular nature of the oligothiophene π -bridge sidechains. Though OPV active-layer stability is not a focus of this study, it is worth mentioning that molecular structures with increased interdigitation have conferred higher thermal stabilities for OPV materials.^[149] Upon the addition of fullerenes, longer sidechains have been shown to exacerbate the degree of phase separation between the donor material and added fullerenes, with the larger interchain distances conferring a greater rate of diffusion during film formation.^[56, 58, 150] This in turn allows higher rates of demixing between the two semiconducting materials, and as such increases the size of the pure crystalline domains formed – albeit at the cost of a lower interfacial surface area.

The large disparity between the observed OPV device performance of the BT_xR series can be primarily attributed to the increased crystallization induced by the longer octyl sidechains of **BT₈R**. In small molecular substrates large-scale phase separation and the corresponding improvement of crystallinity has been shown to result in premature exciton recombination due to the incongruence between the crystallized domain sizes and exciton diffusion distances. The bound charges of the exciton are not harnessed and is thus is a crucial factor limiting photocurrent generation, ultimately manifesting in the observed decreased J_{SC} and FF.^[151] It has been stressed previously that through sidechain engineering an optimal balance can be found between the intermixing and crystallization of nanoscale domains, and from this study it seems likely that this balance point for the BTR substrate is attained with hexyl-length sidechains on the oligothiophene π -bridge.

Table 4: Summary of data calculated from GIWAXS scattering patterns of BT_xR analogues

Sample	Processing Conditions	d (100) [nm]	CCL (100) [nm]	d (010) [nm]	S (100)	S (010)
BT ₄ R	Neat, As-Cast	1.73	21.3	0.37	0.03	-0.07
	Blend, As-Cast	1.73	11.9	0.38	0.00	-0.02
	Blend, SVA (THF)	1.89	13.4	0.37	-0.01	0.68
BTR	Neat, As-Cast	1.88	29.5	0.38	-0.13	0.05
	Blend, As-Cast	1.85	18.7	0.38	-0.02	-0.11
	Blend, SVA (THF)	1.84	22.9	0.38	0.01	-0.14
BT ₈ R	Neat, As-Cast	2.03	35.8	0.38	-0.07	-0.10
	Blend, As-Cast	2.03	23.3	0.38	-0.03	-0.02
	Blend, SVA (THF)	2.00	25.9	0.38	-0.03	-0.07

2.7 Chapter conclusion

At the onset of this study, relatively little was known regarding the fundamental structure-property relationships of the novel, high-performing p-type semiconductor **BTR**. As sidechain engineering was seen to

have played a role in the development of **BTR** itself, the work in this chapter describes the design of two analogues with differing oligothiophene π -bridge sidechain lengths, **BT₄R** and **BT₈R**, in order to determine the importance of these structural elements to OPV device performance. A modular pathway able to synthesize analogues on a large scale with industrially-relevant conditions was developed, which proceeded through the use of a borylated 3-alkyl thiophene as a key intermediate. Both final materials underwent rigorous characterization, and were utilized in OPV active layer blends. The sidechain alterations were indeed shown to have a significant impact upon OPV performance, with **BT₄R** and **BT₈R** exhibiting a PCE of 9.0% and 5.2%, respectively, with low J_{SCS} and FFs observed in the case of the latter. X-ray crystallography and GIWAXS experiments were used to investigate the structure-property relationship behind these results, where it was found that the increased sidechain lengths of **BT₈R** a) induced a dimer-like packing motif in the crystalline material with large π - π stacking distances between dimers, potentially hindering intermolecular charge transport, and b) increased the size of crystalline domains within the film bulk through enhanced van der Waal interactions and interdigitation, thereby reducing exciton harvesting efficiencies. A holistic interpretation of the data suggests that **BTR** exists in an ideal ‘goldilocks’ region of sidechain length, with an optimal degree of crystallinity to achieve efficient charge harvesting and transport.

2.8 Experimental and supporting information

2.8.1 Materials and Methods

Unless noted, all materials were reagent grade and used as received without further purification. Anhydrous solvents were prepared by drying HPLC grade solvents using freshly activated molecular sieves. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-vis spectrometer, a Perkin Elmer Lambda 1050 UV-vis-NIR spectrophotometer, or an Agilent 8453 spectrophotometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. ^1H NMR and ^{13}C NMR spectra were carried out on either a Varian 400 MHz spectrometer or a Varian 600 MHz spectrometer. All NMR data was referenced to the chloroform signal, unless stated otherwise, and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublets of doublets, m = multiplet, br = broad). MALDI-TOF mass spectrometry was performed on a Bruker microflex instrument, using chloroform as solvent and DCTB as the assisted matrix. ESI mass spectrometry was performed on a Thermo Scientific Q Exactive Plus Orbitrap LC-MS/MS instrument, using 50% acetonitrile/ 0.1% formic acid as the solvent. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE-440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC at a ramp rate of 10 °C min⁻¹. Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mV/s.

CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag⁺ pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in DCM. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the polymer was drop-casted on the electrode from chlorobenzene solution to form a film. Ferrocene/ferrocenium redox couple was used as the internal standard. The HOMO energy level was calculated from the onset of the oxidation potential of the donor materials using the following: $E_{\text{HOMO}} = -(4.8 + E_{\text{ox onset}})$ eV. Polarized optical microscopy was performed on a Linkham TMS 94 variable temperature stage was mounted on an Olympus BH2 fluorescence microscope. Samples were mounted using standard glass microscope slides with a cover slip and located in the microscope focus. A high resolution Luminera Infinity 4-11C 10.7 megapixel CCD camera was mounted on the microscope for image capture using the transmission light source of the microscope.

2.8.1.1 Device fabrication and characterization:

Organic photovoltaic devices were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. The conventional devices were fabricated with a device geometry of glass/ITO/PEDOT:PSS/active layer/Ca/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone and isopropyl alcohol for 15 minutes each and subsequently treated in UV–Ozone for 15 minutes. A thin layer of PEDOT:PSS was spin-coated onto the ITO surface. After being baked at 150 °C for 10 minutes, the substrates were transferred into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated from blend chloroform solutions (32 mg/mL) with weight ratio of BTR analogue and PC₇₁BM at 1:1 and the active layer thicknesses of all films were measured as 210–260 nm. Then, the substrates were placed in a glass Petri dish containing 1 mL THF for solvent vapour annealing (SVA). After SVA treatment, the films were transferred to a metal evaporation chamber and a bilayer cathode consisted of Ca (30 nm) capped with Al (100 nm) was deposited through a shadow mask (active area was 0.1 cm²) at approximately 1×10^{-6} Torr.

2.8.1.2 X-ray crystallography and scattering studies:

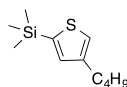
Samples were prepared for GIWAXS by spin-coating solutions of BTR analogue blends onto PEDOT:PSS coated Si substrates using the same deposition condition and annealing conditions as for the photovoltaic devices. The Si wafers had been sonicated in acetone and isopropanol for 30 minutes each followed by 15 minutes of UV/Ozone treatment. GIWAXS experiments were performed at the Australian Synchrotron on the SAXS/WAXS beamline under ambient conditions. A Pilatus 200K detector was used for 2D diffraction pattern collection. The energy of the incident beam was 11 keV at a range of incident angles from $\theta = 0.02 - 0.20^\circ$. The sample-to-detector range was 28 cm. Data from GIWAXS experiments was gathered from the SAXS/WAXS beamline of the Australian Synchrotron and analysed using a customized version of NIKA 2D

based in IgorPro.^[144] Crystals were grown from slow diffusion of IPA into a solution of the BTR analogues in chloroform, and the data was gathered from the MX1 beamline at the Australian Synchrotron^[141, 152]

2.8.2 Synthesis

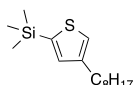
Full experimental details for the synthesis of the BT_xR analogues and material characterization have been previously published,^[39a] and are replicated here.

2.8.2.1 (4-butylthiophen-2-yl)trimethylsilane (**2a**)



1a (3-butylthiophene) and diisopropylamine were dried by passage through an alumina column then degassed by bubbling dinitrogen through the reagents for 30 minutes. A solution of *n*-BuLi (100 mL, 2.5 M, 250 mmol) was added drop wise over 1 hour to a solution of **1a** (31.5 g, 225 mmol) and diisopropylamine (34.15 g, 337.5 mmol) in 250 mL of THF at -78°C. The reaction mixture was allowed to warm to RT, then cooled to -78°C when chlorotrimethylsilane (28.93 g, 266 mmol) was slowly added. The reaction mixture was allowed to warm to RT and stirred for 1 hour. The reaction was deactivated by addition of 250 mL of water. The THF was removed under rotary evaporation and was followed by the addition of 200 mL of diethyl ether. The organic phases were separated, washed with water (2 x 100 mL) then dried over MgSO₄. The slurry was filtered to remove the MgSO₄, the solvent removed under vacuum and the crude product distilled at 90°C at 700 mTorr to yield the product as a clear oil (44.1 g, 208 mmol, 94 %). ¹H NMR (600 MHz, CDCl₃) δ = 7.17 (s, 1 H), 7.08 (s, 1 H), 2.65 (t, *J* = 7.8 Hz, 2 H), 1.68-1.59 (m, 2 H), 1.40-1.37 (m, 2 H), 0.95 (t, *J* = 6.7 Hz, 3 H), 0.33 (s, 9 H). ¹³C NMR (400 MHz, CDCl₃) δ = 144.6, 140.0, 135.5, 125.3, 32.9, 29.7, 22.5, 13.9, 0.01. IR (neat) ν = 2956, 2929, 2859, 1248, 1006, 820 cm⁻¹. MS (ESI) *m/z* [*M*+H]⁺ = 212.1494. Elemental analysis calculated for C₁₁H₂₀SSi: Calculated: C, 62.19; H, 9.49; S, 15.09; Si, 13.22; found: C, 62.12; H, 9.64; S, 14.92

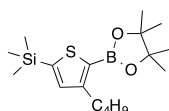
2.8.2.2 (4-octylthiophen-2-yl)trimethylsilane (**2b**)



1b (3-octylthiophene) and diisopropylamine were dried by passage through an alumina column then degassed by bubbling dinitrogen through the reagents for 30 minutes. A solution of *n*-BuLi (100 mL, 2.5 M, 250 mmol) was added drop wise over 1 hour to a solution of **1b** (44.2 g, 225 mmol) and diisopropylamine (34.15 g, 337.5 mmol) in 250 mL of THF at -78°C. The reaction mixture was allowed to warm to RT, then cooled to -78°C when chlorotrimethylsilane (28.93 g, 266 mmol) was slowly added. The reaction mixture was allowed to warm to RT and stirred for 1 hour. The reaction was deactivated by addition of 250 mL of water. The THF was removed under rotary evaporation and was followed by the addition of 200 mL of diethyl ether. The organic phases were separated, washed with water (2 x 100 mL) then dried over MgSO₄. The slurry was filtered to remove the MgSO₄, the solvent removed under vacuum and the crude product distilled at 102°C

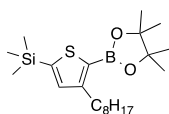
at 610 mTorr to yield the product as a clear oil (52.7 g, 186 mmol, 84 %). ^1H NMR (600 MHz, CDCl_3) δ = 7.17 (s, 1 H), 7.08 (s, 1 H), 2.65 (t, J = 7.8 Hz, 2 H), 1.68-1.59 (m, 2 H), 1.40-1.24 (m, 6 H), 0.91 (t, J = 6.7 Hz, 3 H), 0.33 (s, 9 H). ^{13}C NMR (400 MHz, CDCl_3) δ = 144.7, 140.0, 135.5, 125.3, 31.9, 30.7, 30.3, 29.5, 29.4, 29.3, 2276, 14.1, -0.01. IR (neat cm^{-1}) 2956, 2924, 2854, 1248, 1006, 820; MS (ESI) m/z $[\text{M}+\text{H}]^+$ = 269.1751. Elemental analysis calculated for $\text{C}_{15}\text{H}_{28}\text{SSi}$: Calculated: C, 67.09; H, 10.51; S, 11.94; Si, 10.46, found: C: 67.03; H, 10.63

2.8.2.3 (4-butyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylsilane (**3a**)



A solution of *n*-BuLi (64 mL, 2.5 M, 160 mmol) was added drop wise over 1 hour to a solution of **2a** (30 g, 141 mmol) in THF (100 mL) at -78°C . The mixture was allowed to react for 1 hour then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (62.6 g, 160 mmol) was slowly added. The reaction mixture was allowed to warm to RT and stirred for 1 hour. The reaction was deactivated by addition of 100 mL of water. The THF was removed and diethyl ether (100 mL) was added with the organic phases separated, washed with water (2 x 100 mL) then dried over MgSO_4 . The slurry was filtered to remove the MgSO_4 , the solvent removed under vacuum and the crude product distilled at 150°C at 700 mTorr to yield a clear, viscous oil (36.0 g, 106 mmol, 76 %). ^1H NMR (600 MHz, CDCl_3) δ = 7.13 (s, 1 H), 2.88 (t, J = 6 Hz, 2 H), 1.58-1.56 (m, 2 H), 1.34-1.32 (m, 2 H), 1.32 (s, 12H) 0.93 (t, J = 7 Hz, 3 H), 0.30 (s, 9 H). ^{13}C NMR (400 MHz, CDCl_3) δ = 155.5, 147.1, 137.17, 83.5, 34.1, 29.6, 24.8, 22.5 13.92, 0.01. IR (neat) ν = 2977, 2956, 2929, 2859, 1523, 1436, 1330, 1249, 1142, 1006, 1006, 996, 820, 775 cm^{-1} ; MS (ESI) m/z $[\text{M}+\text{H}]^+$ = 339.1977. Elemental analysis calculated for $\text{C}_{17}\text{H}_{31}\text{BO}_2\text{SSi}$: Calculated: C, 60.34; H, 9.23; B, 3.19; O, 9.46; S, 9.48; Si, 8.30; found: C, 60.20; H, 9.42; S, 9.29

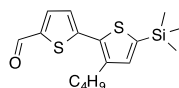
2.8.2.4 (4-octyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylsilane (**3b**)



A solution of *n*-BuLi (76 mL, 2.5 M, 190 mmol) was added drop wise over 1 hour to a solution of **2b** (45 g, 167.6 mmol) in THF (125 mL) at -78°C . The mixture was allowed to react for 1 hour then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35.4 g, 190 mmol) was slowly added. The reaction mixture was allowed to warm to RT and stirred for 1 hour. The reaction was deactivated by addition of 250 mL of water. The THF was removed and diethyl ether (200 mL) was added with the organic phases separated, washed with water (2 x 100 mL) then dried over MgSO_4 . The slurry was filtered to remove the MgSO_4 , the solvent removed under vacuum and the crude product distilled at 150°C at 730 mTorr to yield a clear, viscous oil (51.9 g, 131.6 mmol, 79 %). ^1H NMR (600 MHz, CDCl_3) δ = 7.13 (s, 1 H), 2.87 (t, J = 6 Hz, 2 H), 1.61-1.57 (m, 2 H), 1.32 (s, 12 H), 1.29-

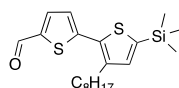
1.23 (m, 10H) 0.89 (t, $J = 7$ Hz, 3 H), 0.30 (s, 9 H). ^{13}C NMR (400 MHz, CDCl_3) $\delta = 155.6, 147.1, 137.18, 83.5, 31.9, 30.0, 29.5, 29.4, 29.3, 24.8, 14.1, -0.01$. IR (neat) $\nu = 2956, 2924, 2855, 1330, 1249, 1142, 996, 820\text{ cm}^{-1}$; MS (ESI) m/z $[\text{M}+\text{Ag}(\text{I})]^+ = 501.1575$. Elemental analysis calculated for $\text{C}_{21}\text{H}_{38}\text{SSiBO}_2$: Calculated: C, 63.94; H, 9.96; B, 2.74; O, 8.11; S, 8.13; Si, 7.12, found: C: 64.21 H: 9.98.

2.8.2.5 3'-butyl-5'-(trimethylsilyl)-[2,2'-bithiophene]-5-carbaldehyde (**4a**)



A mixture of **3a** (20 g, 59.14 mmol), 5-bromothiophen-2-ylcarboxaldehyde (11.3 g, 59.14 mmol), THF (100 mL) and 2.0 M K_3PO_4 (89 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, $\text{Pd}_2(\text{dba})_3$ (680 mg, 0.74 mmol) and $\text{P}(o\text{-tol})_3$ (900 mg, 2.95 mmol) was added and the reaction mixture was stirred at 60°C for 18 h. The reaction mixture was filtered through celite filter aid and the THF removed under vacuum. Diethyl ether (100 mL) was added and the organic phase separated, washed with water (2 x 100 mL) and dried over MgSO_4 and filtered. After removing the solvent the crude product was purified twice by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1.5, then petroleum spirits:ethyl acetate = 5:1) to give the pure product as a brown oil (15.8 g, 48.0 mmol, 82%). ^1H NMR (600 MHz, CDCl_3) $\delta = 9.88$ (s, 1 H), 7.70 (d, $J = 3.9$ Hz, 1 H), 7.23 (d, $J = 3.9$ Hz, 1 H), 7.07 (s, 1 H), 2.81 (t, $J = 7.9$ Hz, 2 H), 1.66-1.64 (m, 2 H), 1.44-1.40 (m, 2H), 0.95 (t, $J = 7.08$ Hz, 3 H), 0.33 (s, 9H). ^{13}C NMR (400 MHz, CDCl_3) $\delta = 182.7, 146.8, 143.1, 142.2, 141.5, 137.5, 136.8, 134.5, 126.0, 32.7, 29.2, 22.7, 13.9, -0.22$. IR (neat) $\nu = 2955, 2930, 1664, 1510, 1446, 1417, 1249, 1224, 1011, 820, 754\text{ cm}^{-1}$; MS (ESI) m/z $[\text{M}+\text{H}]^+ = 323.0953$. Elemental analysis calculated for $\text{C}_{16}\text{H}_{22}\text{OS}_2\text{Si}$: Calculated: C, 59.58; H, 6.87; O, 4.96; S, 19.88; Si, 8.71; found: C, 59.79; H, 6.95; S, 19.92

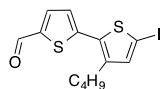
2.8.2.6 3'-octyl-5'-(trimethylsilyl)-[2,2'-bithiophene]-5-carbaldehyde (**4b**)



A mixture of **3b** (35 g, 88.2 mmol), 5-bromothiophen-2-ylcarboxaldehyde (16.8 g, 88.2 mmol), THF (350 mL) and 2.0 M K_3PO_4 (122 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, $\text{Pd}_2(\text{dba})_3$ (1 g, 1.12 mmol) and $\text{P}(o\text{-tol})_3$ (1.35 g, 4.2 mmol) was added and the reaction mixture was stirred at 60°C for 18 h. The reaction mixture was filtered through celite filter aid and the THF removed. Diethyl ether (300 mL) was added and the organic phase separated, washed with water (2 x 150 mL) and dried over MgSO_4 and filtered. After removing the solvent the crude product was purified twice by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1, then petroleum spirits:ethyl acetate = 10:1) to give the pure product as a brown oil (26.34 g, 69.68 mmol, 79%). ^1H NMR (600 MHz, CDCl_3) $\delta = 9.88$ (s, 1 H), 7.69 (d, $J = 3.9$ Hz, 1 H), 7.23 (d, $J = 3.9$ Hz, 1 H), 7.07 (s, 1 H), 2.80 (t, $J = 7.9$ Hz, 2 H), 1.69-1.56 (m, 2 H), 1.38-1.34 (m, 2H), 1.34-1.26 (m, 8H) 0.875 (t, $J = 7.08$ Hz, 3 H), 0.33 (s, 9H). ^{13}C NMR (400 MHz, CDCl_3) $\delta = 182.7, 146.8, 143.1, 142.2, 141.5, 137.5, 136.8, 134.5, 126.0, 31.8, 30.5, 29.6, 29.5, 29.4, 29.2, 22.7, 14.1, -0.22$. IR

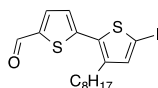
(neat) $\nu = 2954, 2925, 2855, 1668, 1446, 1250, 1225, 820 \text{ cm}^{-1}$; MS (ESI) m/z $[M+H]^+ = 379.1586$. Elemental analysis calculated for $C_{20}H_{30}SiOS_2$: Calculated: C, 63.44; H, 7.99; S, 16.94. Found: C, 63.68; H, 8.03; S, 16.71

2.8.2.7 3'-butyl-5'-iodo-[2,2'-bithiophene]-5-carbaldehyde (**5a**)



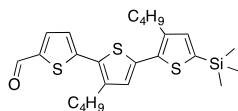
A solution of ICl (3.8 g, 23.3 mmol) in DCM (25 mL) was added slowly to a solution of **4a** (7.5 g, 23.3 mmol) in DCM (100 mL) under dinitrogen at -15°C (ice/acetone). The solution was allowed to react for one hour then deactivated by addition of 2 M K_2CO_3 then a 1 M solution of Na_2SO_3 . The biphasic reaction mix was filtered through celite, and then the organic phase separated, washed with water (2 x 100 mL) and then dried over $MgSO_4$. The solvent was removed and a crude product obtained by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1) as a pale yellow liquid. The pure product was obtained by silica gel column chromatography (petroleum spirit : ethyl acetate = 7:3) to give the product as a brown oil which crystallized as yellow, needle-like crystals under vacuum (7.4 g, 19.67 mmol, 84%). 1H NMR (600 MHz, $CDCl_3$) $\delta = 9.88$ (s, 1 H), 7.69 (d, $J = 3.95$ Hz, 1 H), 7.14 (d, $J = 3.27$ Hz, 1 H), 7.12 (s, 1 H), 2.75 (t, $J = 7.8$ Hz, 2 H), 1.64-1.59 (m, 2 H), 1.38-1.33 (m, 2H), 1.31-1.25 (m, 8H) 0.88 (t, $J = 7.08$ Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 182.6, 144.8, 143.6, 142.7, 140.4, 136.6, 135.5, 126.5, 74.5, 32.5, 28.9, 22.5, 13.9$. IR (neat) $\nu = 2956, 2926, 1666, 1443, 1223, 1057, 801 \text{ cm}^{-1}$; MS (ESI) m/z $[M+H]^+ = 376.9526$. Elemental analysis calculated for $C_{13}H_{13}OS_2I$: Calculated: C, 41.50; H, 3.48; I, 33.73; O, 4.25; S, 17.04; found: C, 41.42; H, 3.53; S, 17.28

2.8.2.8 3'-octyl-5'-iodo-[2,2'-bithiophene]-5-carbaldehyde (**5b**)



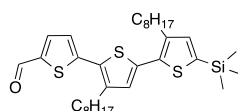
A solution of ICl (6.47 g, 39.67 mmol) in DCM (50 mL) was added slowly to a solution of **4b** (15 g, 39.67 mmol) in DCM (250 mL) under dinitrogen at -15°C (ice/acetone). The solution was allowed to react for one hour then deactivated by addition of 2 M K_2CO_3 then a 1 M solution of Na_2SO_3 . The biphasic reaction mix was filtered through celite, and then the organic phase separated, washed with water (2 x 100 mL) and then dried over $MgSO_4$. The solvent was removed from the filtered solution and a crude product obtained by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1) as a pale yellow liquid. The pure product was obtained by silica gel column chromatography (petroleum spirit : ethyl acetate = 9:1) to give the product as yellow, needle-like crystals (14.05 g, 32.53 mmol, 82%). 1H NMR (600 MHz, $CDCl_3$) $\delta = 9.88$ (s, 1 H), 7.69 (d, $J = 3.95$ Hz, 1 H), 7.14 (d, $J = 3.27$ Hz, 1 H), 7.12 (s, 1 H), 2.75 (t, $J = 7.8$ Hz, 2 H), 1.64-1.59 (m, 2 H), 1.38-1.33 (m, 2H), 1.31-1.25 (m, 8H) 0.88 (t, $J = 7.08$ Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 182.6, 144.8, 143.7, 142.7, 140.3, 136.6, 135.5, 126.5, 74.5, 31.8, 30.3, 29.4, 29.3, 29.2, 29.1, 22.6, 14.1$. IR (neat) $\nu = 2924, 2853, 1668, 1443, 1222 \text{ cm}^{-1}$; MS (ESI) m/z $[M+H]^+ = 433.0137$. Elemental analysis calculated for $C_{17}H_{21}IOS_2$: Calculated: C, 47.22; H, 4.90; I, 29.35; O, 3.70; S, 14.83; found: C: 46.92, H: 4.91.

2.8.2.9 3',3''-dibutyl-5''-(trimethylsilyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (**6a**)



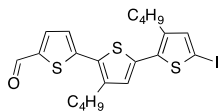
A mixture of **3a** (5.7 g, 15.32 mmol), **5a** (5.8 g, 15.32 mmol), THF (100 mL) and 2.0 M K₃PO₄ (35 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, Pd₂(dba)₃ (340 mg, 0.38 mmol) and P(*o*-tol)₃ (466 mg, 1.53 mmol) was added and the reaction mixture was stirred at 60 °C for 18 h. The reaction mixture was filtered through celite filter aid and the THF removed under vacuum. Diethyl ether (100 mL) was added and the organic phase separated, washed with water (2 x 50 mL) and dried over MgSO₄ and filtered. After removing the solvent the crude product was purified twice by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1, then petroleum spirit: ethyl acetate = 7:3) to give the pure product as a brown oil which crystallized into yellow needles under high pressure (5.6 g, 12 mmol, 80%). ¹H NMR (600 MHz, CDCl₃) δ = 9.88 (s, 1 H), 7.70 (d, *J* = 4.0, 1 H), 7.23 (d, *J* = 4.0 Hz, 1 H), 7.04 (s, 1H), 6.99 (s, 1 H), 2.82 (t, *J* = 7.8 Hz, 2 H), 2.78 (t, *J* = 7.8 Hz, 2 H), 1.71-1.62 (m, 4 H), 1.46-1.41 (m, 4 H), 0.96 (m, 6 H), 0.33 (s, 9H). ¹³C NMR (δ, CDCl₃) 182.6, 146.4, 142.4, 142.0, 141.4, 139.5, 137.3, 136.9, 136.7, 135.0, 129.1, 128.9, 125.7, 32.8, 32.4, 29.5, 29.0 22.8, 22.6, 13.9, -0.16. %). IR (neat) ν = 2955, 2924, 1666, 1449, 1453, 1251, 1221, 1057, 1005, 837, 827 cm⁻¹; MS (ESI) *m/z* [M+H]⁺ = 461.1456. Elemental analysis calculated for C₂₄H₃₂OSiS₃: Calculated: C, 62.56; H, 7.00; O, 3.47; S, 20.88; Si, 6.10; found: C, 62.48, H, 7.12

2.8.2.10 3',3''-dioctyl-5''-(trimethylsilyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (**6b**)



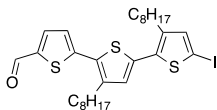
A mixture of **3b** (7.3 g, 18.51 mmol), **5b** (8 g, 18.51 mmol), THF (125 mL) and 2.0 M K₃PO₄ (42 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, Pd₂(dba)₃ (421 mg, 0.46 mmol) and P(*o*-tol)₃ (570 mg, 1.85 mmol) was added and the reaction mixture was stirred at 60 °C for 18 h. The reaction mixture was filtered through celite filter aid and the THF removed under vacuum. Diethyl ether (200 mL) was added and the organic phase separated, washed with water (2 x 50 mL) and dried over MgSO₄ and filtered. After removing the solvent the crude product was purified twice by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1, then petroleum spirit: ethyl acetate = 10:1) to give the pure product as a brown oil (9.1 g, 15.91 mmol, 86%). ¹H NMR (600 MHz, CDCl₃) δ = 9.88 (s, 1 H), 7.70 (d, *J* = 4.0, 1 H), 7.23 (d, *J* = 4.0 Hz, 1 H), 7.05 (s, 1H), 6.99 (s, 1 H), 2.82 (t, *J* = 7.8 Hz, 2 H), 2.78 (t, *J* = 7.8 Hz, 2 H), 1.71-1.63 (m, 4 H), 1.42-1.36 (m, 4 H), 1.36-1.23 (m, 16H), 0.88 (dd, *J* = 7.0 Hz, 2.3 Hz, 6 H), 0.33 (s, 9H). ¹³C NMR (δ, CDCl₃) 182.5, 146.4, 142.5, 142.0, 141.5, 139.5, 137.3, 136.9, 136.7, 135.0, 129.1, 128.9, 125.7, 31.9, 31.8, 30.7, 30.2, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 22.6, 14.09, -0.1. IR (neat) ν = 2954, 2924, 2854, 1665, 1444, 1249, 1225, 1003, 820 cm⁻¹; MS (ESI) *m/z* [M+H]⁺ = 573.2683. Elemental analysis calculated for C₃₂H₄₈SiOS₃: Calculated: C, 67.08; H, 8.44; O, 2.79; S, 16.79; Si, 4.90; found: C, 67.12; H, 8.58; S, 16.54.

2.8.2.11 3',3''-dibutyl-5''-iodo-[2,2':5',2''-terthiophene]-5-carbaldehyde (**7a**)



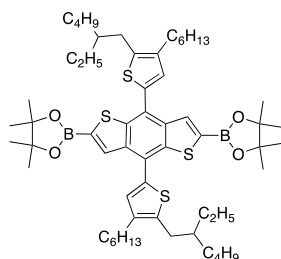
A mixture of **6a** (0.5 g, 1.08 mmol), *n*-iodosuccinimide (0.36 g, 1.63 mmol) and sodium acetate (0.5 g, 3 mmol) was dissolved in a solution of chloroform (15 mL) and acetic acid (15 mL), then cooled to 0 °C. The mixture was stirred for 1 hour, then poured into H₂O (50 mL). The mixture was then extracted with DCM (2 x 50 mL) and the combined organic phase was washed with saturated NaHCO₃ (2 x 50 mL) before being dried over MgSO₄. The solvent was removed from the filtered solution and purified twice by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1, then petroleum spirit: ethyl acetate = 4:1) to give the product as yellow needles (0.43 g, 0.83 mmol, 77%). ¹H NMR (600 MHz, CDCl₃) δ = 9.88 (s, 1 H), 7.71 (d, *J* = 4.0, 1 H), 7.23 (d, *J* = 4.0 Hz, 1 H), 7.08 (s, 1H), 6.92 (s, 1 H), , 2.78 (t, *J* = 7.8 Hz, 2 H), 1.71-1.62 (m, 4 H), 1.46-1.41 (m, 4 H), 0.96 (m, 6 H). ¹³C NMR (δ, CDCl₃) 182.6, 145.9, 142.4, 142.3, 142.0, 140.0, 136.8, 135.8, 135.0, 129.7, 129.5, 126.0, 72.4, 32.7, 32.4, 29.4, 28.7, 22.6, 22.5, 13.9, 13.9. IR (neat) ν = 2925, 2854, 1666, 1456, 1434, 1260, 1225, 764 cm⁻¹; MS (ESI) *m/z* [M+H]⁺ = 515.0028. Elemental analysis calculated for C₂₁H₂₃OIS₃: Calculated: C, 49.02; H, 4.51; I, 24.67; O, 3.11; S, 18.70; found: C, 49.06; H, 4.77; S, 18.54.

2.8.2.12 3',3''-dioctyl-5''-iodo-[2,2':5',2''-terthiophene]-5-carbaldehyde (**7b**)



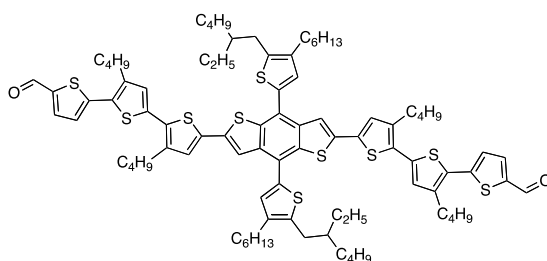
A mixture of **6b** (6.0 g, 10.5 mmol), *n*-iodosuccinimide (2.3 g, 10.5 mmol) and sodium acetate (3.5 g, 21 mmol) was dissolved in a solution of chloroform (100 mL) and acetic acid (100 mL), then cooled to 0 °C. The mixture was stirred for 1 hour, then poured into H₂O (50 mL). The mixture was then extracted with DCM (2 x 150 mL) and the combined organic phase was washed with saturated NaHCO₃ (2 x 150 mL) before being dried over MgSO₄. The solvent was removed and purified twice by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1, then petroleum spirit: ethyl acetate = 10:1) to give the pure product as a brown, viscous oil (5.4 g, 8.61 mmol, 82%). ¹H NMR (600 MHz, CDCl₃) δ = 9.88 (s, 1 H), 7.71 (d, *J* = 4.0, 1 H), 7.23 (d, *J* = 4.0 Hz, 1 H), 7.08 (s, 1H), 6.92 (s, 1 H), 2.82 (t, *J* = 7.8 Hz, 2 H), 2.78 (t, *J* = 7.8 Hz, 2 H), 1.71-1.63 (m, 4 H), 1.42-1.36 (m, 4 H), 1.36-1.23 (m, 16H), 0.88 (dd, *J* = 7.0 Hz, 2.3 Hz, 6 H). ¹³C NMR (400MHz, CDCl₃) δ = 182.55, 145.89, 142.40, 142.32, 142.07, 139.94, 136.77, 135.81, 134.96, 129.74, 129.45, 126.00, 72.36, 31.86, 31.84, 30.53, 30.25, 29.69, 29.52, 29.42, 29.40, 29.35, 29.22, 28.98, 22.66, 14.10. IR (neat) ν = 2925, 2854, 1666, 1456, 1434, 1260, 1225, 764 cm⁻¹; MS (ESI) *m/z* [M+H]⁺ = 627.1286. Elemental analysis calculated for C₂₉H₃₉IOS₃: Calculated: C, 55.58; H, 6.27; I, 20.25; O, 2.55; S, 15.35; found: C, 57.60; H, 6.64; S, 14.64

2.8.2.13 2,2'-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**13**)



To a 50 ml Schlenk flask was added **12** (2.00 g, 2.68 mmole) and the flask heated under vacuum for 2 hours at 60°C. Dry, degassed DME (20 mL) was added and the temperature raised to 85 °C. The following were added in the order, i) [Ir(COD)₂OMe]₂ (90 mg, 0.136 mmole), ii) B₂Pin₂ (1.04 g, 4.1 mmole), and iii) bis-*tert*-butylbipyridine (112 mg, mmole) and the reaction stirred for 2 hours. The reaction vessel was cooled to RT and IPA (15 mls) added and the DME removed under vacuum. A further 20 mL of IPA were added and the product allowed to precipitate over night. The crude product was collected by filtration, washed with IPA, dried under vacuum and used without further purification. Yield (2.43 g, 2.43 mmol, 91%). ¹H NMR (δ, CDCl₃) 8.164 (s, 2 H), 7.181 (s, 2 H), 2.735 (dd, *J* = 7.1 & 1.9 Hz, 4 H), 2.588 (t, *J* = 7.7 Hz, 4 H), 1.63-1.59 (m, 6 H), 1.45-1.30 (m, 52 H), 0.96-0.65 (m, 18 H); ¹³C NMR (δ, CDCl₃) 142.5, 139.3, 138.8, 138.1, 135.0, 133.8, 129.8, 124.9, 84.4, 41.6, 32.6, 32.2, 31.8, 30.8, 29.3, 28.9, 28.4, 25.8, 24.7, 23.0, 22.6, 14.2, 14.1, 10.9; MS (ESI +) *m/z* 998.58614 [M⁺]. Elemental analysis calculated for C₅₈H₈₈B₂O₄S₄: C, 69.72; H, 8.88; S, 12.84. Found C, 69.74; H, 8.90; S, 12.90.

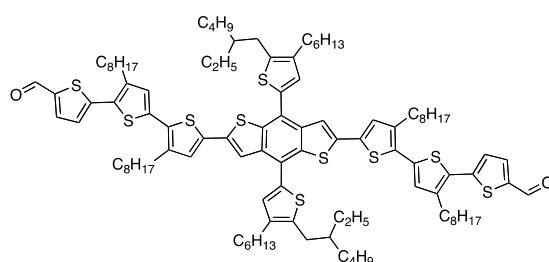
2.8.2.14 5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dibutyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (**15a**)



A mixture of **13** (0.5 g, 0.5 mmol), **7a** (0.62 g, 1.2 mmol), THF (30 mL) and 2.0 M K₃PO₄ (15 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, Pd₂(dba)₃ (23 mg, 0.025 mmol) and P(*o*-tol)₃ (30.5 mg, 0.1 mmol) was added and the reaction mixture was stirred at 60°C for 12 h. The reaction mixture was filtered through celite filter aid and the THF removed. Diethyl ether (40 mL) was added and the organic phase separated, washed with water (2 x 20 mL) and dried over MgSO₄ and filtered. The crude product was purified by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1) to give the pure product as a red solid (0.77 g, 0.42 mmol, 59%). ¹H NMR (600 MHz, CDCl₃) δ = 9.89 (s, 2H), 7.72 (d, *J* = 4.0,

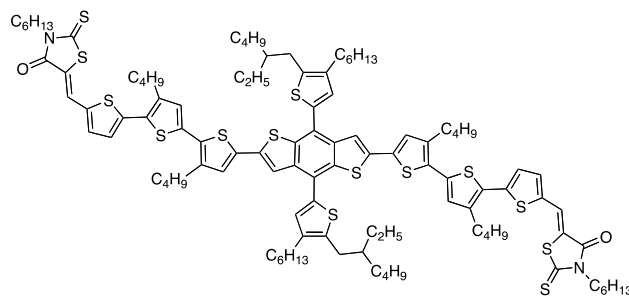
2H), 7.68 (s, 2H), 7.24 (d, J = 4.0, 2H), 7.23 (s, 2H), 7.12 (s, 2H), 7.02 (s, 2H), 2.80 (m, 12H), 2.65 (m, 4H), 1.69 (m, 16H), 1.47-1.37 (m, 32H), 1.00-0.88 (m, 30H). ^{13}C NMR (400MHz, CDCl_3) δ = 182.55, 142.47, 141.12, 139.54, 138.97, 138.58, 137.24, 136.84, 135.99, 135.74, 134.78, 129.78, 129.09, 128.31, 125.88, 123.51, 119.50, 41.69, 32.67, 32.54, 32.37, 31.84, 30.76, 29.47, 29.33, 29.19, 28.95, 28.44, 26.05, 23.09, 22.68, 22.64, 14.21, 14.15, 13.93, 11.05. IR (neat) ν = 2957, 2926, 1646, 1434, 1264, 1230, 1058, 754, 703 cm^{-1} . MS (MALDI) calculated for $\text{C}_{88}\text{H}_{110}\text{O}_2\text{S}_{10}$ m/z = 1518.571, Found 1520.262 $[\text{M}+\text{H}^+]$ Elemental analysis calculated for $\text{C}_{88}\text{H}_{110}\text{O}_2\text{S}_{10}$: Calculated: C, 69.51; H, 7.29; O, 2.10; S, 21.09; found: C, 69.90; H, 7.49; S, 20.88

2.8.2.15 5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (**15b**)



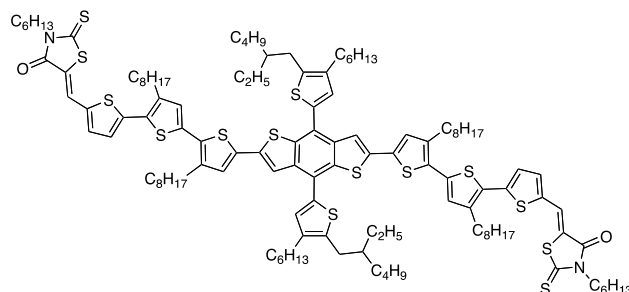
A mixture of **13** (0.5 g, 0.5 mmol), **7b** (0.63 g, 1 mmol), THF (30 mL) and 2.0 M K_3PO_4 (15 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, $\text{Pd}_2(\text{dba})_3$ (23 mg, 0.025 mmol) and $\text{P}(o\text{-tol})_3$ (30.5 mg, 0.1 mmol) was added and the reaction mixture was stirred at 60°C for 12 h. The reaction mixture was filtered through celite filter aid and the THF removed under vacuum. Diethyl ether (40 mL) was added and the organic phase separated, washed with water (2 x 20 mL) and dried over MgSO_4 and filtered. After removing the solvent the crude product was purified by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1) to give the pure product as a red solid (0.71 g, 0.41 mmol, 81%). ^1H NMR (600 MHz, CDCl_3) δ = 9.89 (s, 2H), 7.72 (d, J = 4.0, 2H), 7.68 (s, 2H), 7.24 (d, J = 4.0, 2H), 7.23 (s, 2H), 7.12 (s, 2H), 7.01 (s, 2H), 2.80 (m, 14H), 2.65 (m, 4H), 1.69 (m, 18H), 1.38-1.27 (m, 62H), 1.00-0.88 (m, 30H). ^{13}C NMR (400 MHz, CDCl_3) δ = 182.55, 142.47, 141.12, 139.54, 138.97, 138.58, 137.24, 136.84, 135.99, 135.74, 134.78, 129.78, 129.09, 128.31, 125.88, 123.51, 119.50, 41.69, 32.66, 32.35, 31.85, 30.75, 30.43, 30.25, 29.76, 29.56, 29.41, 29.23, 28.95, 28.43, 26.04, 23.09, 22.66, 14.22, 14.15, 14.10, 11.04. IR (neat) ν = 2955, 2930, 1664, 1510, 1446, 1417, 1249, 1224, 1011, 820, 754 cm^{-1} ; MS (MALDI) calculated for $\text{C}_{104}\text{H}_{142}\text{O}_2\text{S}_{10}$ m/z = 1742.822, found 1744.288 $[\text{M}+\text{H}]^+$. Elemental analysis calculated for $\text{C}_{104}\text{H}_{142}\text{O}_2\text{S}_{10}$: Calculated: C, 71.59; H, 8.20; O, 1.83; S, 18.38; found: C, 71.81; H, 8.34; S, 18.42.

2.8.2.16 5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dibutyl-[2,2':5',2''-terthiophene]-5-hexylrhodanine) (**BT⁴R**)



A solution of **16a** (0.3 g, 0.2 mmol), **14** (0.434 g, 2 mmol) and 1 drop of DBU was stirred in chloroform (5 mL). The reaction mixture was then stirred at room temperature for 3 hours. The solvent was then removed via rotary evaporation and the crude product purified via column chromatography (petroleum spirit: dichloromethane = 1:1) and then washed with isopropanol to yield a red powder. This was then further purified via size-exclusion chromatography (toluene, BioBeads 100) to yield a purple solid (366 mg, 0.17 mmol, 40%). ¹H NMR (600 MHz, CDCl₃) δ = 7.80 (s, 2H), 7.63 (s, 2H), 7.32 (d, J = 4.0, 2H), 7.24 (s, 2H), 7.17 (d, J = 4.0, 2H), 7.08 (s, 2H), 6.98 (s, 2H), 4.08, (t, J = 7.8, 4.0, 4H), 2.80 (m, 12H), 2.65 (m, 4H), 1.70 (m, 20H), 1.47-1.37 (m, 46H), 1.00-0.88 (m, 36H). ¹³C NMR (400MHz, CDCl₃) δ = 192.16, 167.42, 144.24, 141.77, 140.88, 139.46, 138.95, 138.50, 137.18, 136.96, 135.62, 135.57, 134.85, 134.56, 130.45, 129.82, 129.67, 128.96, 128.23, 126.45, 124.94, 123.39, 120.09, 119.39, 44.83, 41.71, 32.71, 32.47, 32.37, 31.88, 31.32, 30.81, 29.55, 29.44, 29.24, 28.98, 28.49, 26.91, 26.45, 26.06, 23.14, 22.73, 22.71, 22.51, 14.26, 14.19, 14.00, 13.97, 11.08. IR (neat) ν = 2953, 2928, 2856, 1700, 1578, 1412, 1328, 1184, 820 cm⁻¹; MS (MALDI) m/z = 1919.429. Elemental analysis calculated for C₁₀₆H₁₃₆N₂O₂S₁₄: Calculated: C, 66.34; H, 7.14; N, 1.46; S, 23.39; found: C, 66.19; H, 7.13; N, 1.40; S, 23.28

2.8.2.17 5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dioctyl-[2,2':5',2''-terthiophene]-5-hexylrhodanine) (**BT⁸R**)



A solution of **16b** (0.35 g, 0.2 mmol), **14** (0.434 g, 2 mmol) and 1 drop of DBU was stirred in chloroform (20 mL). The reaction mixture was then stirred at room temperature for 3 hours. The solvent was then removed via rotary evaporation and the crude product purified via column chromatography (petroleum spirit: dichloromethane = 1:1) and then washed with isopropanol to yield a red powder. This was then further

purified via size-exclusion chromatography (toluene, BioBeads 100) to yield a purple solid (356 mg, 0.17 mmol, 83%). ^1H NMR (600 MHz, CDCl_3) δ = 7.80 (s, 2H), 7.63 (s, 2H), 7.32 (d, J = 4.0, 2H), 7.24 (s, 2H), 7.17 (d, J = 4.0, 2H), 7.08 (s, 2H), 6.98 (s, 2H), 4.08 (t, J = 7.8, 4.0, 4H), 2.80 (m, 14H), 2.65 (m, 4H), 1.69 (m, 22H), 1.38-1.27 (m, 74H), 1.00-0.88 (m, 36H). ^{13}C NMR (400 MHz, CDCl_3) δ = 192.16, 167.42, 144.24, 141.77, 140.88, 139.46, 138.95, 138.50, 137.18, 136.96, 135.62, 135.57, 134.85, 134.56, 130.45, 129.82, 129.67, 128.96, 128.23, 126.45, 124.94, 123.39, 120.09, 119.39, 44.83, 41.69, 32.67, 32.36, 31.88, 31.33, 30.76, 30.40, 29.80, 29.61, 29.40, 29.25, 28.95, 28.45, 26.94, 26.44, 26.05, 23.10, 22.68, 22.49, 14.11, 13.99, 11.04. IR (neat) ν = 2957, 2870, 1698, 1579, 1460, 1425, 1378, 1185, 1019, 888, 824 cm^{-1} ; MS (MALDI) m/z $[\text{M}+\text{H}]^+$ = 2143.229. Elemental analysis calculated for $\text{C}_{122}\text{H}_{168}\text{N}_2\text{O}_2\text{S}_{14}$: Calculated: C, 68.36; H, 7.90; N, 1.31; S, 20.94; found: C, 67.54; H, 7.89; N, 1.21; S, 19.72.

2.8.2.18 Direct Arylation - initial reaction #1

A mixture of **2a** (300 mg, 1.41 mmol), $\text{Pd}(\text{OAc})_2$ (5.75 mg, 0.026 mmol, tricyclohexylphosphine tetrafluoroborate (18.5 mg, 0.05 mmol), pivalic acid (39.2 mg, 0.38 mmol) and 5-bromothiophen-2-ylcarboxaldehyde (245 mg, 1.28 mmol) in toluene (5 mL) was stirred while being degassed under dinitrogen for 30 minutes. The reaction mixture was then stirred for 4 hours at 100 °C. The reaction mixture was filtered through celite filter aid and the solvent removed under vacuum. NMR analysis of the crude material showed a yield of ~1%.

2.8.2.19 Direct Arylation - initial reaction #2

A mixture of **2a** (300 mg, 1.41 mmol), $\text{Pd}(\text{OAc})_2$ (16 mg, 0.07 mmol, triphenylphosphine (37.0 mg, 0.14 mmol), K_2CO_3 (292 mg, 2.12 mmol) and 5-bromothiophen-2-ylcarboxaldehyde (245 mg, 1.28 mmol) in dimethylformamide (10 mL) was stirred while being degassed under dinitrogen for 30 minutes. The reaction mixture was then stirred for 6 hours at 120 °C. The reaction mixture was filtered through celite filter aid and the solvent removed under vacuum. Diethyl ether (20 mL) was added and the organic phase separated, washed with water (2 x 20 mL) and dried over MgSO_4 and filtered. After removing the solvent the crude product was purified by silica gel column chromatography (petroleum spirit: dichloromethane = 2:3) to give the pure product as a brown oil (0.04 g, 0.13 mmol, 10%).

2.8.2.20 Direct Arylation - initial reaction #3

A mixture of **2a** (300 mg, 1.41 mmol), $\text{Pd}(\text{OAc})_2$ (5.8 mg, 0.028 mmol), diphenylphosphinobutane (11.9 mg, 0.028 mmol) and KOAc (137 mg, 1.4 mmol) were degassed under dinitrogen for 30 minutes. A solution of 5-bromothiophen-2-ylcarboxaldehyde (534 mg, 2.8 mmol) in DMAc (5 mL) was stirred, degassed under dinitrogen for 30 minutes and introduced to the other reagents. The reaction mixture was then stirred for 5 hours at 120 °C. The reaction mixture was filtered through celite filter aid and the solvent removed under vacuum. Diethyl ether (20 mL) was added and the organic phase separated, washed with water (2 x 20 mL) and dried over MgSO_4 and filtered. After removing the solvent the crude product was purified by silica gel

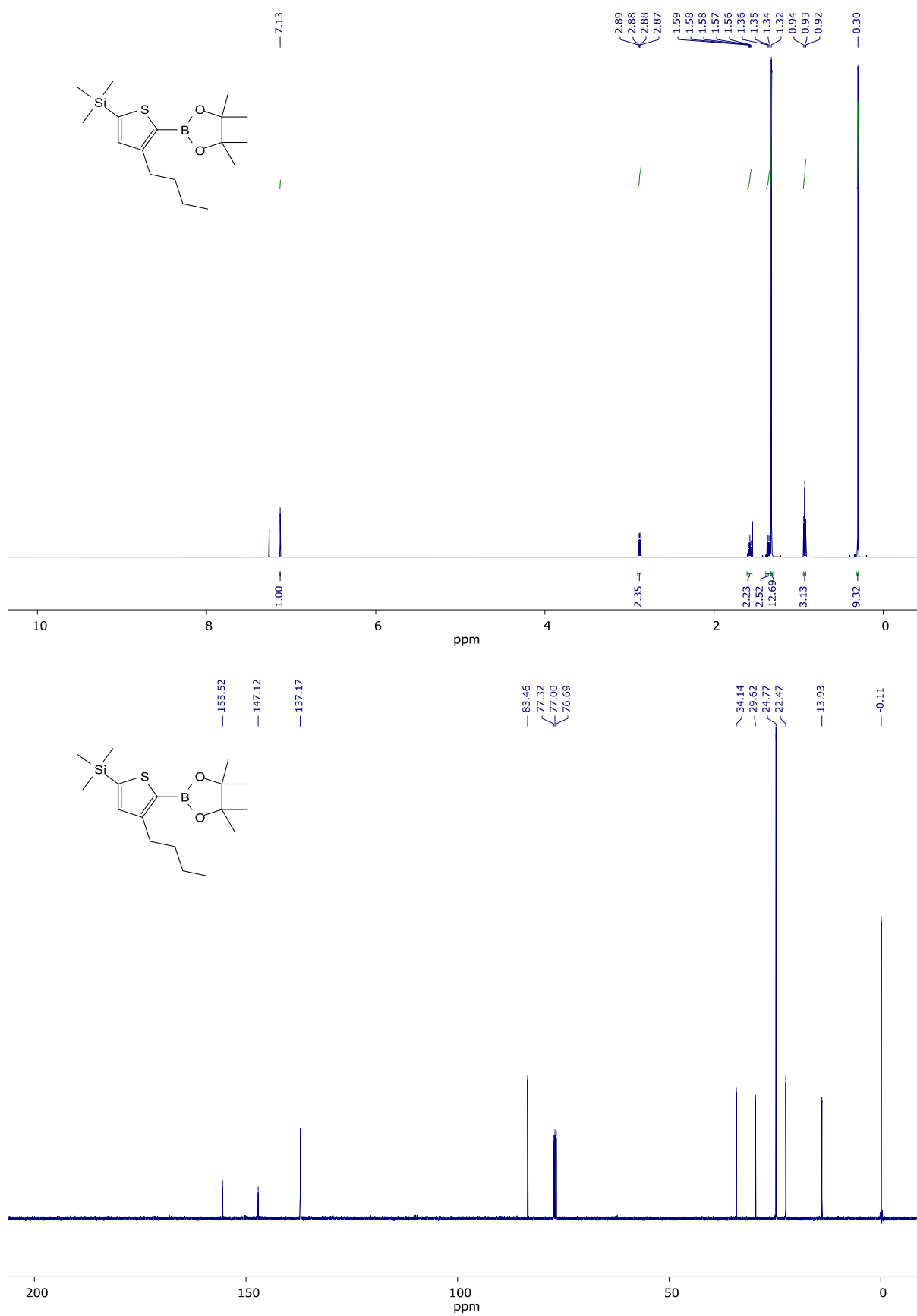
column chromatography (petroleum spirit: dichloromethane = 2:3) to give the pure product as a brown oil (0.15 g, 0.45 mmol, 32%).

2.8.2.21 High-throughput catalyst screening

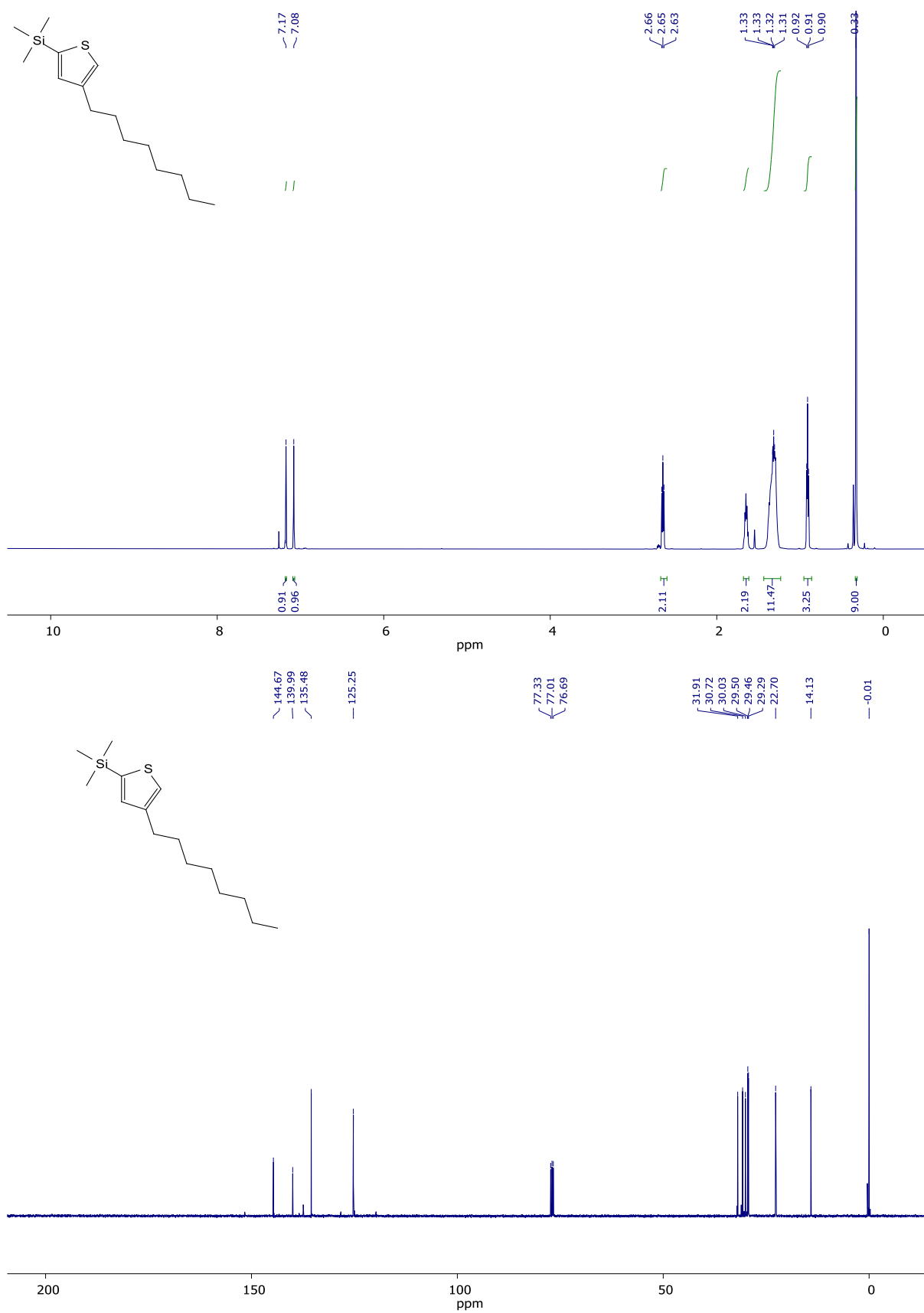
A stock solution containing the reagents 3-hexyl-5-trimethylsilyl-thiophene (6.8 g, 28.4 mmol) and 5-bromo-2-thiophenecarboxaldehyde (2.42 g, 14.2 mmol) was prepared in 100-mL of anhydrous dimethylacetamide. A set of ligands (Table 1) were screened to find the highest performing reaction conditions. For each reaction, 0.028 mmol of the ligand, Pd(OAc)₂ (5.8 mg, 0.028 mmol) and KOAc (137 mg, 1.40 mmol) were introduced to 5 mL of the stock solution. The reaction was stirred and heated at 120°C for 5 hours. Following this, the commercially available dye Coumarin 6 (2.0 mL, 17.5 mM) was added to the crude mixture to act as an internal standard. This solution was separated into 10 mL of petroleum spirits and 10 mL of water. 1 mL was extracted from the organic layer and filtered through a plug of glass wool with 5 mL of chloroform. 1 mL of this filtered solution was added to 4 mL of a 1:1 solution of chloroform and petroleum spirits to be analysed via HPLC. The flow rate through the silica column was 1 mL/minute, the mobile phase was 1:1 hexane/chloroform, the injection volume was 100 µL and the UV/vis wavelengths used to detect the analytes were 254 nm, 301 nm, 350 nm and 450 nm. The yield of the coupled product was calculated from the HPLC traces by determining the ratios of the integrated peak areas of the Coumarin 6 internal standard, target product 3'-hexyl-5'-(trimethylsilyl)-[2,2'-bithiophene]-5-carbaldehyde, starting material 5-bromo-2-thiophenecarboxaldehyde and the desilylated impurity 3'-hexyl-[2,2'-bithiophene]-5-carbaldehyde.

2.8.3 ^1H and ^{13}C spectra

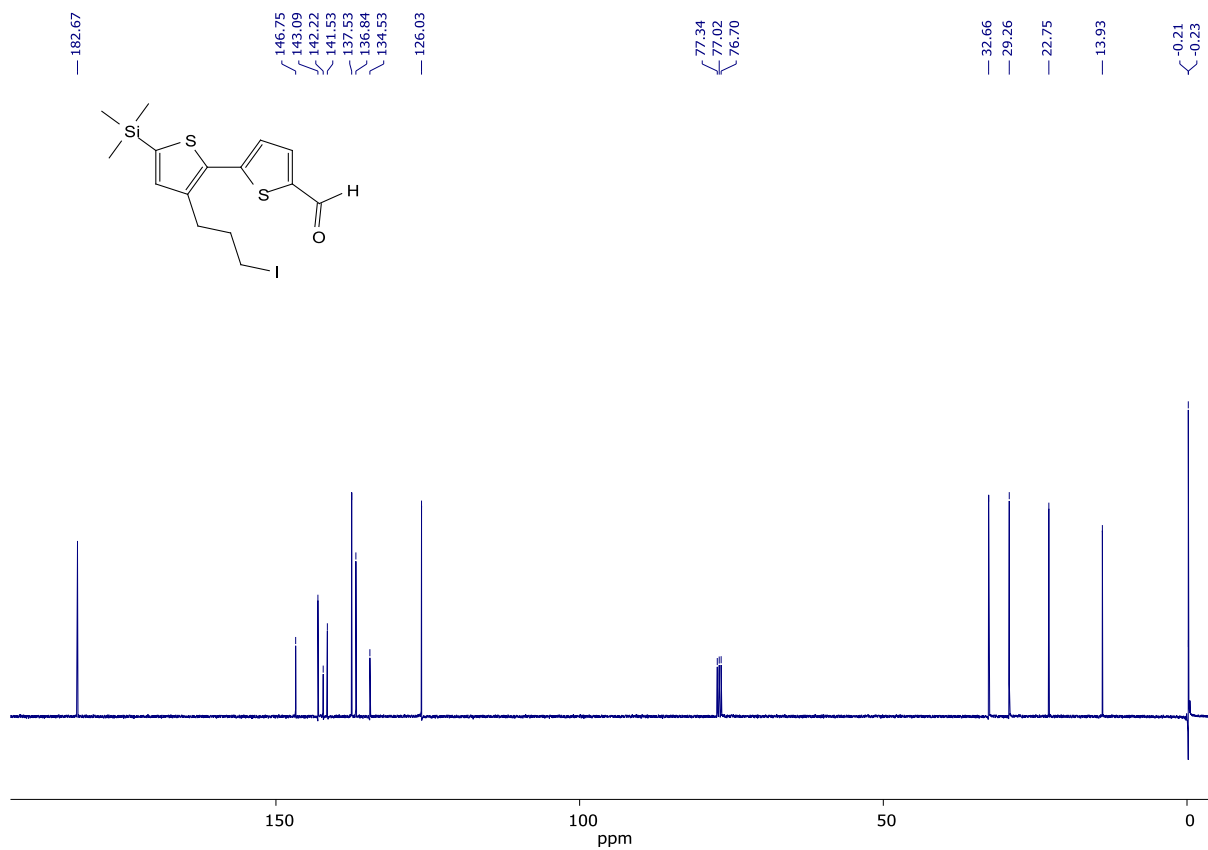
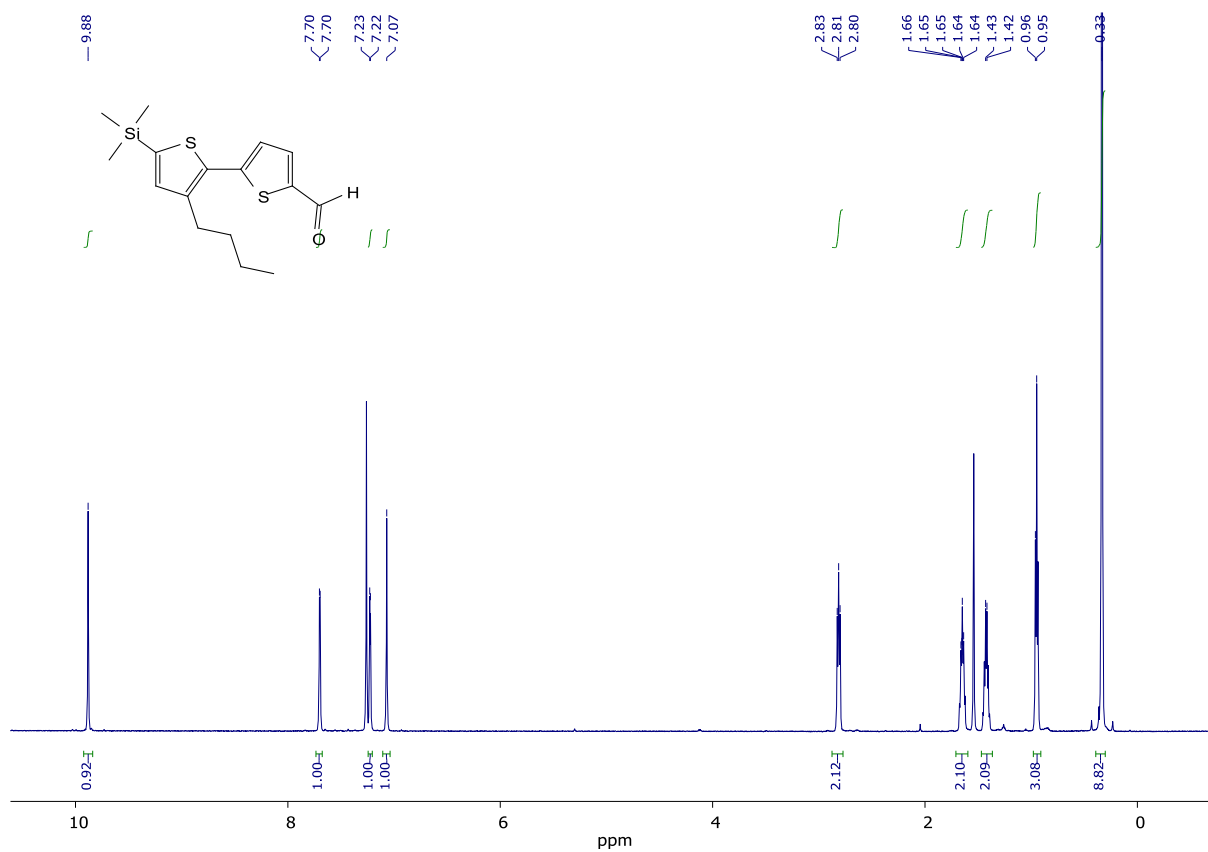
2.8.3.1 (4-butyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylsilane



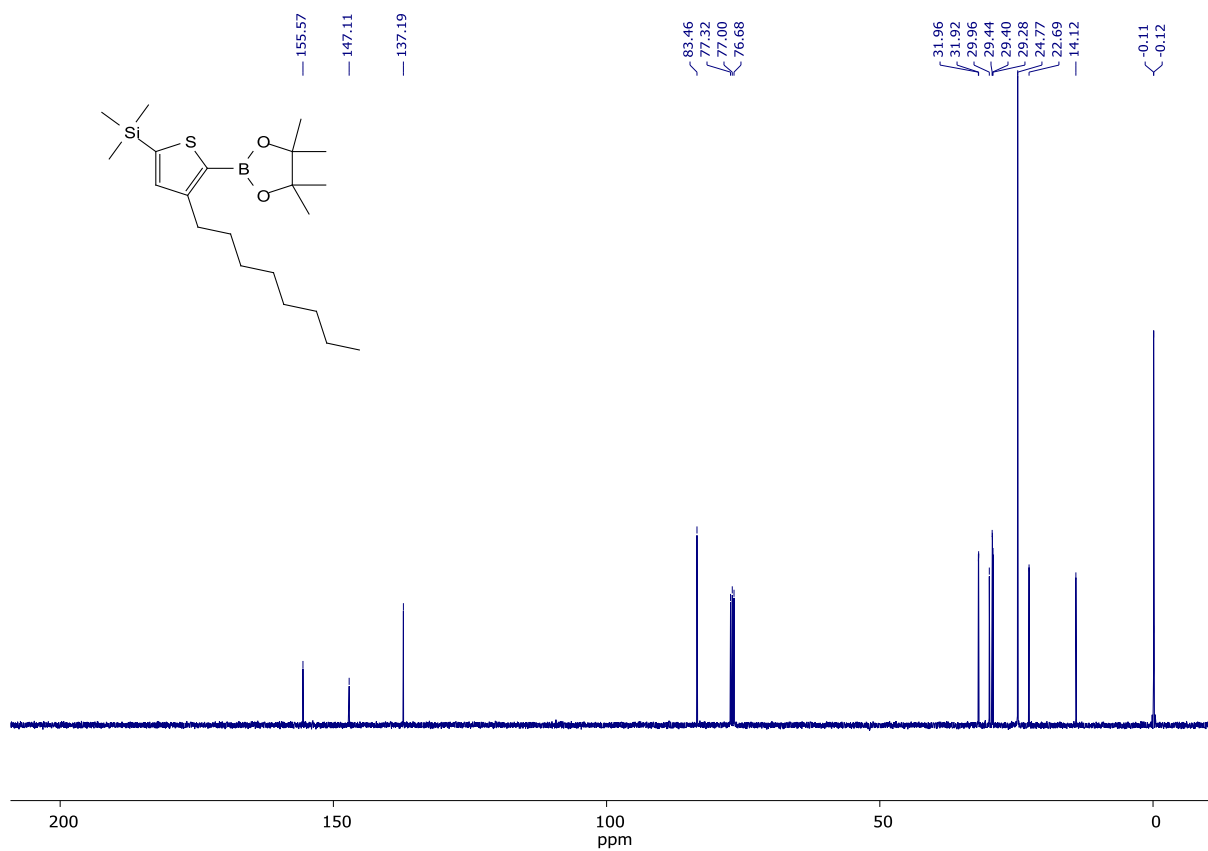
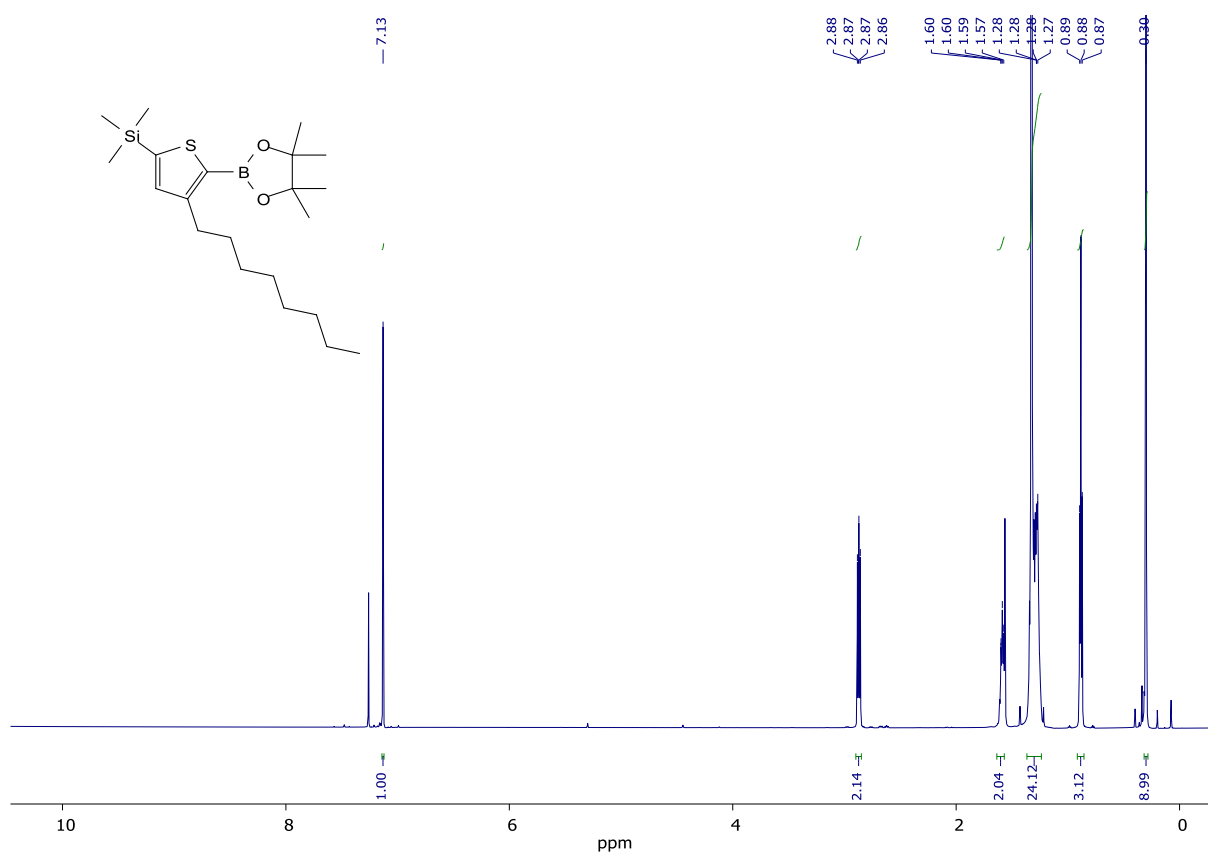
2.8.3.2 (4-octylthiophen-2-yl)trimethylsilane



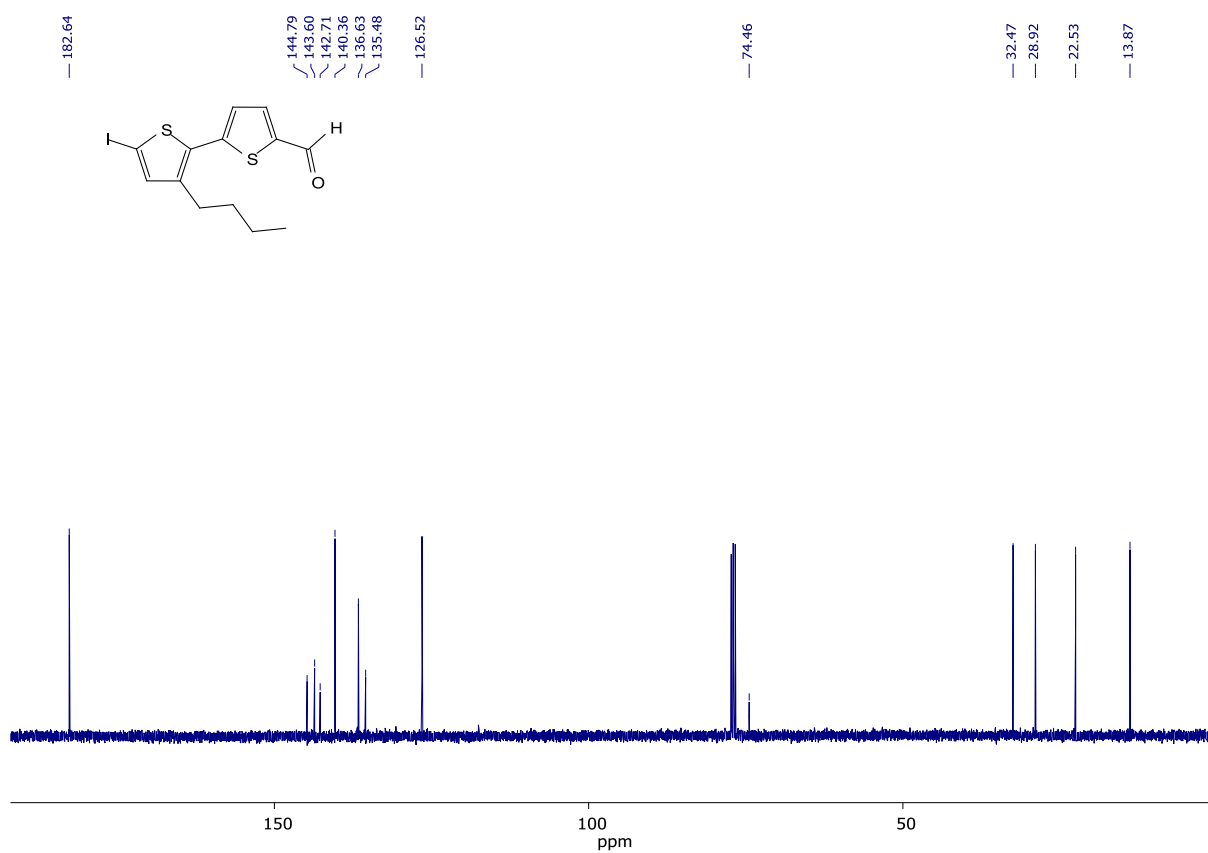
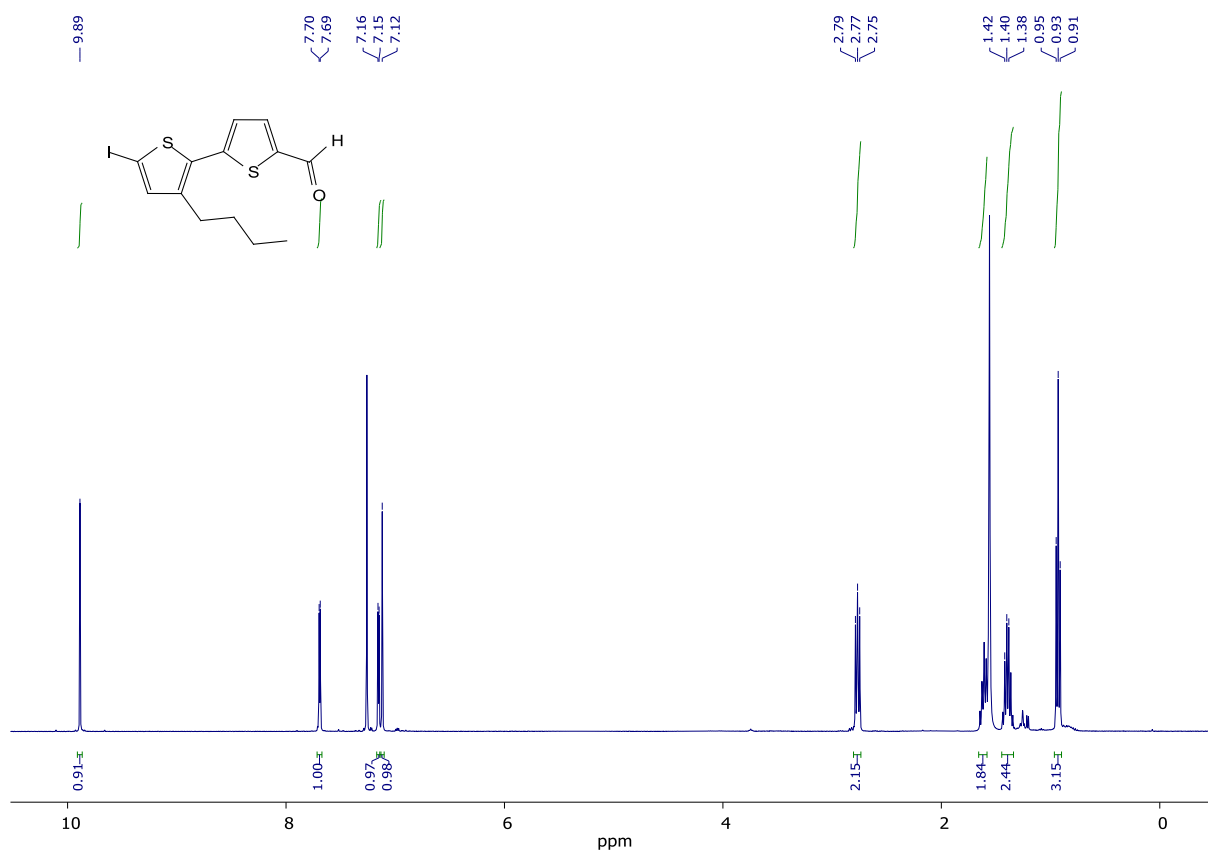
2.8.3.3 3'-butyl-5'-(trimethylsilyl)-[2,2'-bithiophene]-5-carbaldehyde



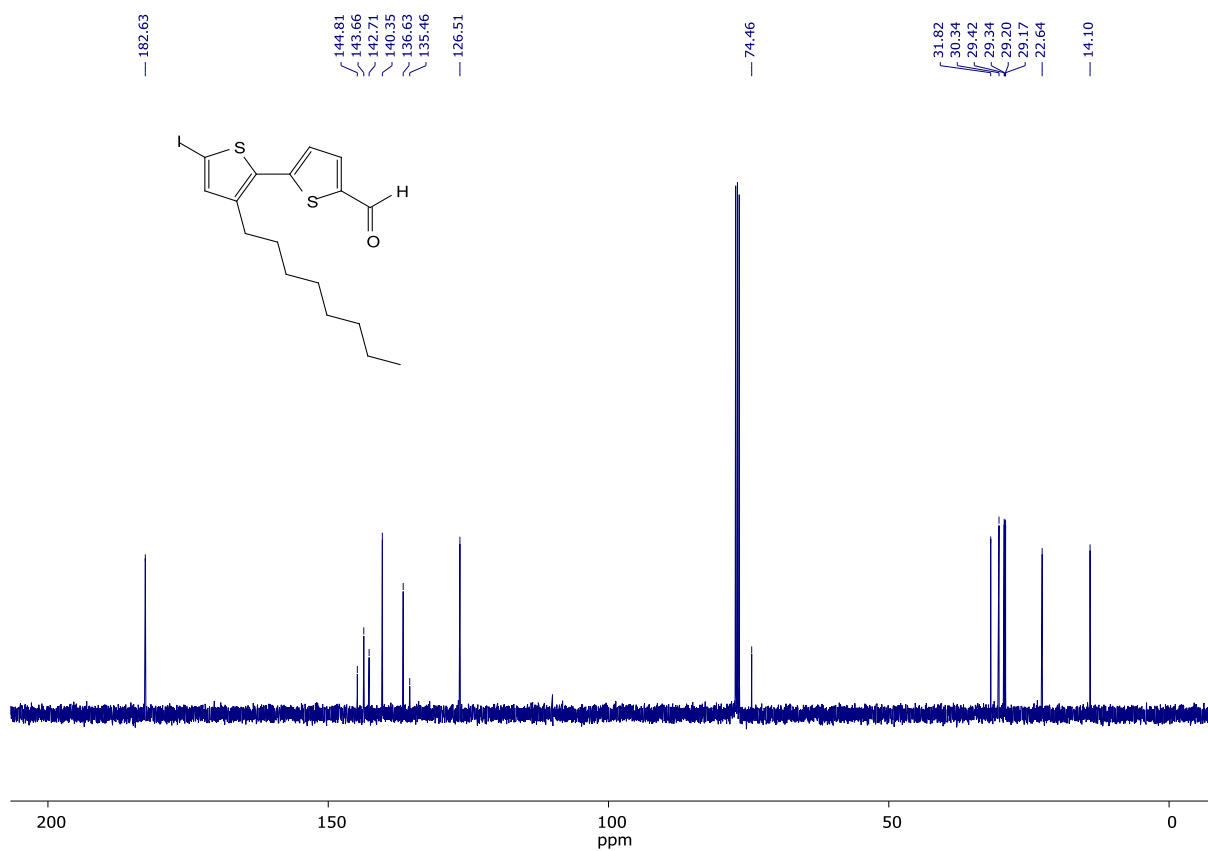
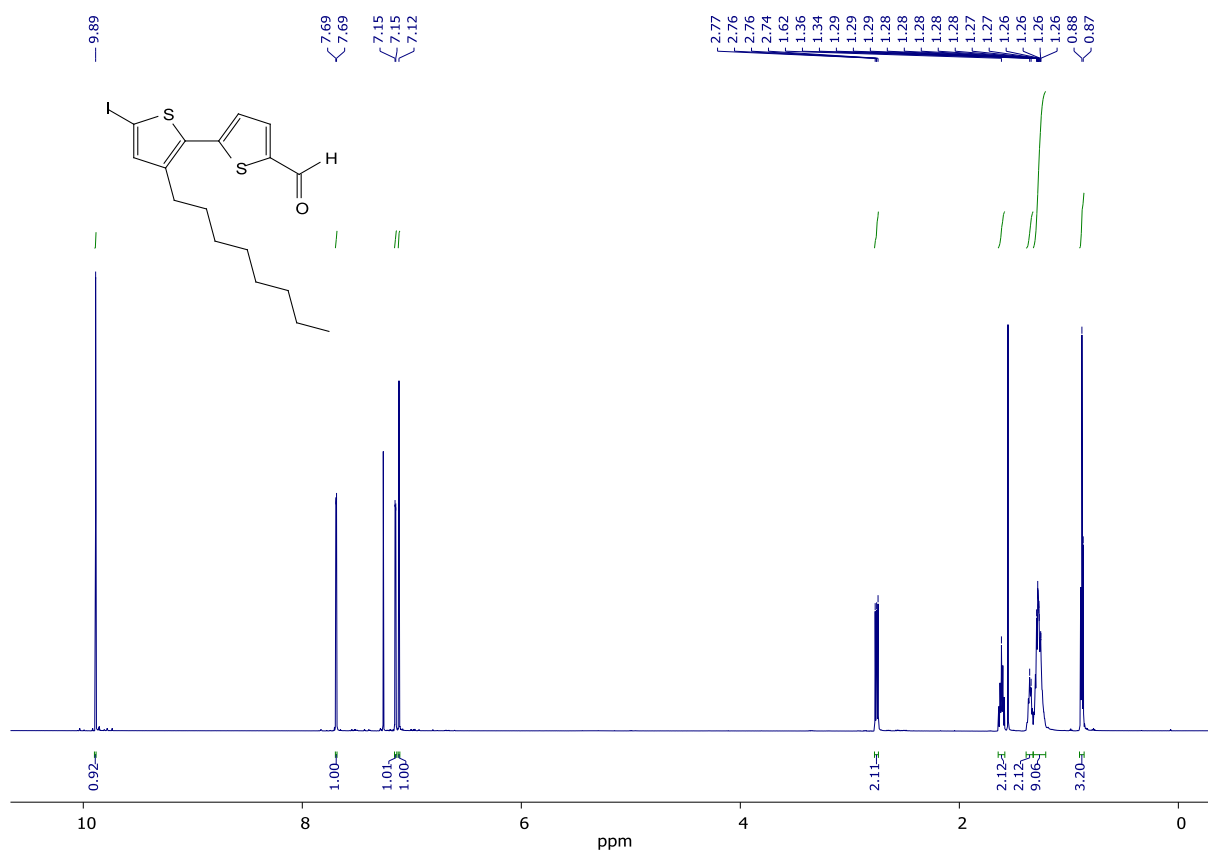
2.8.3.4 (4-octyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylsilane



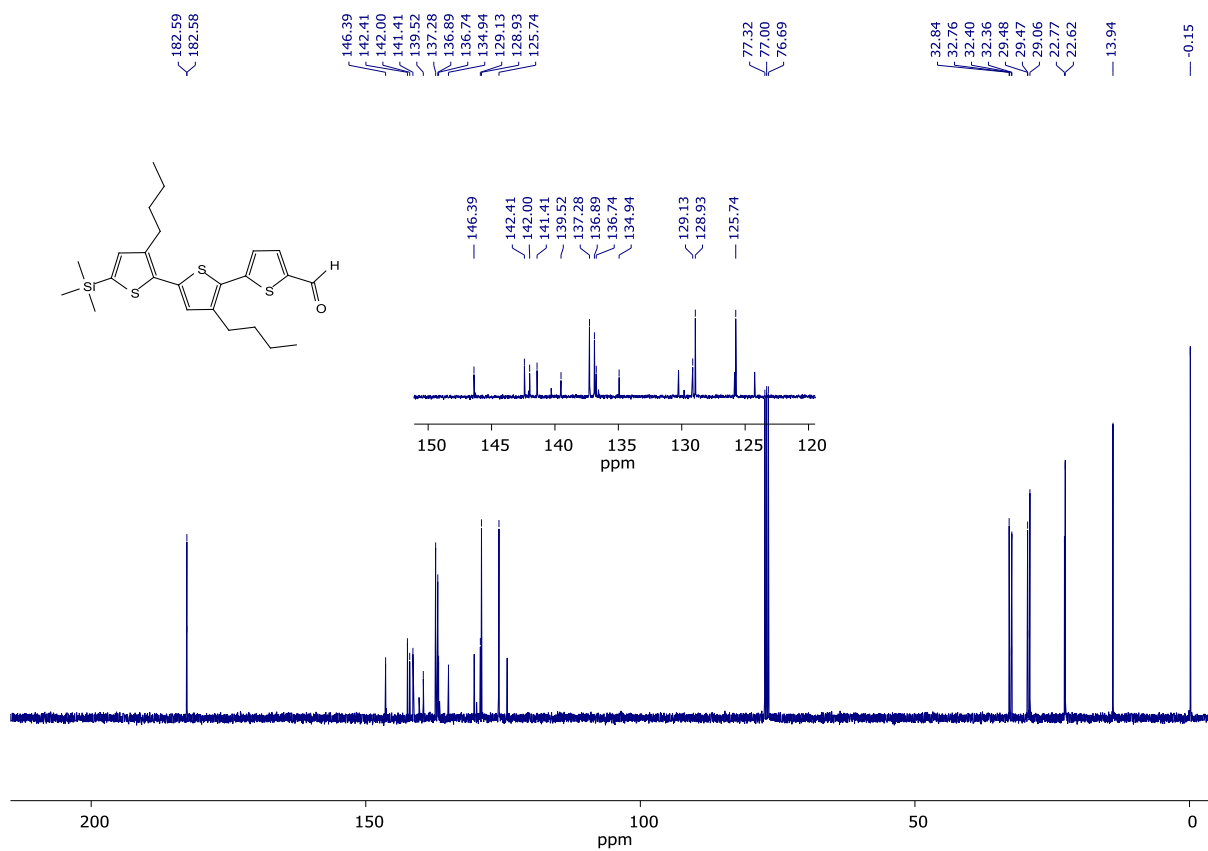
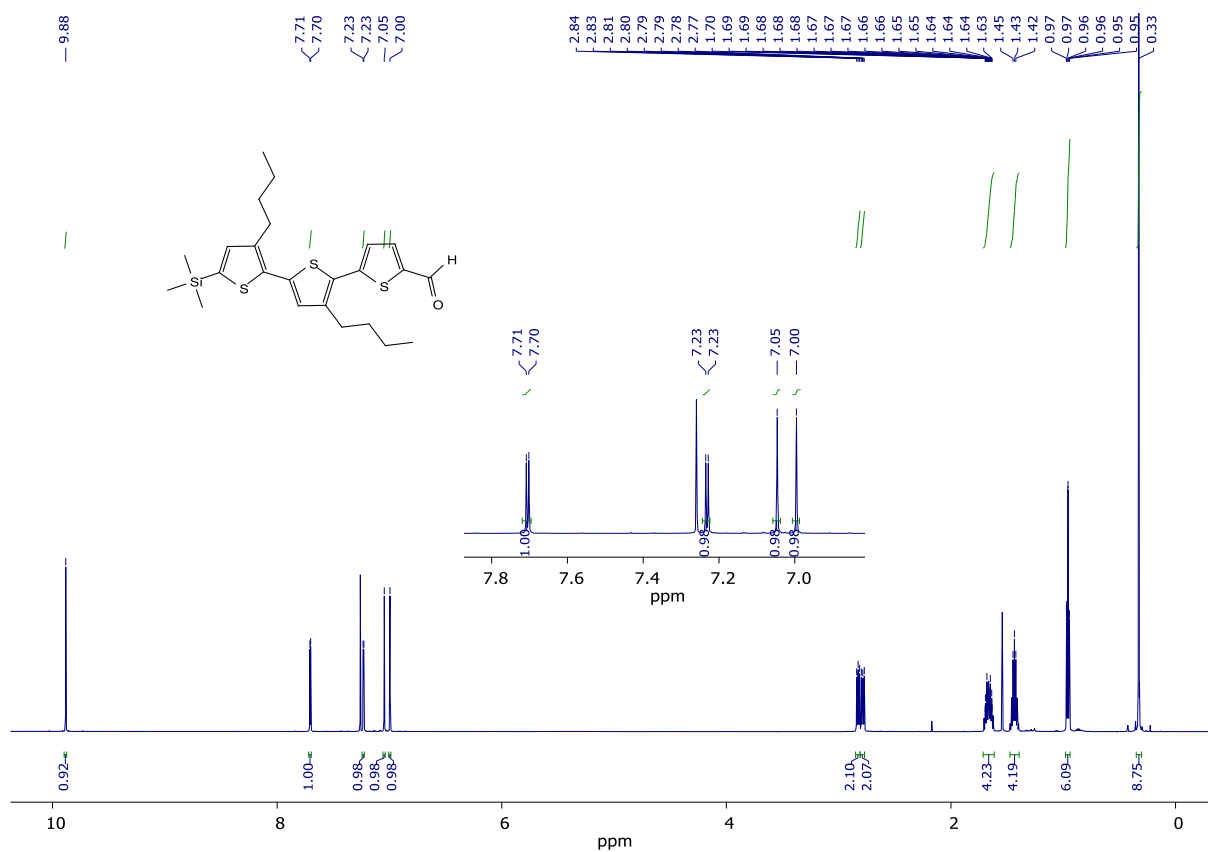
2.8.3.5 3'-butyl-5'-iodo-[2,2'-bithiophene]-5-carbaldehyde



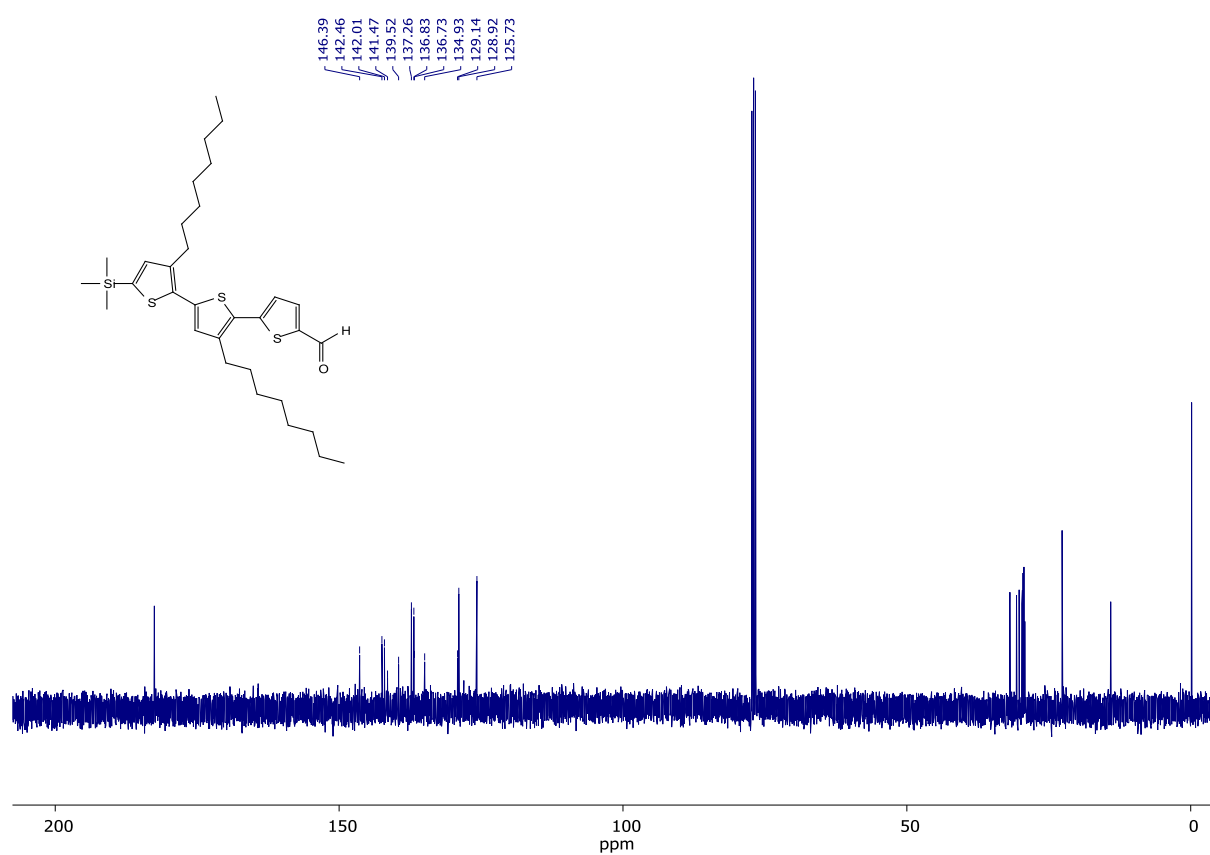
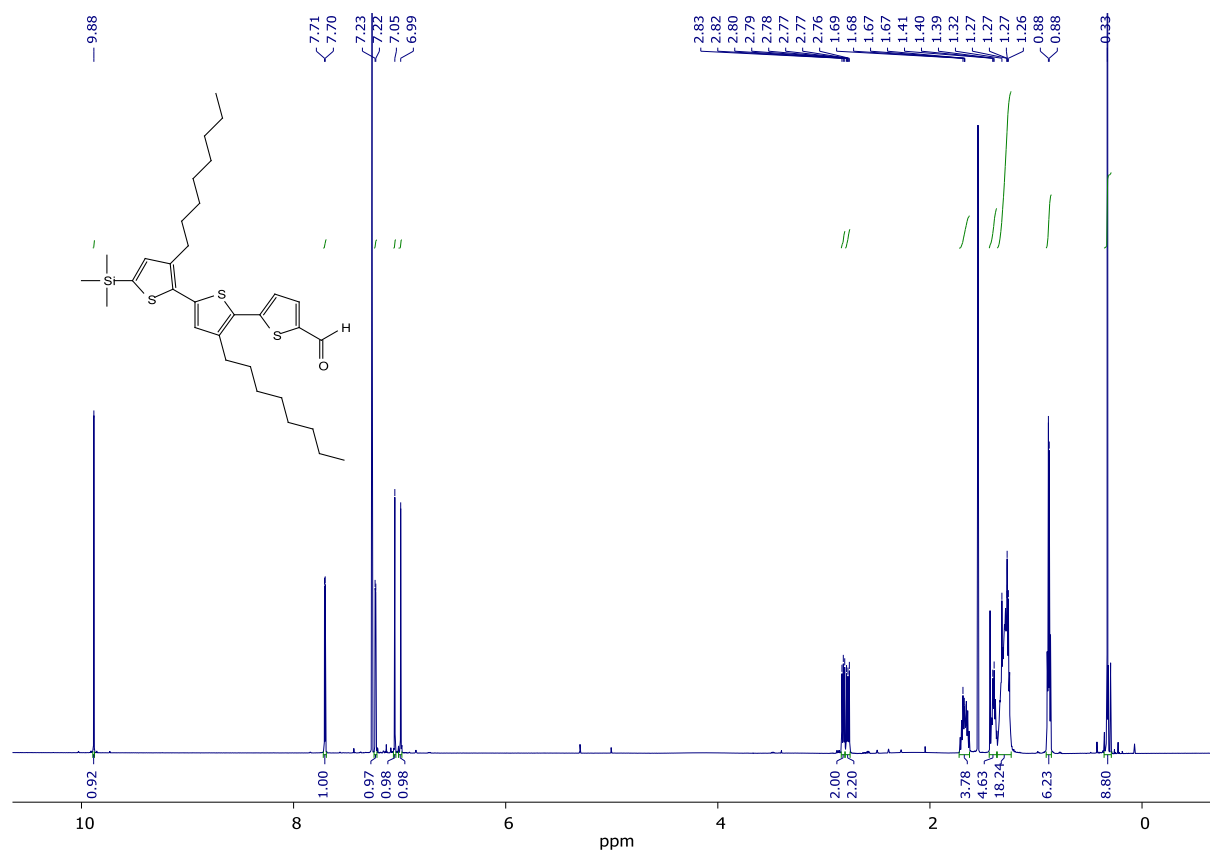
2.8.3.6 3'-octyl-5'-iodo-[2,2'-bithiophene]-5-carbaldehyde



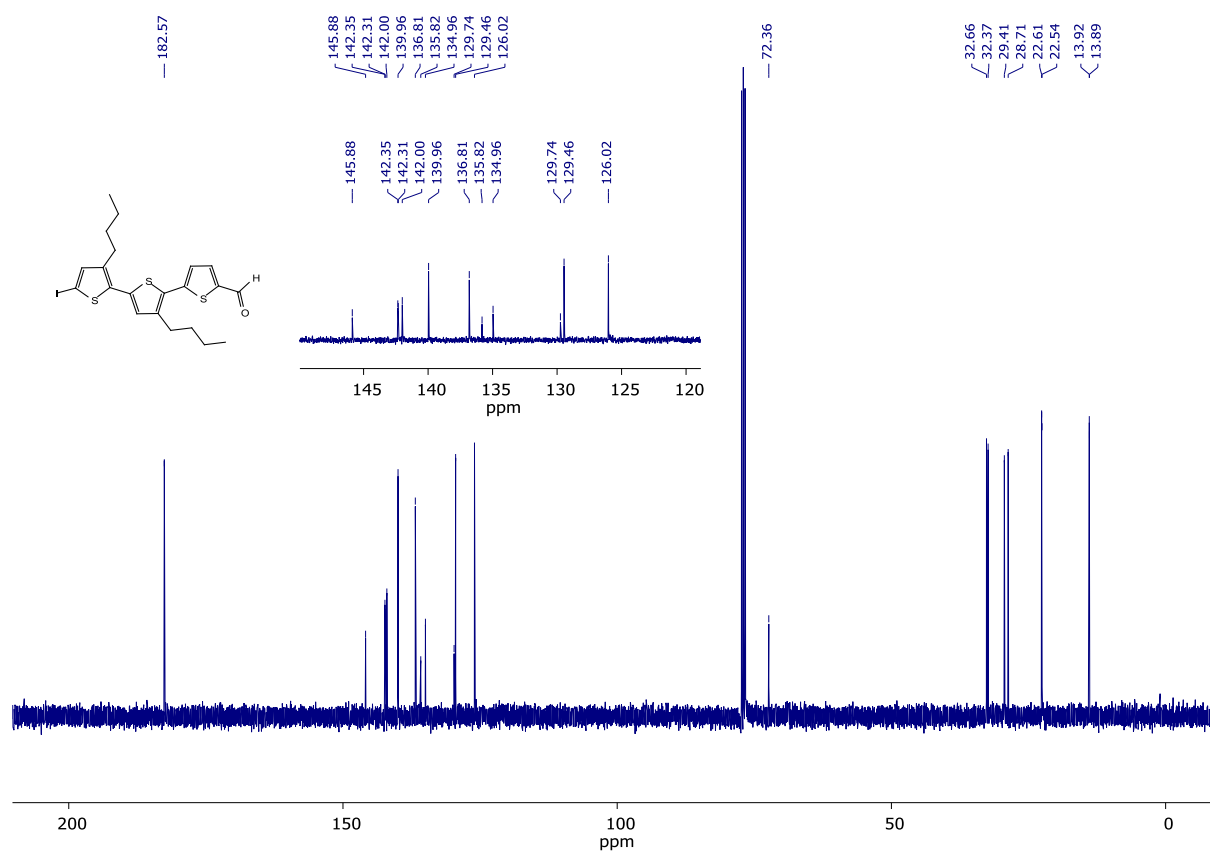
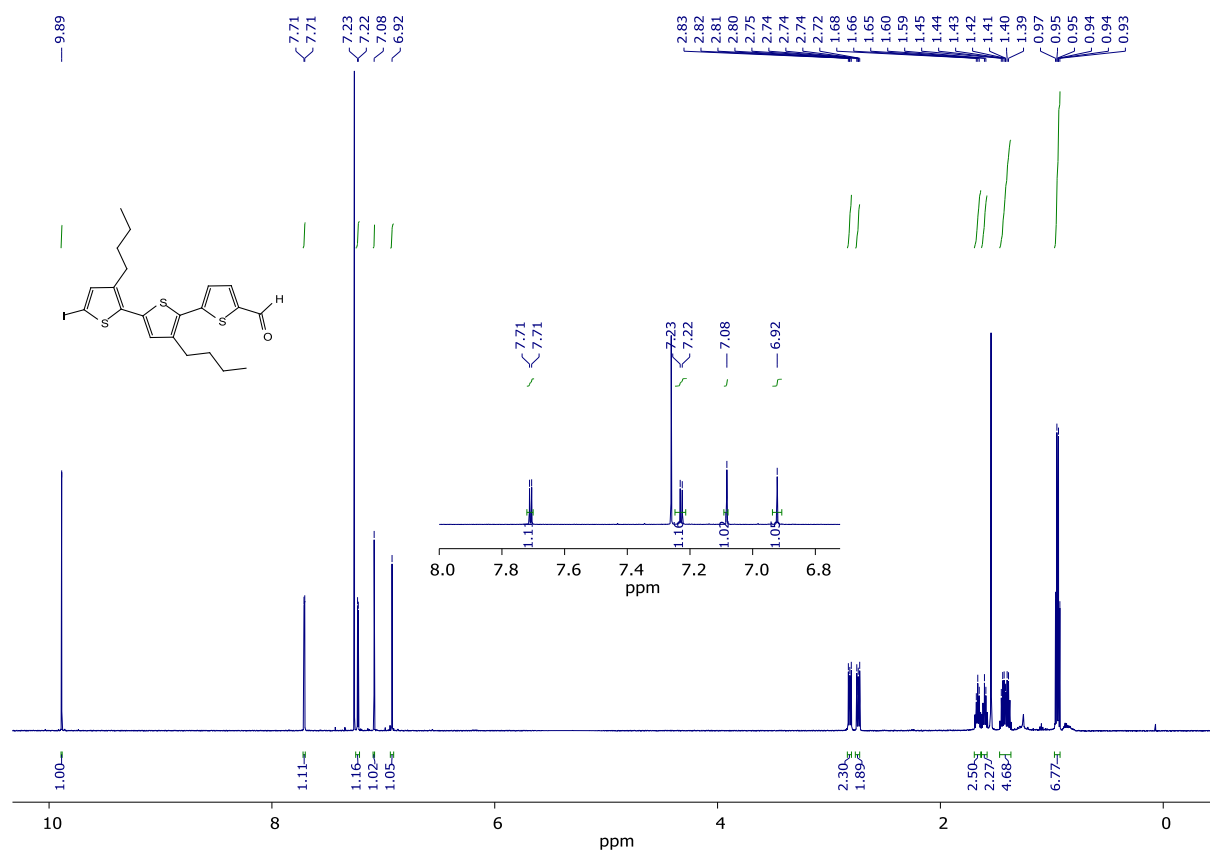
2.8.3.7 3',3''-dibutyl-5''-(trimethylsilyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde



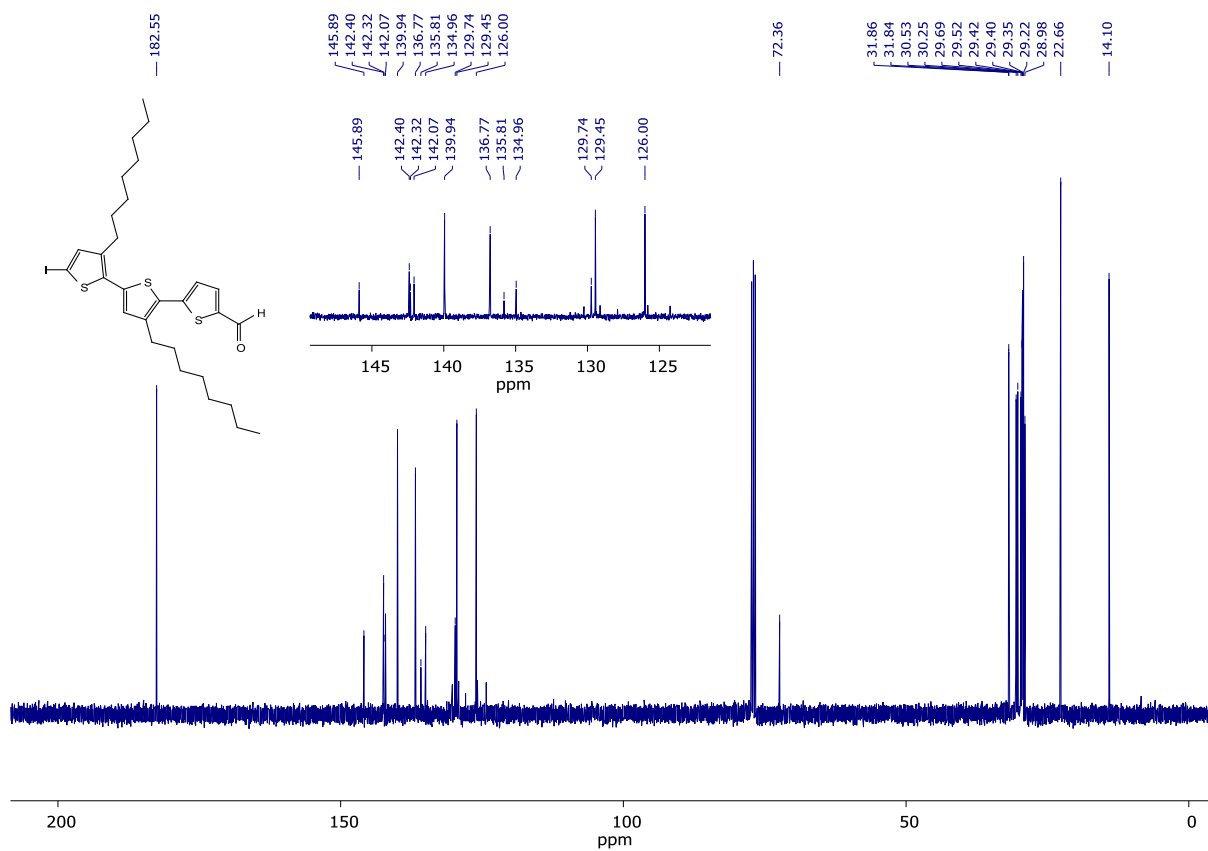
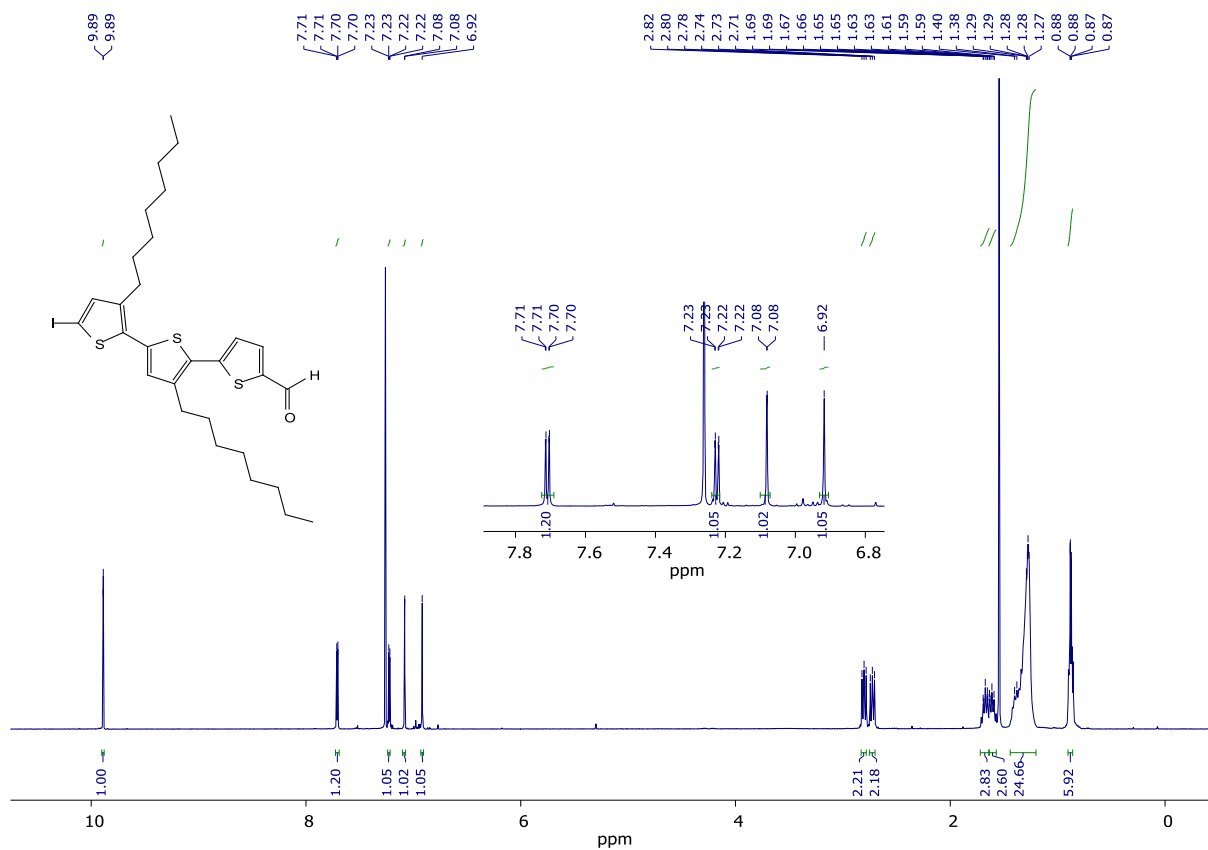
2.8.3.8 3',3''-dioctyl-5''-(trimethylsilyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde



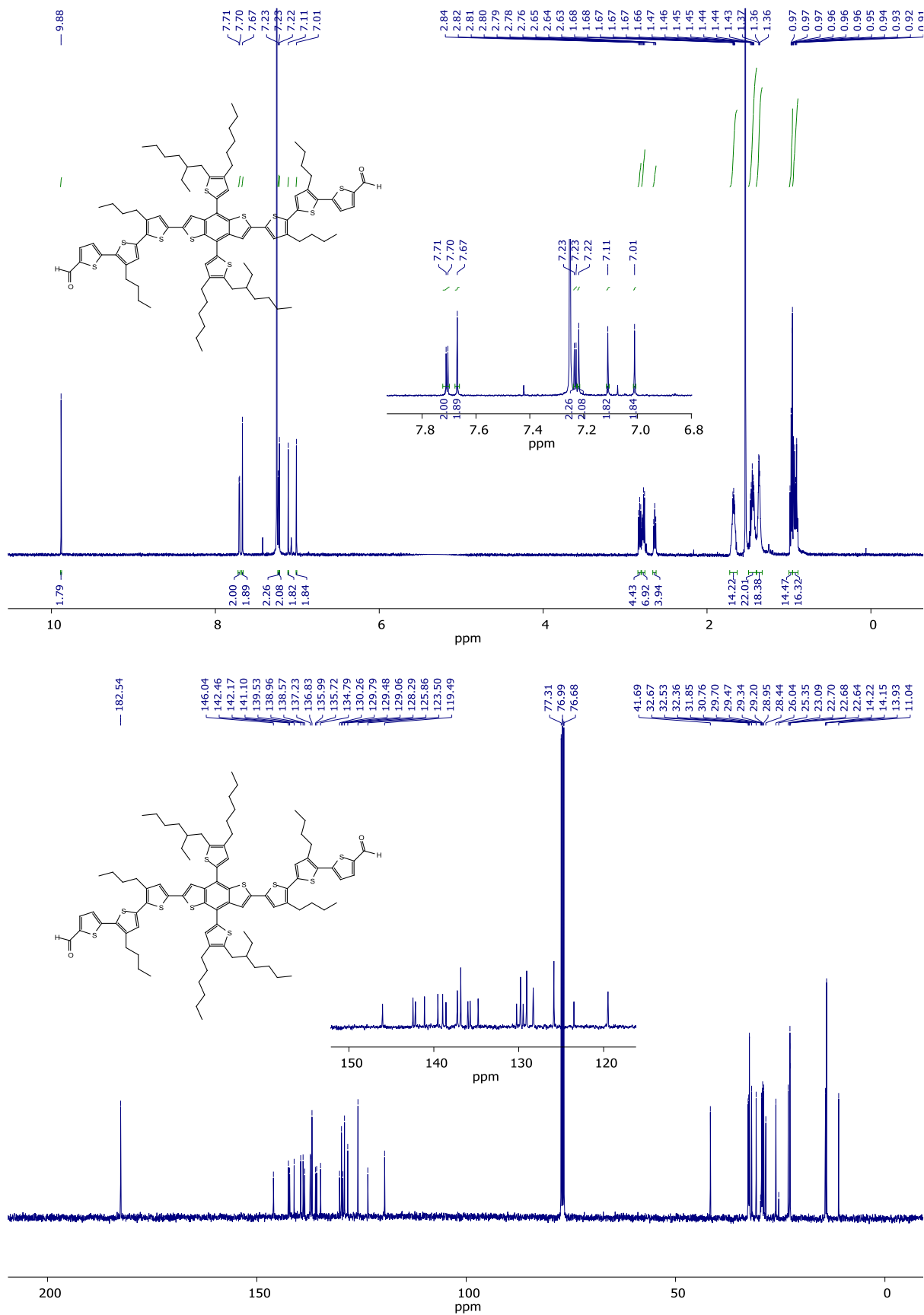
2.8.3.9 3',3''-dibutyl-5''-iodo-[2,2':5',2''-terthiophene]-5-carbaldehyde



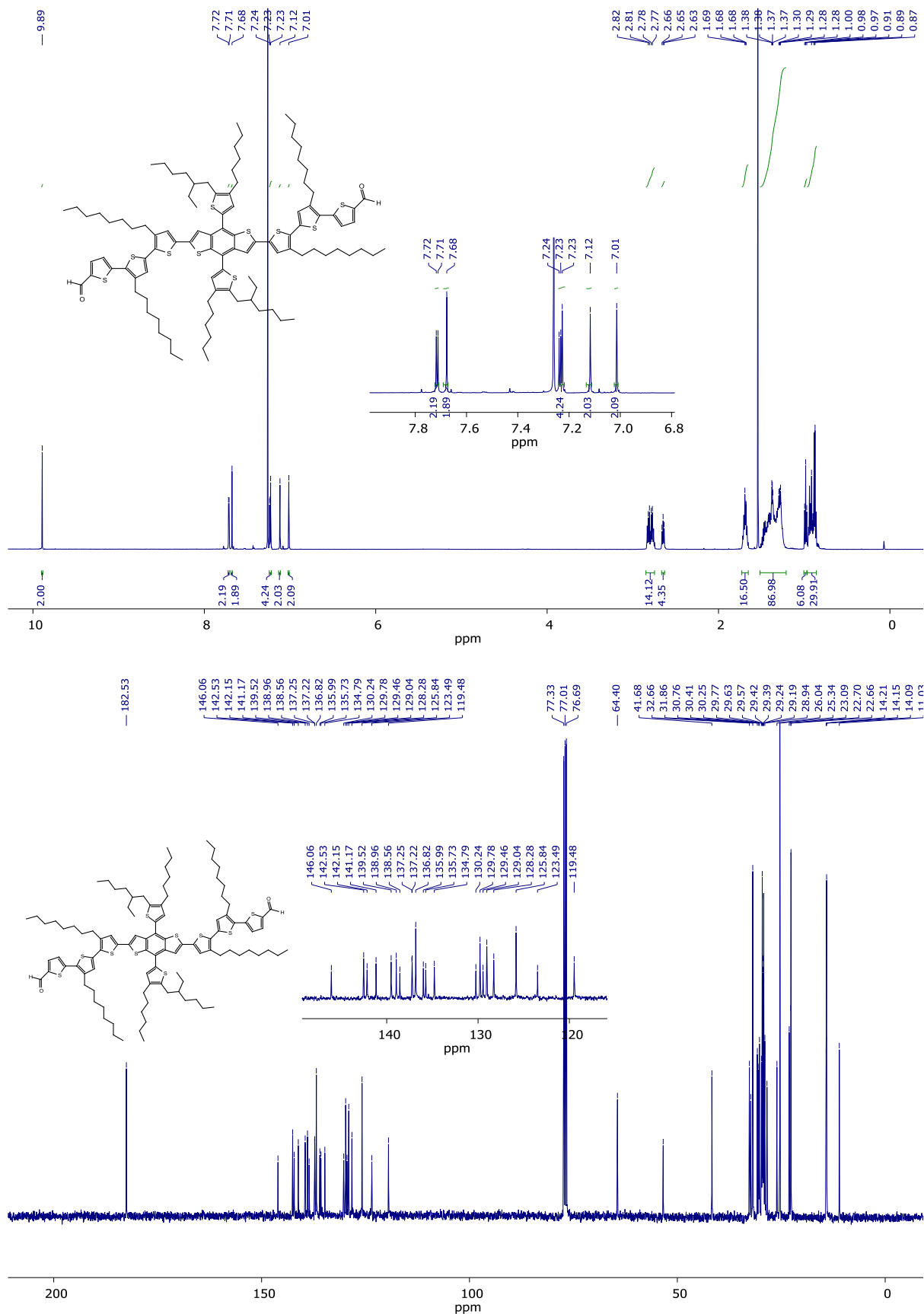
2.8.3.10 3',3''-dioctyl-5''-iodo-[2,2':5',2''-terthiophene]-5-carbaldehyde



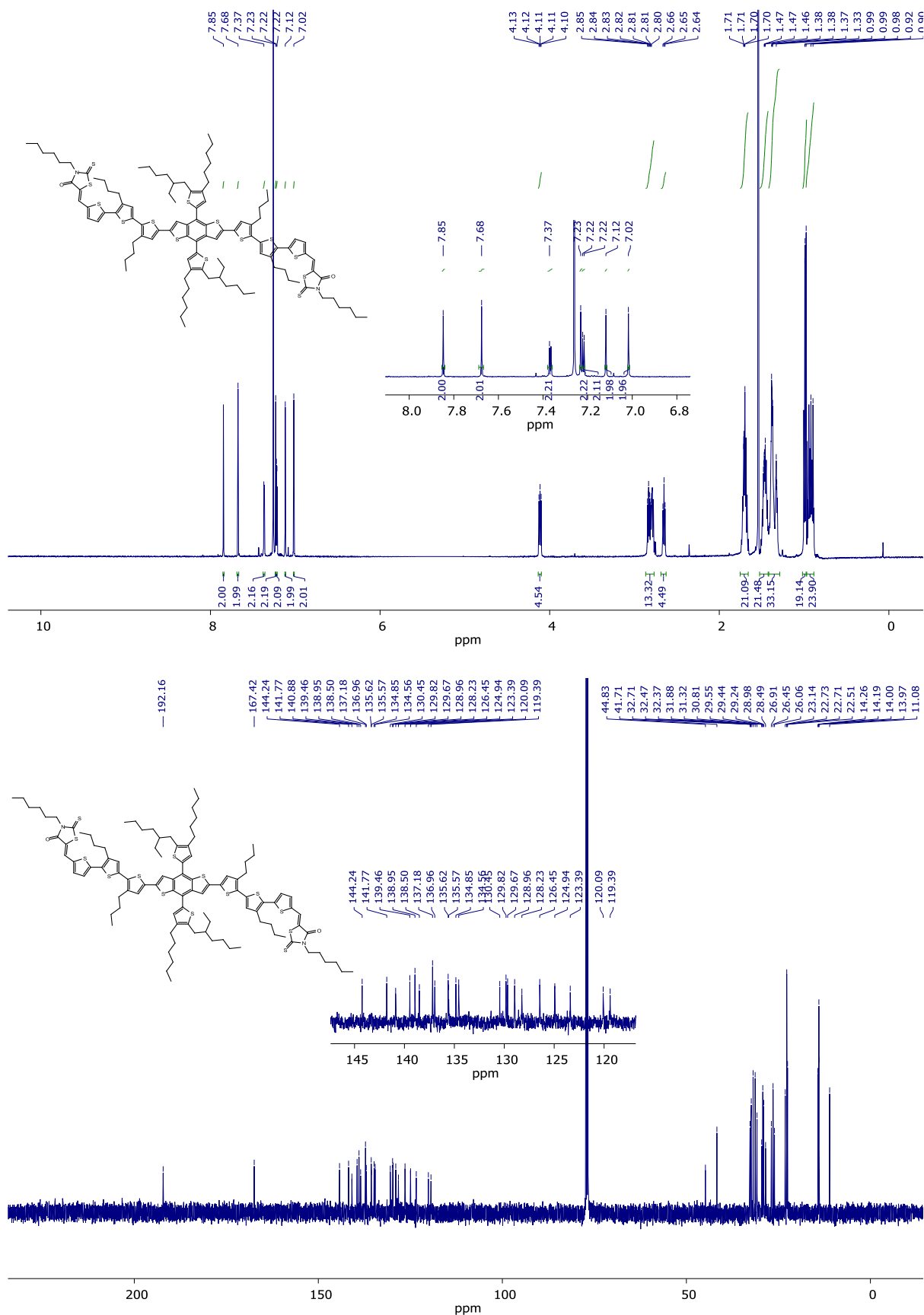
2.8.3.11 5'',5'''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dibutyl-[2,2':5',2''-terthiophene]-5-carbaldehyde)



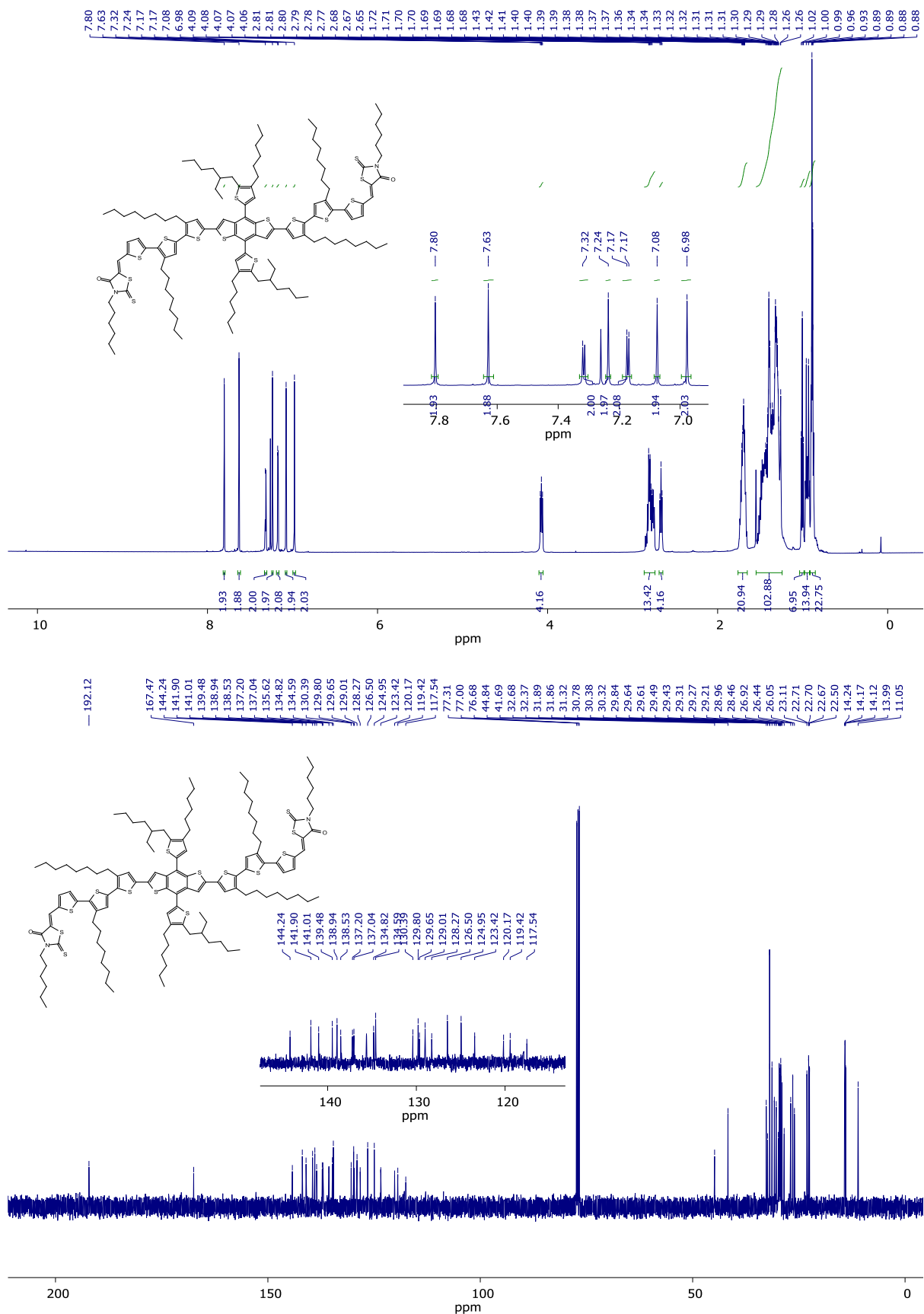
2.8.3.12 5'',5'''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde)



2.8.3.13 5Z,5'Z)-5,5'-((5'',5'''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dibutyl-[2,2':5',2''-terthiophene]-5'',5'-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)

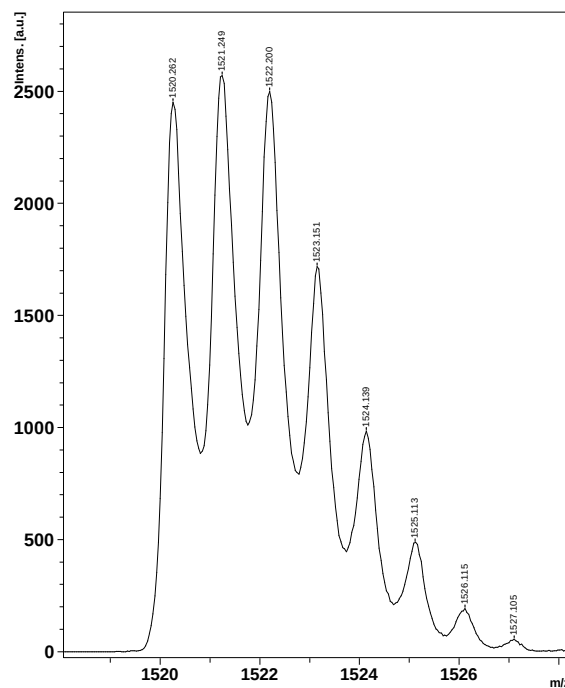


2.8.3.14 (5Z,5'Z)-5,5'-((5'',5'''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5'-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)

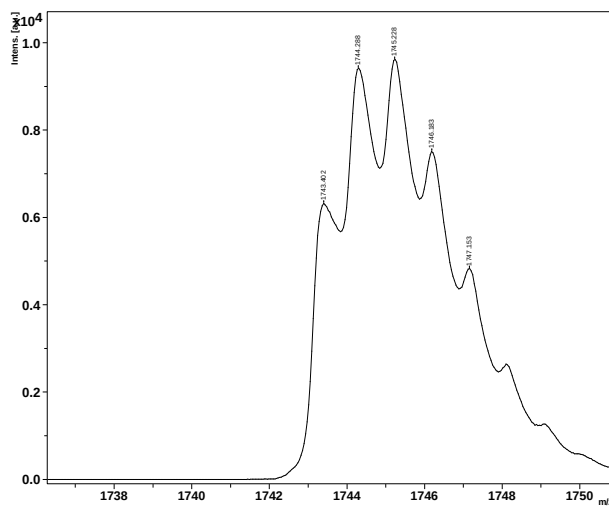


2.8.4 MALDI mass spectra

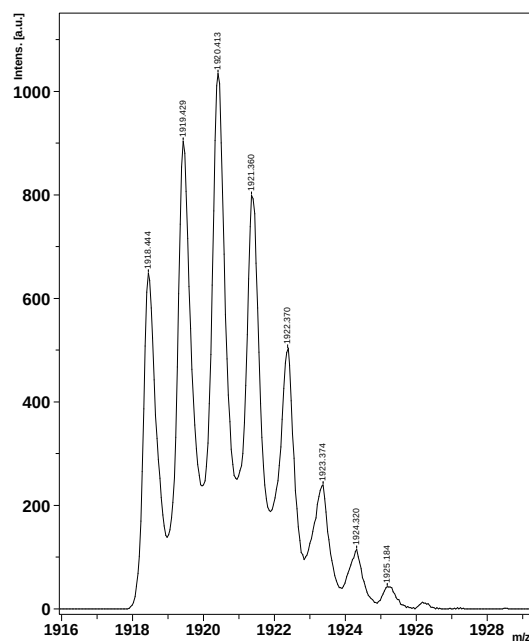
2.8.4.1 5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dibutyl-[2,2':5',2''-terthiophene]-5-carbaldehyde)



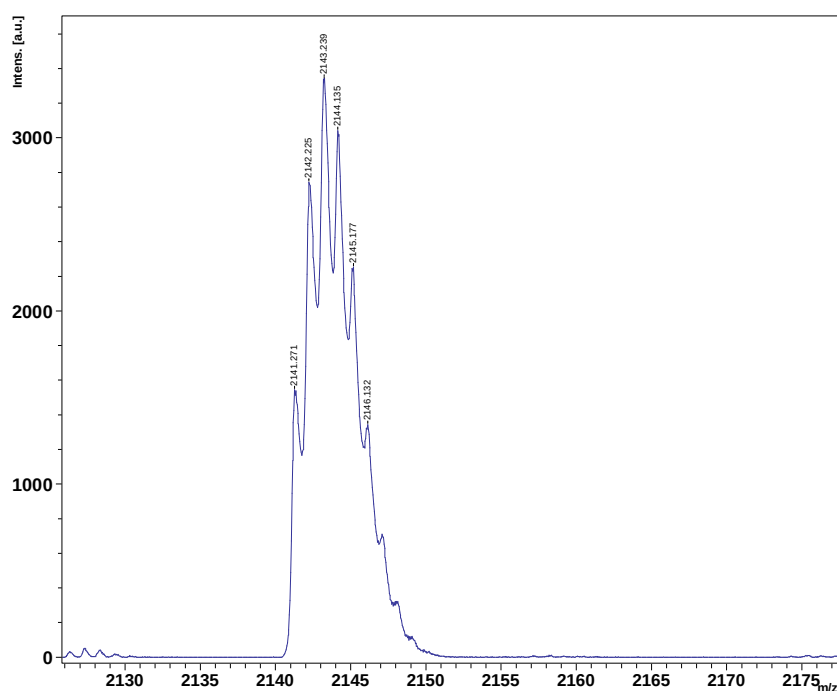
2.8.4.2 5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde)



2.8.4.3 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dibutyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)



2.8.4.4 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one)



2.8.5 Thermogravimetric Analysis Thermograms

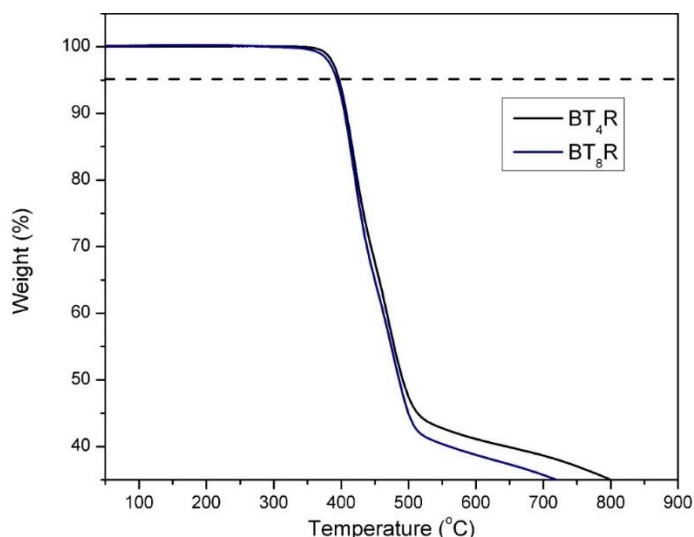


Figure 2-16: TGA thermograms for the BT_xR analogue materials. Samples were heated under N₂ at rate of 10°C min⁻¹

2.8.6 Polarized optical microscopy heating profiles

Table 5: Heating and cooling profiles utilized to capture images of the phase changes of BT₄R

BT ₄ R sample [Transmission imaging]					
Heating Process			Cooling Process		
Temperature (°C)	Heating rate (°C min ⁻¹)	Hold time (min)	Temperature (°C)	Cooling rate (°C min ⁻¹)	Hold time (min)
25	10	1	210	1	5
205	1	10	200	1	10
206	1	10	198.5	1	10
210	1	5	193.5	1	10
			25	10	1

2.8.7 Cyclic voltammetry

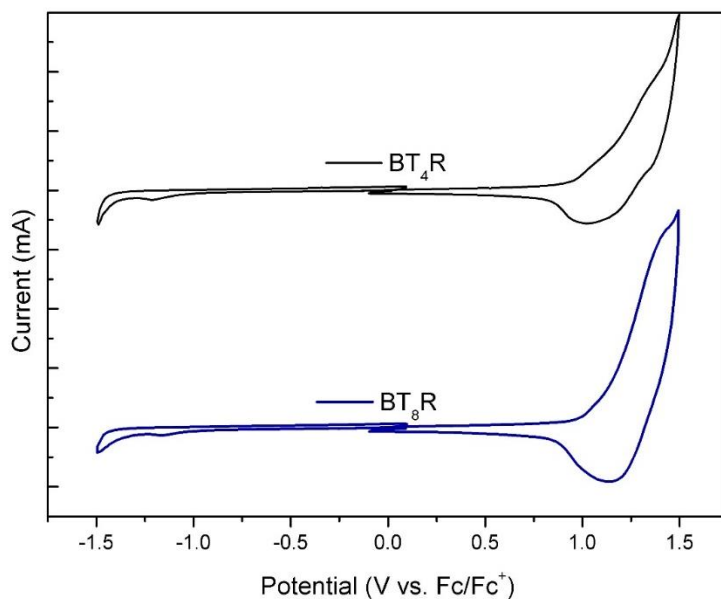


Figure 2-17: Normalized thin film cyclic voltammograms for BT_xR analogue materials, referenced to ferrocene.

2.8.8 X-ray crystallography

Crystal data for **BT₄R**. C₁₀₆H₁₃₆N₂O₂S₁₄ $M = 1829.93$, $T = 130.01(10)$ K, $\lambda = 1.54184$ Å, Triclinic, space group $P-1$, $a = 7.5742(6)$, $b = 18.3131(19)$, $c = 20.291(3)$ Å, $\alpha = 64.565(13)^\circ$, $\beta = 87.825(9)^\circ$, $\gamma = 84.211(7)^\circ$, $V = 2528.6(6)$ Å³, $Z = 2$, $D_c = 1.258$ Mg M⁻³, $\mu = 3.163$ mm⁻¹, $F(000) = 1024$, crystal size 0.7584 x 0.0634 x 0.0095 mm. $\theta_{\max} = 74.557^\circ$, 15219 reflections measured, 9782 independent reflections ($R_{\text{int}} = 0.0877$) the final $R = 0.0989$ [$I > 2\sigma(I)$, 15002 data] and $wR(F^2) = 0.2895$ (all data) GOOF = 1.039.

Chapter 3

Benzodithiophene core substituents and the impact of solubility on film morphology

3.1 Chapter introduction

In an ongoing effort to establish the structure-property relationships of the high-performing BTR molecular substrate, and with the importance of the oligothiophene-appended alkyl sidechains to BTR analogue device morphology established in Chapter 2, attention was turned to the nature of the 2D substituent on the benzodithiophene core moiety and what influence it had with respect to molecular packing, thin-film behaviour and OPV device performance. Interest in the study of these core substituents came about from two primary observations: the first was that sidechain engineering on the thienyl core moiety, and specifically the re-engineering of this moiety from a mono-alkylated to a di-alkylated one (Figure 3-1), had been one of the alterations made that resulted in the design of **BTR** itself, and therefore potentially a vital contributing factor to its high charge transport.

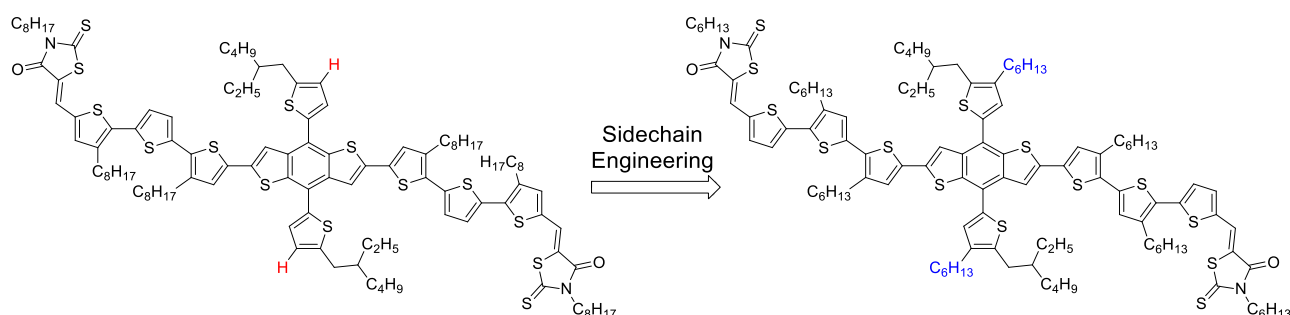


Figure 3-1: Sidechain engineering alterations made to known chromophore SMPV1 (left) resulting in BTR (right).

The second observation was one made from the study of the single-crystal determined structures of the BT_xR analogues in Chapter 2 (section 2.6.1). It was observed that, intuitively, the length of alkyl sidechains affected the degree of spacing between alkyl lamellar layers. This lamellar spacing, however, was itself seen to influence the benzodithiophene core-to-core offset between these lamellar layers (Figure 3-2a). This in turn seemed to result in a series of cascading impacts upon intermolecular packing, affecting factors such as the torsional angle of the thienyl substituent, the torsional angle of the oligothiophene π -bridge, and both the π - π stacking motif and distance. Though the direct cause and effects of these individual factors on intermolecular interactions are decidedly non-trivial to deconvolute, it is logical that an increasing torsional angle between the BDT core and the thienyl core moiety can be linked to an increasing amount of 3D space and steric volume taken up by this core substituent, with this potentially hindering π - π stacking. Following this, it was theorized that this relationship between the lamellar spacing and the steric volume of the core

substituent could potentially be a two-way street – that by altering the nature of the core moiety and reducing its steric volume, perhaps both the degree of core-to-core offset and interlamellar spacing could be reduced, and thereby increasing intermolecular packing. Following on from this, the ultimate goal of this study was to assess the feasibility of designing a core substituent with an optimal steric presence to allow a π -stacking motif that resulted in cofacial orbital overlap of the conjugated backbone not only within the π -stacked intra-lamellar layer (longitudinal displacement) but also across the inter-lamellar distance (transverse displacement), as seen in Figure 3-2b. This would allow greater delocalization of charges through an expanded 3D pathway, thereby increasing charge-carrier mobility within the OPV active layer.

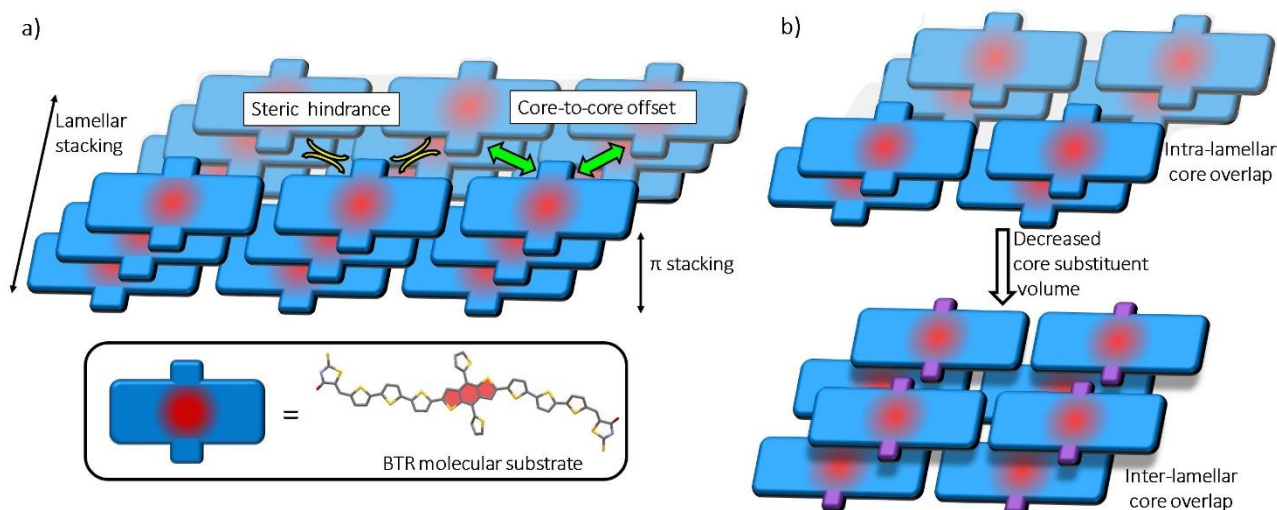


Figure 3-2: Schematic showing a) the benzodithiophene core offset present in the intermolecular packing motif of BTR molecular substrates, and b) a transition to the desired π -stacked packing structure with enhanced overlap via alteration of the core substituent

Substantial efforts have been made in the literature to promote increased pi-overlap to achieve these enhanced charge -carrier mobilities, with this particularly challenging for molecular substrates with a clear director axis along the conjugated backbone and a large aspect ratio.^[143] It has previously been shown in the literature that altering the degree of π -overlap for the maximization of charge transport is indeed possible through the rational application of molecular design. Liu et al conducted a series of studies on substituted quarterthiophenes, where the introduction of sidechain substituents with varying degrees of hydrogen-bonding capabilities resulted in a controllable degree of both longitudinal and transverse displacement.^[153] Of note was that achieving decreased intermolecular lamellar and π -stacking distances was subordinate in effect on charge mobility to optimal displacement and positioning of the aryl cores. In a separate study, Han et al have shown through both experimentally-determined single-crystal structures and computational simulations that modulation of the end-group moiety on an ITIC-based non-fullerene acceptor -featuring 2D conjugation in a similar manner to **BTR**- resulted in partial three-dimensional molecular overlap through π - π stacking interactions in thin-film packing. This was found to confer high electron mobilities through an isotropic network, and was superior to mobilities obtained from the single-crystal, which did not feature this 3D overlap.^[154]

3.2 BTR core-substituted materials: initial findings

Four different BDT core substituents of varying steric bulk (Figure 3-3) were investigated for their impact upon the intermolecular packing of the BTR substrate. These substituents are all widely used in the literature and can be seen to range from a triisopropylsilyl ethynyl (**BTR-TIPS**) and 2-ethylhexylthio moiety (**BTR-TE**), to a 2-hexyl- (**BTR-H**) and a 2-(2-ethylhexyl)-thienyl (**BTR-EH**) moiety reminiscent of **SMPV1**, the precursor to **BTR**. The TIPS substituent is well known for its solubilizing properties and contributions to enhanced π -orbital overlap, with its use in conjunction with the BDT core having resulted in high charge mobilities when incorporated into both OFET and OPV devices.^[155] Single crystal diffraction studies of TIPS-functionalized acene substrates have also demonstrated the potential for transverse overlap,^[156] and when coupled with its smaller volume relative to the dialkylated thienyl substituent on **BTR** lead to its selection for use in the current study. The alkylthio substituent was also considered for this same reason, with the lack of an aromatic ring within this moiety significantly reducing its surface area. Alkylthio core substituents, when coupled to benzodithiophene cores, have resulted in molecular substrates featuring some of the highest reported OPV performances, due to both lower HOMO levels and optimized molecular packing from sulfur-sulfur interactions.^[157] In the case of the two mono-alkylthienyl core substituents, the removal of a single alkyl chain was theorized to also result in a decreased steric presence, with this fine-tuned decluttering of the inter-lamellar space potentially allowing for an a) increased planarization of the thienyl moiety relative to the BDT core, and b) increased interdigitation of the alkyl sidechains.

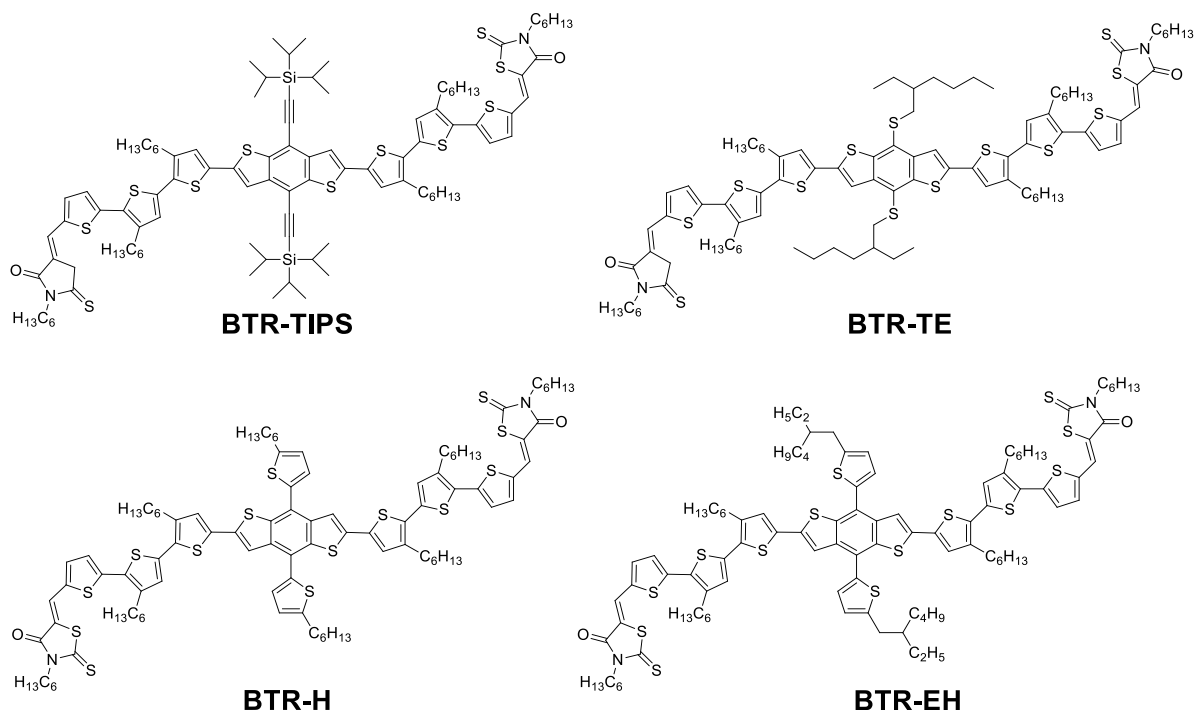


Figure 3-3: Chemical structures of the BTR-X series.

Unfortunately, single-crystal structures were unable to be obtained for all analogues in the series, and as such this hypothesis was unable to be conclusively proven. Structures for the analogues from which crystals

were able to be grown -namely **BTR-TIPS** and **BTR-EH**, Figures 3-4 and 3-5, respectively- however show that while the lamellar spacing does decrease relative to the 19.04 Å reported for **BTR**, the degree of transverse offsets and π -stacking motifs observed preclude any inter-lamellar π -orbital overlap. This is likely due to a) the core substituents utilized still possessing excess steric bulk, and b) the twist along the oligothiophene π -bridge apparently inherent to this molecular substrate preventing complete planarity. Nevertheless, an intriguing relationship was discovered through studies of the thin-film morphology, linking molecular structure, bulk properties and device performance. This resulted in a paper currently undergoing a peer-review process, the text and supporting information of which comprises the remainder of this chapter.

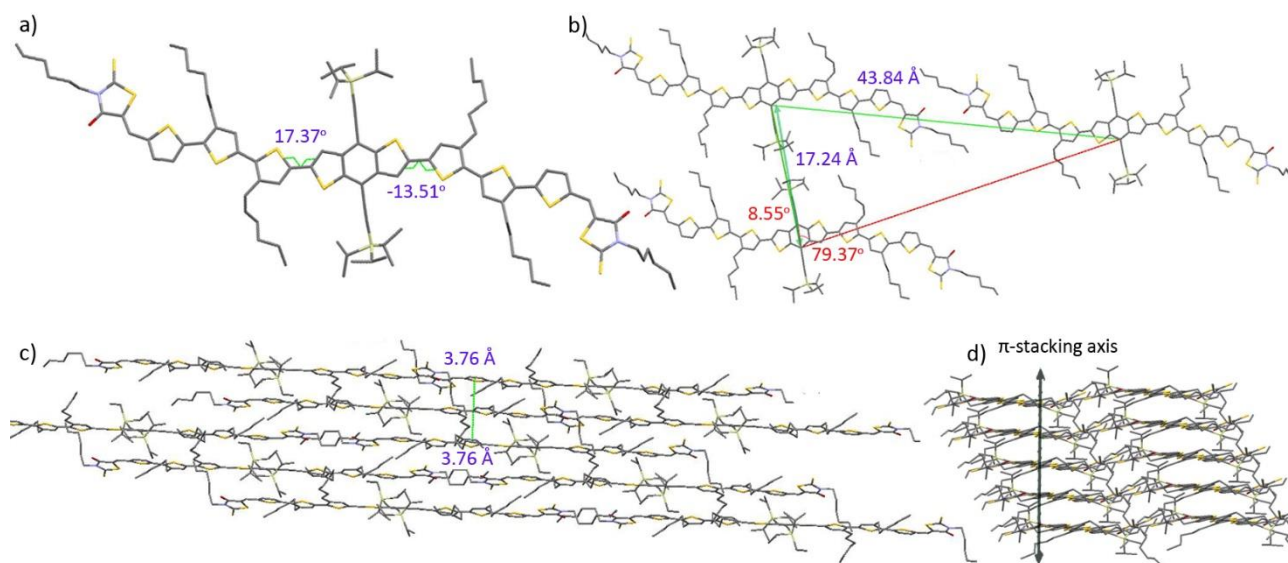


Figure 3-4: Single crystal structures of BTR-TIPS, seen a) as a single unit with dihedral angles labelled, b) as packing across alkyl lamellar layers with the core-core distance (purple) and angles (red) labelled, and c) as a 2-molecule long π -stacked layer with π -stacking widths labelled. Hydrogens and some alkyl chains have been omitted for clarity.

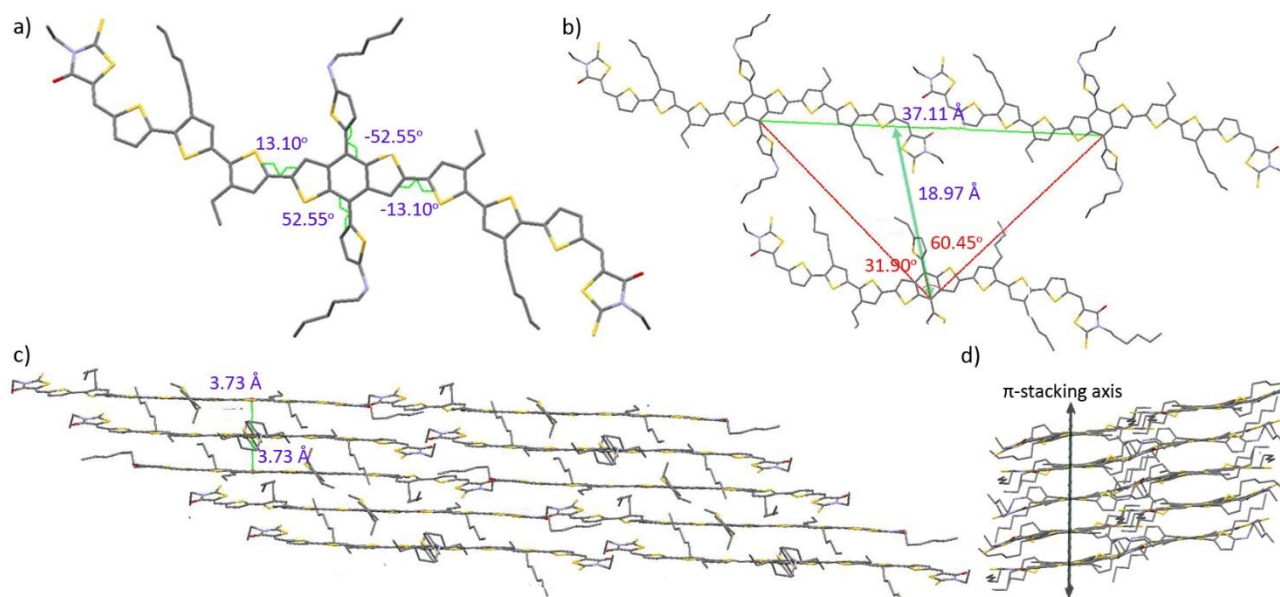


Figure 3-5: Single crystal structures of BTR-EH, seen a) as a single unit with dihedral angles labelled, b) as packing across alkyl lamellar layers with the core-core distance (purple) and angles (red) labelled, and c) as a 2-molecule long π -stacked layer with π -stacking widths labelled. Hydrogens and some alkyl chains have been omitted for clarity.

3.3 GIWAXS depth profiling measurements

As the work within the following manuscript heavily involves the use of depth-dependant studies, a brief description of the technique and its underlying principle seems prudent.

The discussion on and interpretation of GIWAXS data in Chapter 1 presupposed that the grazing angle of the incident beam (θ_x) was matched with the critical angle for total external reflection (θ_c) of the material in the thin-films. This critical angle, as defined by Snell's law of refraction, is the point below which the total reflection of X-rays occur for all angles when passing from a medium with a higher refraction index, (i.e. the air) to one of a lower refraction index (i.e. a layer of organic semiconducting material). This critical angle depends on the material being probed, but as most organic semiconducting materials have a refractive index extremely close to 1, critical angles for these samples are both very close to zero (i.e. less than 0.20°) and largely similar due to the weak interactions of X-rays with matter.^[77] Practically speaking, typical GIWAXS experiments approximate this critical angle by performing a range of scans at a stepped series of incident angles between $0-0.20^\circ$, with it determined as the angle conferring the maximum scattered intensity.

Refraction of incident X-rays at the air/sample interface can generate X-ray standing wave (XSW, or 'waveguiding') effects by the interference between incident and scattered X-ray beams previously mentioned in Chapter 1, and these effects are highly dependent on the incident angle. These incident angles determine where in the sample film the X-ray electric field intensity (XEFI) of the XSW reaches its maximum, essentially creating a node of high-intensity X-rays at a specific depth (hence 'waveguiding').^[158] Angularly-dependant XEFI distributions from a specific sample can be modelled using the distorted wave Born approximation (DWBA) theory by inputting film thickness and X-ray absorptivity parameters, which can be fit to the experimentally-determined angularly-dependant XEFI profile and as such quantitatively inform on the crystalline structure of samples as a function of their vertical depth, however this modelling is technically challenging and has only been performed a few times in the literature.^[158-159] Far more common is the approximation of the XEFI distribution in organic samples during X-ray scattering measurements to perform qualitative depth profiling -of the sort utilized for the publication in this chapter- which nonetheless is still able to distinguish between surface-sensitive and bulk-sensitive measurements.^[160]

Below the critical angle, as mentioned, the incident beam undergoes total external reflection and does not penetrate the film, save for a short-range evanescent wave where the intensity is reduced by a factor of $1/e$ as a function of depth, thereby enhancing the surface sensitivity of the measurement.^[78, 160a, 161] XEFI simulations performed on films of polymeric organic semiconducting materials using a DWBA framework (Figure 3-6) suggest that measurements made at incident angles below the critical angle ($\theta_x < \theta_c$) are restricted to the top 5 nm of the sample, and as X-ray absorption constants are similar for most organic semiconductors at the hard X-ray energies utilized, it is likely that this depth holds true for the BTR-X analogues measured in this chapter. At the air/sample critical angle ($\theta_x = \theta_c$) the transmitted beam probes a much larger scattering

volume, accounting for the strong increase in scattering intensity, and through the waveguiding effects is essentially trapped between the air/sample and sample/substrate interfaces, thus producing scattering patterns from structures throughout the depth of the film.

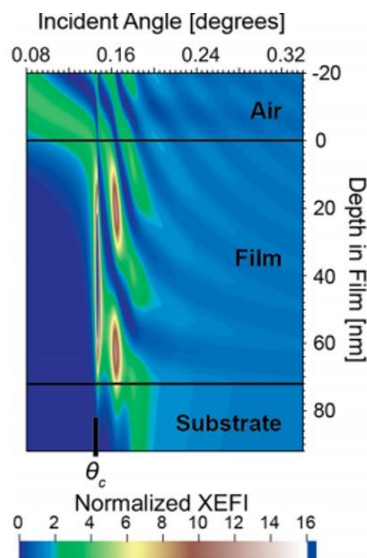


Figure 3-6: The measured XEFI throughout a thin film system consisting of 72 nm of an organic semiconductor on silicon substrate. Reprinted (adapted) with permission from E. Gann, M. Caironi, Y.-Y. Noh, Y.-H. Kim, C. R. McNeill, *Macromolecules* 2018, 51, 2979. Copyright (2018) American Chemical Society.

For incident angles above the critical angle ($\theta_x > \theta_c$), depending on the thickness of the film, it has been shown that scattering patterns are produced from structures deep within the film bulk with the measurements able to be deconvoluted from those taken at the film surface, albeit when the sample film thicknesses are on the order of several micrometers.^[162] For the 200-250 nm thick sample films probed in this chapter, the scattering patterns produced are primarily from the same crystalline structures probed at the critical angle itself. It should be noted that the refractive index of most organic semiconductors is smaller than that of the underlying substrate,^[76] with the critical angle for silicon correspondingly larger than that of the probed film. At the typical X-ray wavelengths (9-12 keV) utilized for GIWAXS measurements on organic materials, however, the disparity between the critical angle regions of material to substrate is extremely small, on the order of an additional 0.01-0.05°,^[163] and so care has to be taken not to extend the incident angle past the region of total external reflection of the substrate (i.e. 0.20-0.25°).

In this manner a general guideline can be established for performing depth-dependant measurements of films of nanometer to micrometer thicknesses, where it can be seen that for incident angles at 1) $\theta_x < \theta_c(\text{sample})$, an evanescent regime is in effect and X-ray measurements are localized to the top 5 nm of the surface, 2) $\theta_x = \theta_c(\text{sample})$ the scattering intensity is maximized and measurements made are of structures from the entire film, 3) $\theta_c(\text{sample}) < \theta_x < \theta_c(\text{substrate})$ the scattering intensity decreases with measurements still primarily of the entire film, and 4) $\theta_c(\text{substrate}) < \theta_x$ where a kinematic regime is in effect and scattering is primarily of the film substrate.

3.4 Contribution by the candidate

In the following paper the synthesis and physical characterization, determination of the spectroscopic and electrochemical properties, device fabrication/characterization, AFM and X-ray scattering studies of the BTR core-substituted materials are all described.

The candidate was responsible for the synthesis, purification, and full characterization of all molecules described in the following publication and the associated Supplementary Information except where stated in this paragraph. Professor Jonathan White was responsible for obtaining the single-crystal structures discussed in this chapter, and Dr. Jegadesan Subbiah was responsible for OPV device fabrication and characterization. Sample preparation, data collection/processing and interpretation of the GIWAXS measurements was performed by the candidate, with Dr. Valerie Mitchell, Dr. Xuechen Jiao and Prof. Chris McNeill providing feedback on the interpretations of this data. The candidate was responsible for the preparation, submission and revision of the manuscript.

3.5 Published manuscript

The following manuscript underwent a peer-review process after being submitted to Chemistry of Materials, an ACS publication. The manuscript ID was : cm-2018-04472e. A slightly altered version of this manuscript has since been accepted by the Journal of Materials Chemistry A on the 6th of January, 2019, and published on the 21st of February, 2019 (*J. Mater. Chem. A*, 2019,7, 6312-6326; DOI 10.1039/C9TA00168A).

Solubilizing core modifications on high-performing benzodithiophene-based molecular semiconductors and their influences on thin-film nanostructure and photovoltaic performance

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ABSTRACT: Sidechain engineering of the benzodithiophene-based high-performance organic solar cell (OSC) material **BTR** generated four novel p-type small-molecule semiconducting materials to investigate structure-property relationships in p-type organic semiconductors. Through depth-dependent grazing incidence wide-angle X-ray scattering (GIWAXS) studies, it is found that our best performing materials possess an active-layer morphology comprised of a vertically graded structure with different crystallite orientations. We further establish a correlation between a high solubility in the spin-coating deposition solution and the occurrence of this vertical distribution, whereas materials with lower solubility are found to possess a predominantly edge-on molecular orientation. These results further the understanding of this high-performing class of materials and suggests the importance of solubility considerations to OSC morphology.

INTRODUCTION

Small-molecular organic solar cells (SM-OSCs) are a photovoltaic technology that show great promise for renewable energy applications, and in the last half-decade have affirmed this promise by achieving power conversion efficiencies (PCEs) of >10% for single junction devices and >13% for ternary blends approaching those required for mass-production and commercialization.^[39b-d, 164] SM-OSCs represent an alternative to polymer-based OSCs, and though they tend to lag behind in terms of their PCEs, they are more favored for industrial processing due to their advantages in synthetic and device reproducibility, high degree of structural elucidation and their ability to form films with the degree of crystallinity and order needed for efficient charge transport.^[165]

The bulk heterojunction (BHJ) design dominates the OSC field and consists of an energy-harvesting active-layer comprised of an interpenetrating network of p-type and n-type semiconductors. An ideal BHJ morphology contains pure interpenetrating donor and acceptor domains, which are of sizes consistent with the exciton diffusion length. This morphology facilitates high rates of exciton splitting and minimizes recombination, while maintaining high charge mobility.^[166] As such, some of the most critical factors affecting OSC performance are the crystallinity, size and orientation of domains within the BHJ active layer.^[167]

One of the foremost factors dictating the morphology of the active layer is the molecular structure of the active-layer

materials.^[168] A vast number of organic semiconductors for OSC active-layer applications currently utilize donor-acceptor (D-A) architectures, which consist of covalently-bound electron-rich and electron-poor moieties.^[169] While altering the nature of these moieties can allow the facile tuning of molecular energy levels for optimized solar spectrum harvesting, it is equally important for efficient OSC performance to consider the impacts of these modifications on bulk properties – that is, active-layer nanostructure and film morphology.^[170] Optimal nanoscale-sized domains, generally predicted to be of 10-20 nm in size, are critically important for efficient OSC charge generation and transport. These p- and n-type domains are required to be small enough to allow charge separation within an excitonic lifetime, but large enough to minimize recombination between the separated charges.^[24, 171] Another consideration involves the device architecture of OSCs – this is typically a layered structure, with a light-harvesting layer sandwiched by charge-collecting electrodes.^[172] As such, molecular orientation of the p-type semiconductor with respect to the device substrate can strongly influence photovoltaic performance. Although the optimal ratio of orientations is of some contention in the literature, it is generally accepted that a face-on orientation (Figure 1), where the π -face of the molecular conjugated backbone is parallel to the plane of the substrate, is preferable to an edge-on orientation, where the π -face is perpendicular to the substrate. This is due to intermolecular charge delocalization occurring primarily through π - π interactions, and thus a face-on, vertically π -stacked active layer facilitates charge transport to the electrodes

more so than an edge-on orientation.^[48, 173] As such, factors affecting bulk morphology and molecular orientation must be understood and considered to maximize OSC performance.

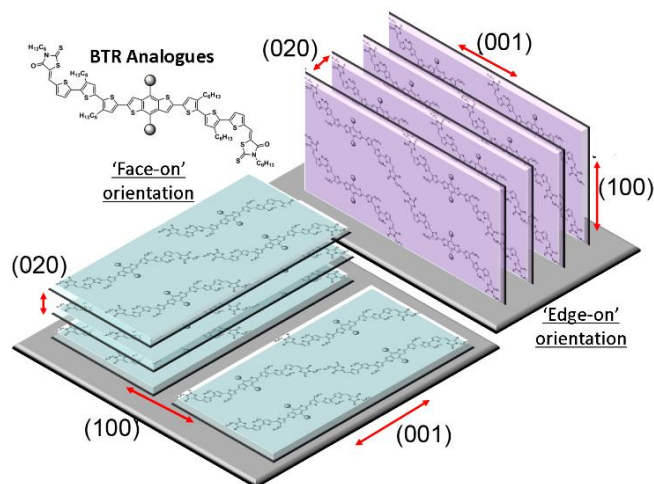


Figure 1. Molecular structure of BTR analogues and schematic illustrations showing common thin-film molecular orientations ('edge-on' and 'face-on') relative to a substrate, as well as Miller indices corresponding to alkyl lamellar spacing (100), π -stacking (020) and backbone spacing (001) for these orientations

Here we examine a series of p-type organic semiconductors based on the electron-rich benzo(1,2-b:4,5-b')dithiophene (BDT) core unit flanked by alkyl-substituted terthiophene π -bridges and end-capped with an electron-poor rhodanine unit, shortened henceforth to '**BTR**'. First utilized in 2008 for OSC active layers, the BDT core unit has since become a structural motif in many high-performing p-type materials due to its nature as a highly planar, electron-dense conjugated unit, capable of relatively high hole transport, and synthetic versatility. Unsurprisingly, five of the six SM-OSCs currently reported with PCEs above 10% contain a benzodithiophene unit.^[109-110, 174] We have recently published several reports on multiple molecular p-type materials utilizing the **BTR** architecture, some of which have produced outstanding PCEs close to 10% with increased thermal stability.^[39a, 119] We partly attribute these high PCEs to optimal morphologies attained by side-chain engineering which allows fast charge transport and a high fill factor (FF). Considering both the demonstrated photovoltaic performance of materials containing the BDT core and the potential for even higher power conversion efficiencies, it is vital to gain a thorough understanding of the structure-property relationship. Our previous studies have focused on altering sidechain length and orientation, as well as conjugation length along the thiophene backbone. We now turn our attention to a study on the impact of BDT core substituents with differing sidechains on active layer morphology, with a specific focus on intermolecular π - π stacking orientation.

To carry out this study we introduced several two-dimensional extensions -referred to from this point onwards as 'headgroups'- of the BDT core perpendicular to the conjugated backbone in order to investigate the impact of differing steric bulk and solubility properties. We carefully selected four headgroup moieties for their intrinsic structural properties,

widespread use in the literature and synthetic versatility. We then appended them to the **BTR** molecular architecture (Figure 2), resulting in four novel p-type molecular semiconductors termed **BTR-TIPS** (triisopropylsilylthynyl), **BTR-TE** (2-ethylhexylthio), **BTR-H** (2-hexylthienyl) and **BTR-EH** (2-(2-ethylhexyl)thienyl).^[110, 165c, 175] We have also included a high-performing (>9% PCE) material, **BTR** from our previous research, in this study as an additional point of data.

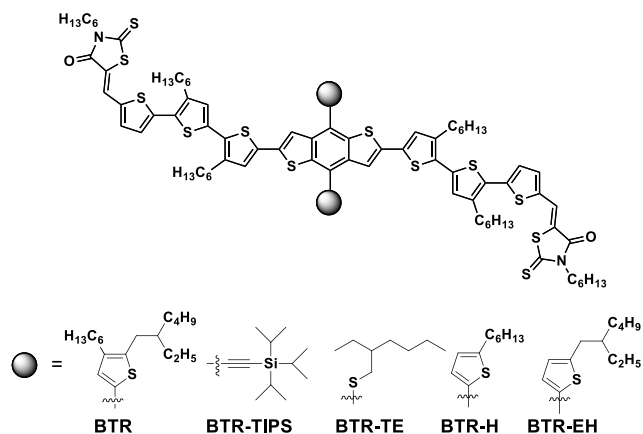


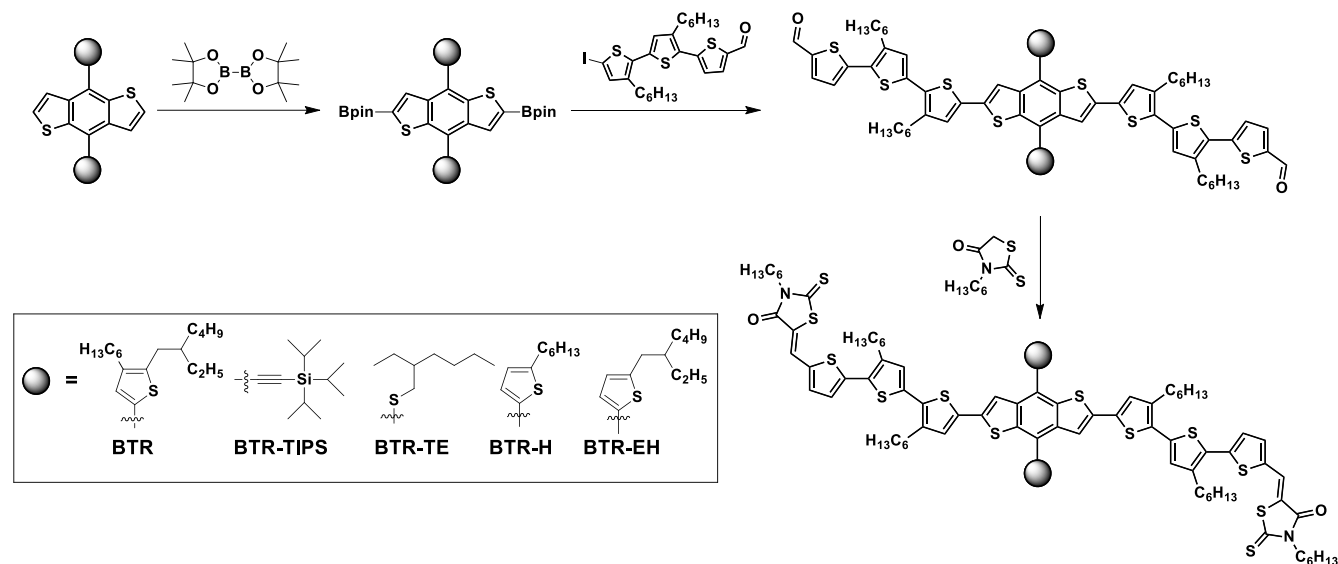
Figure 2. Structures of the previously studied BTR and our four novel BTR-analogue p-type molecular semiconductors.

To be able to elucidate the impact of these different headgroup substitutions on crystalline structure and orientation of BTR-analogue thin films, two-dimensional (2D) grazing-incidence wide-angle X-ray scattering (GIWAXS) was utilized to qualitatively and quantitatively analyze these structures on a nanometer-sized scale. Semiconductor thin-films tend towards paracrystallinity rather than possessing good long-range order and as such GIWAXS measurements typically produce scattering reflections corresponding to d -spacings for specific molecular or intermolecular distances of the reflecting planes, as well as the orientations of these planes with respect to the film substrate.^[81] These d -spacings are usually given in terms of specific Miller indices (see Figure 1) corresponding to different types of molecular packing, i.e. distances between alkyl lamella (100 spacings) or between molecules along the long axis of the conjugated backbone (001 spacings). This information can reveal the π - π stacking orientations vital to OSC performance. Furthermore, depth profiling may be performed simply by altering the angle of incidence of the incoming beam – at shallower incident angles, the depth of penetration of the beam is reduced and scattering is typically limited to the first 5 nm of the film surface.^[78, 160a, 161] We utilize this capability to probe both the film surface as well as its internal structures to obtain a greater understanding of our molecules' orientations as a function of depth.

In this work, we synthesize four novel p-type materials based on the high-performing **BTR** architecture. The solubilities of our materials in chloroform were measured and found to vary significantly as a function of their headgroups. By pairing them with the n-type semiconductor material PC₇₁BM in OSC devices, we show that **BTR-TE** displays outstanding performance as a p-type semiconductor material for OSC applications with a PCE of >9% after solvent vapor annealing (SVA). The morphology and crystallinity of the blends were studied through grazing-incidence wide-angle X-ray scattering

(GIWAXS) studies, from which we observe several distinct pi-stacking orientations across our BTR analogues that we are able to correlate with their OPV performances. Using GIWAXS-enabled depth-profiling we also examine crystallite orientations throughout the vertical distribution of these thin films. When this is considered alongside the solubility of our materials, we hypothesize that the development of crystallite orientation in the films during the spin-coating deposition process could potentially be a result of the intrinsic solubilizing properties of the different headgroup substituents, which can then be further correlated to OSC performance. This then suggests that material solubility is a crucial element for the rational design of enhanced photovoltaic materials.

Results and Discussion



Scheme 1. Generalized reaction pathway to the five BTR-analogues studied in this paper. This pathway begins from headgroup-functionalized BDT cores which are already reported in the literature, and shows the convergent points between the growing BDT core and other key reagents/intermediates utilized.

Thermogravimetric analysis (TGA) was performed to establish the thermal stability of these compounds, all of which display excellent stabilities with 5% weight loss observed at temperature ranges of 366–400 °C (Figure S5.1). Following this, differential scanning calorimetry (DSC) was utilized to probe major phase changes of the materials. (Figure S6.1). **BTR-H** possesses the highest melting point (T_m) of 255 °C and followed by **BTR-TIPS** at 251 °C. As melting points are affected by the force of attraction between molecules, the low T_m of the 2-(2-ethylhexylthienyl) functionalized **BTR-EH** of 227 °C relative to the 2-hexylthienyl functionalized counterpart **BTR-H** is indicative of the strong disruptive influence of the branched alkyl chain. In this same vein it is clear that the thioester functionality also serves to significantly disrupt intermolecular packing contributing to the relatively low T_m of **BTR-TE** recorded at 216 °C. The melting point of **BTR** at 186 °C is consistent with that reported in our previous results. With the exception of **BTR-TIPS**, the solubility of our materials in chloroform – a solvent commonly used in solution-processing for OSC device- follow an inverse trend to that displayed by their melting points, with solubility increasing in the order of **BTR-H** (24 mg/mL) < **BTR-EH** (33 mg/mL) < **BTR-TIPS** (41 mg/mL) < **BTR-TE** (56 mg/mL) < **BTR** (211

Materials synthesis and characterization. The synthesis of our analogues follow a similar procedure to that established in our earlier works (Scheme 1, for full details refer to the Supporting Information).^[39a] We first assemble the benzodithiophene cores with our headgroup moieties, the syntheses of which have been reported in the literature. The BDT core was borylated utilizing our previously published direct iridium-catalyzed C–H activation, followed by a Suzuki coupling to add the alkylated terthiophene aldehyde. The final step is a Knoevenagel condensation between the aldehyde-functionalized BDT molecule and *n*-hexyl rhodanine to yield our target molecules. The synthesis of the terthiophene and rhodanine intermediates are covered in our previous work.^[39a]

mg/mL). These solubilities are derived from concentration and absorption data (Figure S7.1a–d) with the exception of **BTR**, which is taken from the literature.³²

UV-Vis studies and electronic energy levels. UV-vis absorption spectra of our p-type materials were measured in dilute chloroform solution and as thin films cast from chloroform (Figure 3) with the complete data presented in Table 1. No significant differences were observed between the absorption structure of the five compounds in solution, with a uniform broad absorption between 400–600 nm and peak maxima of 510–520 nm. The impact of the structural differences on absorbance between the molecules, however, were readily apparent upon calculation of their molecular absorption coefficients, ϵ . While the three analogues possessing a thienyl headgroup (**BTR**, **BTR-H** and **BTR-EH**) all possessed similar absorption coefficients of 8 to $9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, there is an approximately twofold decrease for **BTR-TE**, with an ϵ_{max} of $4.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The higher absorption coefficient observed for the thienyl-containing analogues we attribute to the presence of extended 2-D conjugation of the structures. Reported single-crystal structures have revealed a $\sim 50^\circ$ dihedral angle between the planes of the conjugated BDT backbone and the thienyl

headgroup, the higher absorption coefficients clearly indicate there is still sufficient interaction to afford electron delocalization.^[175b]

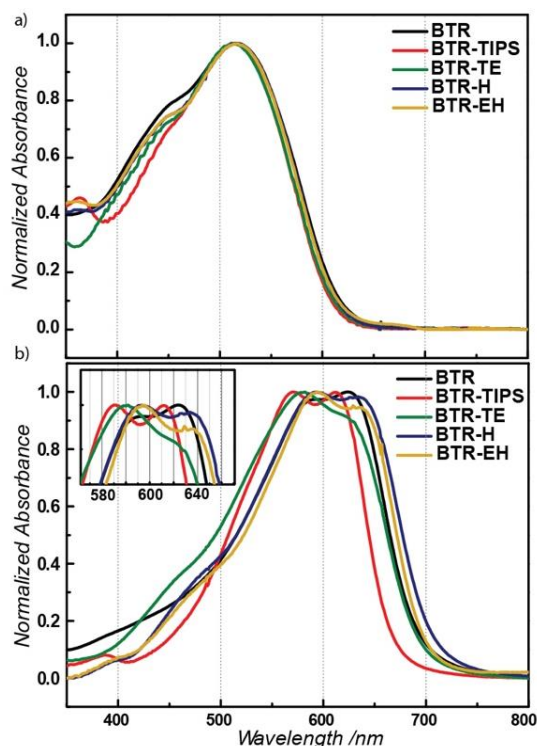


Figure 3. UV-vis absorption spectra of BTR series in a) solution (CHCl₃) and b) as-cast films. Inset: close-up of peak area.

BTR-TIPS possesses a high ϵ_{max} of $1.9 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ that we attribute to the rigid nature and enhanced π -orbital overlap of its triisopropylsilyl headgroups. There is a noticeable change in absorbance upon shifting from solution to as-cast films, with all molecules manifesting redshifts of $\sim 70 \text{ nm}$ along with distinct vibronic shoulders between 630–640 nm. We attribute this new absorption band to an enhanced electronic transition stemming from the increased π - π stacking in the thin-film. Not all our analogues experience these increased interactions to the same degree; **BTR-TE** in particular possesses a relatively diminished shoulder absorption peak, perhaps either due to the relative lack

of two-dimensional conjugation, or that π - π stacking is no longer completely constrained to be along the molecular axis. A lower absorption onset of **BTR-TIPS** (670 nm against ~ 700 –710 nm) relative to the other analogues can be observed. We attribute this to the increased torsional angle between the BDT core and the oligothiophene π -bridges of **BTR-TIPS** of around 20° – as determined by its single-crystal structure (see below) – presumably from the greater steric bulk of the triisopropylsilyl headgroup, resulting in the disruption of conjugation along the backbone.

Steady-state photoluminescence spectra of both neat and SVA-treated blend films (with annealing conditions identical to those for our best-performing devices, see below) were obtained to observe the efficiency of fluorescence quenching with the introduction of the PC₇₁BM n-type semiconductor (Figure S8.1). Relatively similar fluorescence quenching efficiencies are observed from films of all analogues of 83–90%, with these values consistent with the results from Schwarz et al. of a previous study on **BTR**.^[176] As concluded in that work, this suggests efficient exciton quenching at the interface between all our analogues and PC₇₁BM, and may further indicate that a large portion of the domains in the thin-films possess diameters within the exciton diffusion lengths of the BTR analogues.

Cyclic voltammetry (CV) studies (Figure S7.1) were also conducted to further establish the electronic properties of our BTR analogues. This data is summarized in Table 1. From the oxidation/reduction onset potentials ($E_{\text{ox}}^{\text{ons}}$ and $E_{\text{red}}^{\text{ons}}$) we can estimate highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) respectively. Here we reference the oxidation potentials of our compounds against ferrocene, which we determined to be 0.41 V vs Ag/AgCl. These electrochemical studies show that our BTR-analogues all possess roughly equivalent, deep HOMO levels of around -5.3 to -5.4 eV , which are beneficial for the high open-circuit voltages (V_{OC}) needed for OSC devices. From this and the CV-derived LUMO levels we can calculate the HOMO-LUMO energy gap (E_{g}) of our materials. These follow the same trends as established by the calculated optical energy gap from our UV-vis absorption studies. **BTR-TIPS** exhibits a large E_{g} of 2.29 eV, which is detrimental to efficient harvesting of the solar spectrum, and is potentially one of the causes of its low photovoltaic efficiency (discussed further below). All other analogues possess an energy gap of around 2 eV.

Table 1. Absorption and electronic energy levels of BTR-analogues

	Solution λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{ cm}^{-1}$)	Film λ_{max} (nm)	Film λ_{ons} (nm)	Film $E_{\text{g}}^{\text{opt}}$ (eV)	Film E_{HOMO} (eV)	Film E_{LUMO} (eV)	Film E_{g}^{CV} (eV)
BTR	520	9.9×10^4	592	702	1.80	-5.43	-3.46	1.97
BTR-TIPS	515	1.9×10^5	570	673	1.84	-5.42	-3.13	2.29
BTR-TE	512	4.1×10^4	582	695	1.78	-5.39	-3.33	2.06
BTR-H	518	9.4×10^4	593	703	1.76	-5.32	-3.29	2.03
BTR-EH	517	8.4×10^4	594	713	1.73	-5.32	-3.34	1.98

Photovoltaic properties and performance. OSC devices utilizing our BTR-analogues were fabricated using a conventional device architecture (ITO/PEDOT:PSS/BTR-X:PC₇₁BM-(1:1)/Ca/Al) to investigate their photovoltaic properties and efficiencies (Figure 4). The average performances of 10 devices is summarized in Table 2. The high work function PEDOT:PSS interlayer and the low work function Ca interlayer are present as hole- and electron-transport layers, respectively. Devices were spin-coated from chloroform and analyzed both as-cast and after solvent vapor annealing (SVA). The device performance attained using optimized SVA conditions for our materials are given in Table 2. J-V curves under AM 1.5 irradiation are reported in Figure 4. The active layers of all devices were produced without the use of any additives, and as such this presents a potential route to further improvement. As-cast devices exhibited uniformly poor PCEs of <5%, save for BTR-TE which exhibited a surprisingly high PCE of 5.5%. Upon solvent-vapor annealing, improvements were seen in the short-circuit currents (J_{SC}) and

FFs for all analogues, and of the four novel materials **BTR-TE** is seen to possess the best performance, with an excellent PCE of 9.0% due to a high J_{SC} of 14.0 mA cm⁻² and a FF of 70%. The high J_{SC} observed from the thioester-functionalized material is particularly surprising given its lower absorption in the red portion of the solar spectrum, which we attribute to reduced 2D conjugation. The lower performance of **BTR-TIPS** devices is a result of the extremely low J_{SC} of 8.4 mA cm⁻² which can partially be attributed to the large HOMO-LUMO energy gap, resulting in reduced solar spectrum harvesting and photocurrent loss.^[177] THF was found to be the optimal solvent during the vapor annealing process for all materials save for **BTR-TIPS**, which instead yielded non-significant changes to the SVA-treated device performance as compared to the as-cast films. We hypothesized this to be due to limited solubilization and reorganization of the blend by THF, whereas the more solubilizing CHCl₃ -investigated in our previous work- was found to significantly improve performances.

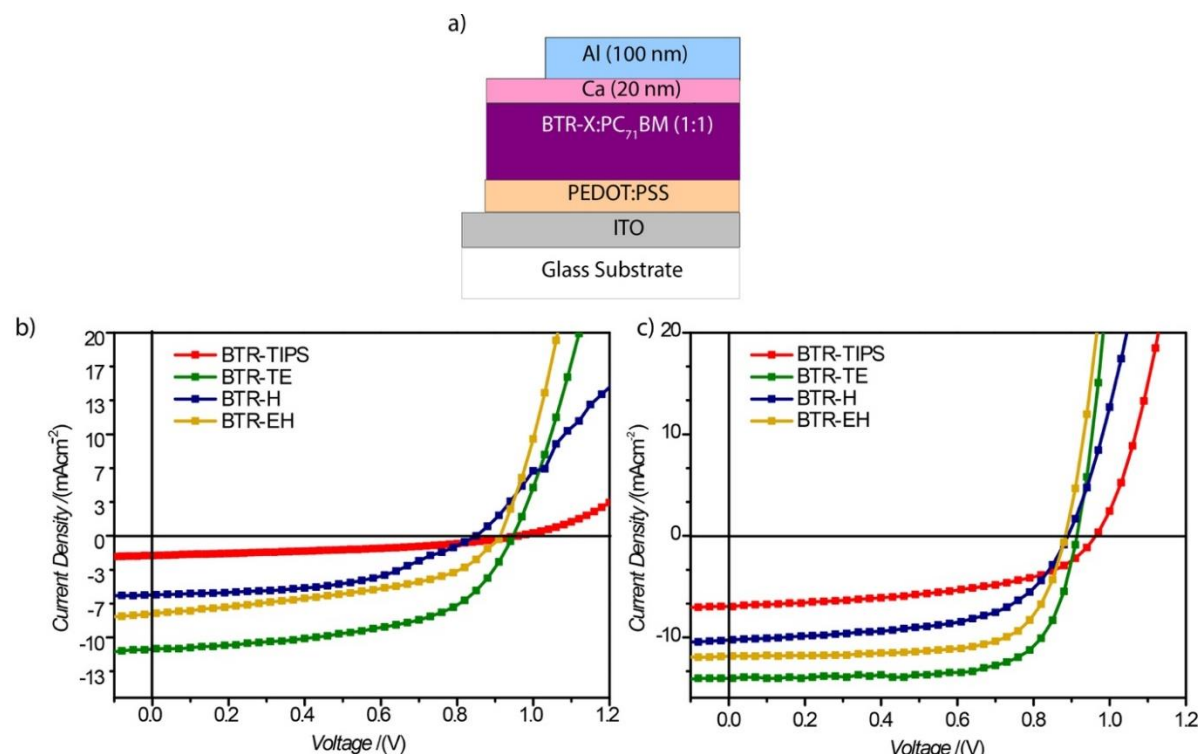


Figure 4. a) Schematic of OSC device architecture, and current-voltage characteristics of BTR-X:PC₇₁BM BHJ solar cell devices b) as-cast and c) after solvent-vapor annealing

Table 2. Photovoltaic performances of BTR:PC₇₁BM BHJ solar cells fabricated under different annealing conditions

Active Layer (1:1 Donor: PC ₇₁ BM)	Annealing Conditions	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
BTR	As-Cast	0.98	10.8	43	4.6*
BTR	SVA – THF (20 sec)	0.92	13.9	72	9.3*
BTR-TIPS	As-Cast	0.94 ± 0.02	1.9 ± 0.25	34 ± 4	0.6 ± 0.15
BTR-TIPS	SVA – CHCl ₃ (20 sec)	0.94 ± 0.02	8.4 ± 0.20	62 ± 2	5.0 ± 0.20
BTR-TE	As-Cast	0.92 ± 0.02	10.7 ± 0.25	54 ± 3	5.5 ± 0.30
BTR-TE	SVA – THF (20 sec)	0.90 ± 0.02	14.0 ± 0.15	70 ± 2	9.0 ± 0.15

BTR-H	As-Cast	0.87 ± 0.02	5.6 ± 0.20	45 ± 3	2.2 ± 0.30
BTR-H	SVA – THF (20 sec)	0.87 ± 0.02	10.1 ± 0.20	58 ± 2	5.1 ± 0.20
BTR-EH	As-Cast	0.90 ± 0.02	7.4 ± 0.30	44 ± 3	3.1 ± 0.15
BTR-EH	SVA – THF (20 sec)	0.89 ± 0.02	11.8 ± 0.20	67 ± 2	7.2 ± 0.20

*Obtained from our previous work^[39a]

The two alkylthienyl-functionalized materials (**BTR-H** and **BTR-EH**) both possess sub-optimal J_{SC} and FFs which, upon GIWAXS analysis of our materials, we hypothesize to be due to poor thin-film morphologies hindering charge transport and collection. This will be discussed in more depth below. **BTR**, from our previous work, still retains the best PCE overall out of all the five compounds studied in this paper, with 9.3%. To investigate one of the causes of this difference in performance, in-depth morphological analysis was undertaken.

Surface topography

We first examine the surface morphology of the films of our analogues through Atomic Force Microscopy (AFM, Figure S10.1). The as-cast film of **BTR-TIPS** shows large aggregates generally over 200 nm in diameter, which visibly crystallize upon SVA but still retain their relatively large widths. **BTR-TE**, **BTR-H** and **BTR-EH** all exhibit much smaller domains with diameters on the order of tens of nanometers, and with a much higher degree of interpenetration.

Molecular nanoscale structure and bulk morphology. 2D-GIWAXS studies were performed to better understand OSC performances of our analogues as a function of their molecular structure. We prepared spin-coated thin films of each analogue under three sets of processing conditions i) neat, ii) in a 1:1 blend with PC₇₁BM, iii) in a 1:1 blend of PC₇₁BM with SVA, using identical conditions to those that gave us the best PCE. A thermally-annealed BTR film is also analyzed, as from our previous studies we have shown that **BTR**:PC₇₁BM blends are not stable under thermal annealing conditions, with a significant PCE loss observed. GIWAXS scattering patterns of **BTR** (Figure 5), **BTR-TIPS** (Figure 6), **BTR-TE** (Figure 7), **BTR-H** (Figure 8) and **BTR-EH** (Figure 9) can be seen along with line cuts of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes. Scattering peaks along the horizontal and vertical axes are indicative of reflections parallel (in-plane) and perpendicular (out-of-plane) to the film substrate, respectively.

Approximate sizes of the crystallites that give rise to coherent scattering are calculated from the full-width-half-maximum (FWHM) of the scattering peaks corresponding to the out-of-plane (100) lamellar reflections using the Scherrer equation (Equation 1) which relates peak width, a shape factor K (for which we have used a value of 1) and the crystallite coherence length (CCL):^[178]

$$CCL = \frac{2\pi K}{FWHM} \quad (1)$$

The orientation distribution of the reflecting planes in the thin-film can be quantified utilizing the Hermans' orientation parameter S .^[82] Here we determine S , from either the (100) or (020) reflections, by considering the intensity of the peak as a function of the polar angle χ .^[81] Using this analysis, for the (100) reflection a value of 1, 0 or -0.5 indicates the reflecting plane is completely parallel, randomly-oriented or completely perpendicular to the substrate, respectively,^[83] while for the

(020) reflection values of 1, 0 or -0.5 indicate a perpendicular, random or parallel orientation. A full summary of our GIWAXS data for films measured at the critical angle containing the calculated Hermans' orientation parameter, CCL and d -spacings for the (100) alkyl lamellar, and (020) π - π stacking distances is given in Table 3.

In our previous work we had reported GIWAXS scattering patterns for as-cast neat **BTR** thin-films.^[119] Here we expand this to include scattering patterns for films that are more representative of those used in OSC devices (Figure 5 b-d). The neat film exhibits a scattering pattern with good long-range order as indicated by the peaks we have assigned to the first, second and third ($h00$) lamellar reflections at $q = 0.33 \text{ \AA}^{-1}$, $0.66 \text{ \AA}^{-1}$ and $1.00 \text{ \AA}^{-1}$ respectively. A peak assigned to the (020) π -stacking reflection can be seen at $q = 1.65 \text{ \AA}^{-1}$ in the vertical axis. For molecular architectures that host alkyl sidechains oriented away from the conjugated backbone, it is expected that the direction of lamellar stacking be normal to that of π -stacking. As such the presence of a vertically-aligned (020) peak alongside the stronger ($h00$) lamellar reflections in the same axis suggests a 'rolling log' molecular orientation, where the **BTR** molecules resemble a 2D 'powder' locked in-plane along the long axis of the conjugated backbone. This shifts the apparent orientations of the lamellar and π -stacking scattering so that they appear to be primarily out-of-plane, whereas these 'rolling log' orientations typically adopt a statistically-random isotropic distribution.^[145b, 179] For a further analysis of these orientations in neat **BTR** films, refer to our earlier work.^[119] Upon addition of the fullerene acceptor, a broad, isotropic reflection at $q = 1.31 \text{ \AA}^{-1}$ is observed corresponding to amorphous PC₇₁BM.^[137b, 175b] The degree of long-range order and crystallinity in the thin-film is reduced, with a broadening of the FWHM for the lamellar reflections and increasing isotropy of the π -stacking reflection (Figure 5b and 5e) indicative of the increasing disorder of the film. CCLs calculated for the as-cast blend films of 18.7 nm are significantly reduced compared to that of the as-cast neat films (29.5 nm). Upon SVA treatment, some of this crystallinity and order is restored, with the appearance of multiple scattering reflections in both axes around $q = 0.6\text{-}0.8 \text{ \AA}^{-1}$ and a decreased FWHM of the (020) peak in the vertical axis. Peak narrowing observed for the (100) peak (Figure 5g) results in increased CCLs of 22.9 nm. This increased crystallinity is not unexpected - the SVA-enabled migration of active-layer components into more-ordered domains is well-documented for **BTR**.^[138] SVA-treated films appear to retain the broader (020) reflection induced by the addition of the fullerene, with a higher degree of molecular isotropy relative to the as-cast neat film. The crystallinity of the blend film is increased again after it is subject to thermal annealing, with multiple off-axis scattering peaks around $q = 0.7\text{-}1.2 \text{ \AA}^{-1}$ observed that are not present in the SVA-treated films (Figure 5h). FWHMs for both the (100) and the (020) reflection intensity peaks are reduced, and a relatively large CCL of 29.7 nm is calculated, surpassing those of the neat **BTR** films. D -spacings for lamellar reflections are

calculated to be 1.88 nm for the neat film, which is reduced to 1.84-1.85 nm for all films after the fullerene acceptor is added with this small change potentially due to a minor aggregation effect within the BTR domains induced by phase separation. The π -stacking distances of 0.38 nm are constant between all films and are typical of that for organic semiconductor

materials. Hermans' orientation parameters of ~ 0.10 - 0.02 are calculated for all **BTR** films and agree with the previous assessment of an isotropically-oriented film. We also see over-crystallised films after thermal annealing that have been shown to lead to poor OSC performance.^[138]

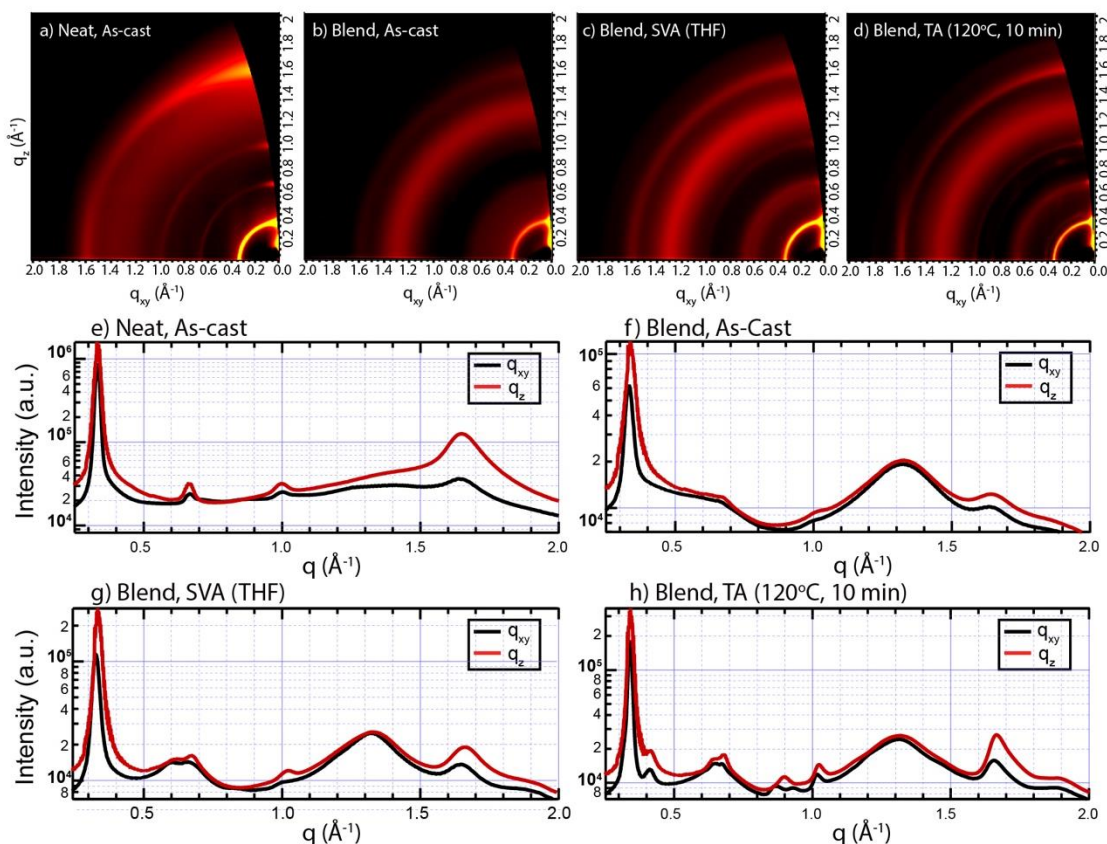


Figure 5. BTR GIWAXS diffractions patterns for films that are: a) neat, as-cast; b) in a 1:1 fullerene blend, as-cast; c) in a 1:1 fullerene blend, solvent-vapor annealed with THF for 20 seconds; d) in a 1:1 fullerene blend, thermally annealed at 120°C for 10 minutes; and their respective sector profiles along the Q_{xy} and Q_z axes (e-h)

As-cast neat films of **BTR-TIPS** exhibit a molecular orientation that is weakly face-on (Figures 6 a, d) with a calculated S of -0.19 . Second and third order lamellar reflections can be distinguished, with calculated (100) d -spacings of 1.69 nm. A CCL of 22.7 nm is obtained. In the as-cast blend film, much like **BTR**, these CCLs are significantly reduced to 12.6 nm. The slight face-on preference of the neat film appears to have been lost as per the stronger (100) peak intensity along the vertical axis, while the (020) peak intensities along the two axes indicates a large population of isotropically oriented crystallites. After SVA treatment a significant change in film morphology can be observed in the scattering pattern with the development of multiple off-axis reflections (Figures 6c, e) and analysis of the (020) reflection again suggests that the SVA-treated film, like **BTR**, also exhibits a ‘rolling log’ orientation. Most notably however is the apparent shifting of the out-of-plane lamellar packing from $q = 0.36 \text{ \AA}^{-1}$ (in the as-cast blend) to at $q = 0.48 \text{ \AA}^{-1}$, with a corresponding decrease of the d -spacing from 1.72 nm to 1.31 nm. The in-plane lamellar peak however remains at a similar position to that in the as-cast blend at $q = 0.37 \text{ \AA}^{-1}$, with this suggesting the formation of two

lamellar polymorphs, each with relatively anisotropic (100) reflections. Here we denote the polymorph characterized by a higher population (as determined by peak intensity) and an out-of-plane packing with a d -spacing of 1.31 nm as polymorph 1, and the polymorph with a lower population and in-plane packing with a d -spacing of 1.68 nm as polymorph 2. Polymorph 1 is calculated to have a relatively large CCL of 23.9 nm, suggesting that SVA treatment has resulted in the partial reorganization of the film into larger crystallites that show tight packing between lamellar planes. The theoretical (100) reflection (calculated from the simulated powder diffraction pattern from the unit cell of the single-crystal structure, Figure 6g, Figure S12.1) corresponds well to the experimental (100) reflection obtained from polymorph 2 in the SVA annealed film. This suggests that the packing structure adopted by polymorph 1, induced by the annealing process, is a deviation away from the packing structure of the single-crystal. Additionally, as seen from the single-crystal structure unlike **BTR** - as shown from our previous publication- the BDT cores of **BTR-TIPS** are highly offset in the π -stacking axis, with each core sandwiched between terminal thiophenes of the

oligothiophene bridge, and do not stack into the centrosymmetric π -dimers that **BTR** exhibits.^[119] This could

theoretically contribute to the lower J_{SC} observed but would need charge mobility measurements to quantify.

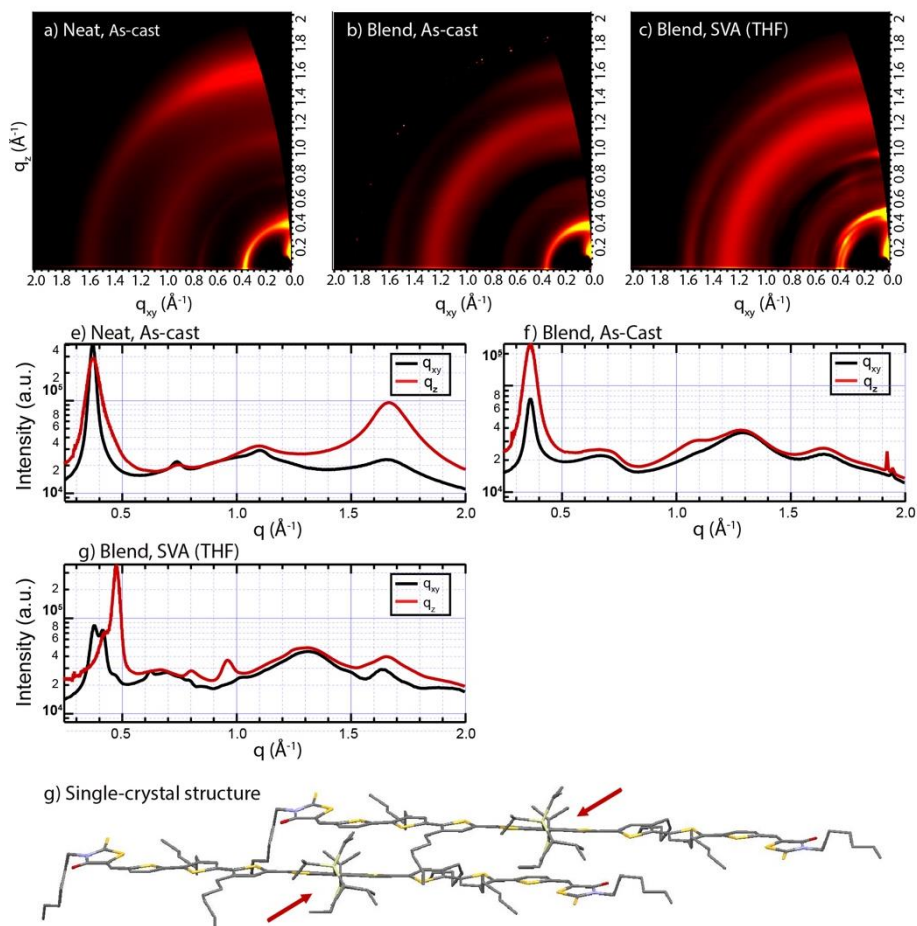


Figure 6. **BTR-TIPS** film GIWAXS scattering patterns that are: a) neat, as-cast; b) in a 1:1 fullerene blend, as-cast; c) in a 1:1 fullerene blend, solvent-vapor annealed with CHCl_3 for 20 seconds; and their respective sector profiles along the Q_{xy} and Q_z axes (d-f), as well as g) the solid-state geometry of BTR-TIPS as determined by its single-crystal structure. The two π -stacked molecules are viewed perpendicular to the long axis of the backbone. The benzodithiophene cores are marked out.

BTR-TE behaves morphologically in a similar manner to **BTR**, with the neat as-cast film exhibiting narrowly-distributed lamellar reflections in the vertical axis and a broad, halo-like distribution of the (020) π -stacking reflection. The as-cast blend film possesses decreased long-range order, molecular orientation and overall crystallinity. PC_{71}BM addition to the donor material again serves to reduce crystallite size, with a

decrease from 27.3 nm to 12.2 nm. D -spacing also remains largely unaffected, with a lamellar spacing of ~ 1.70 nm calculated for all **BTR-TE** films regardless of processing conditions. SVA treatment increases the overall crystallinity of the donor material, with an increased CCL of 19.3 nm, although it also confers a higher degree of isotropy to the (020) π -stacking reflection that the as-cast film lacks.

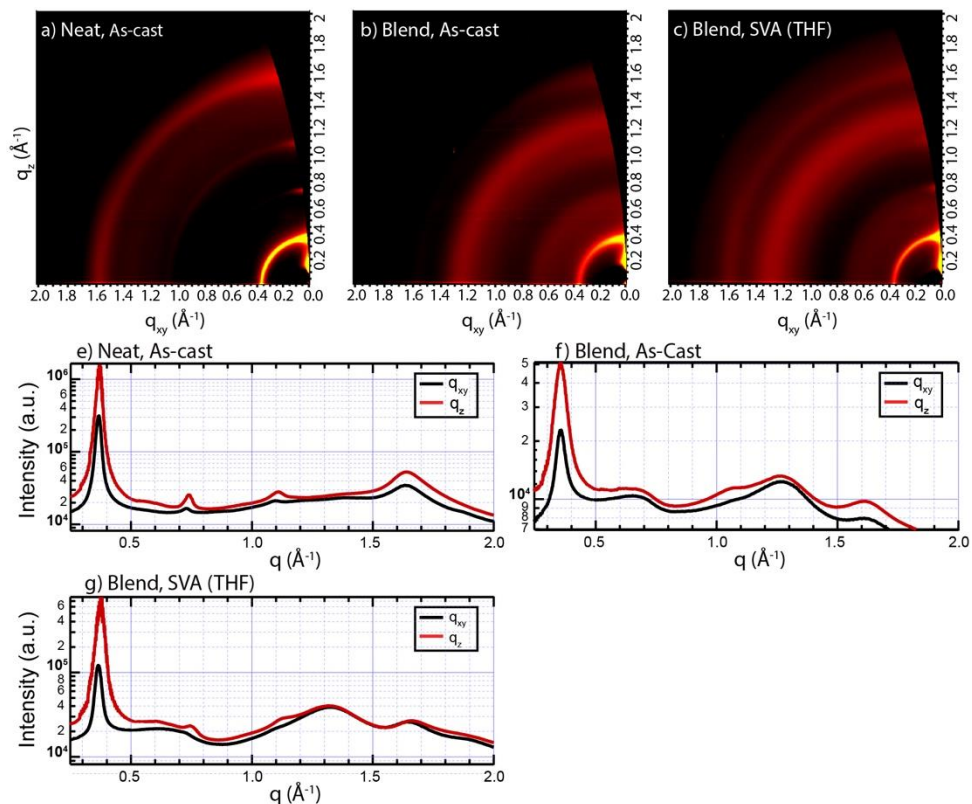


Figure 7. BTR-TE film GIWAXS scattering patterns that are: a) neat, as-cast; b) in a 1:1 fullerene blend, as-cast; c) in a 1:1 fullerene blend, solvent-vapor annealed with CHCl_3 for 20 seconds; and their respective sector profiles along the Q_{xy} and Q_z axes (d-f)

Unlike the other BTR-analogues, **BTR-H** and **BTR-EH** share an unambiguous edge-on molecular orientation, which is clearly visible in the neat films (Figures 8a and 9a) and persists throughout the addition of PC_{71}BM and SVA. Scattering patterns for both analogues exhibit long-range lamellar reflections in the vertical axes that appear to be typical for our BTR-type molecules, from which we can calculate d -spacings that decrease in length to ~ 1.85 nm in SVA-treated films from the neat, as-cast films. Curiously enough, unlike our other analogues crystalline order is maintained in our blend, as-cast

films, as evidenced by the clearly-visible, narrowly-distributed (200) and (300) reflections in Figures 8b and 9b. (020) reflections are almost exclusively observed in the horizontal Q_{xy} axis at $q = 1.68 \text{ \AA}^{-1}$ for all films. Relatively high Hermans' orientation parameters of ~ 0.2 - 0.25 as calculated from the (100) reflections support this edge-on conjecture. CCLs calculated for both analogues follow the familiar trend of decreasing upon the addition of PC_{71}BM , and increasing upon SVA treatment to 20.5 and 22.1 nm for **BTR-H** and **BTR-EH**, respectively.

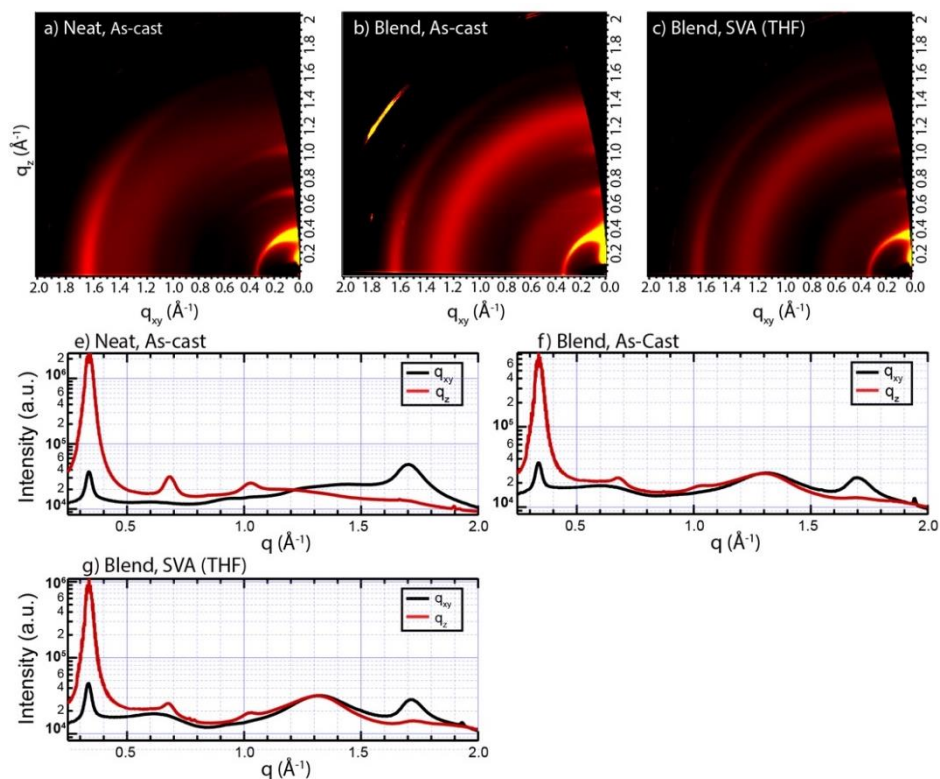


Figure 8. BTR-H film GIWAXS scattering patterns that are: a) neat, as-cast; b) in a 1:1 fullerene blend, as-cast; c) in a 1:1 fullerene blend, solvent-vapor annealed with CHCl_3 for 20 seconds; and their respective sector profiles along the Q_{xy} and Q_z axes (d-f)

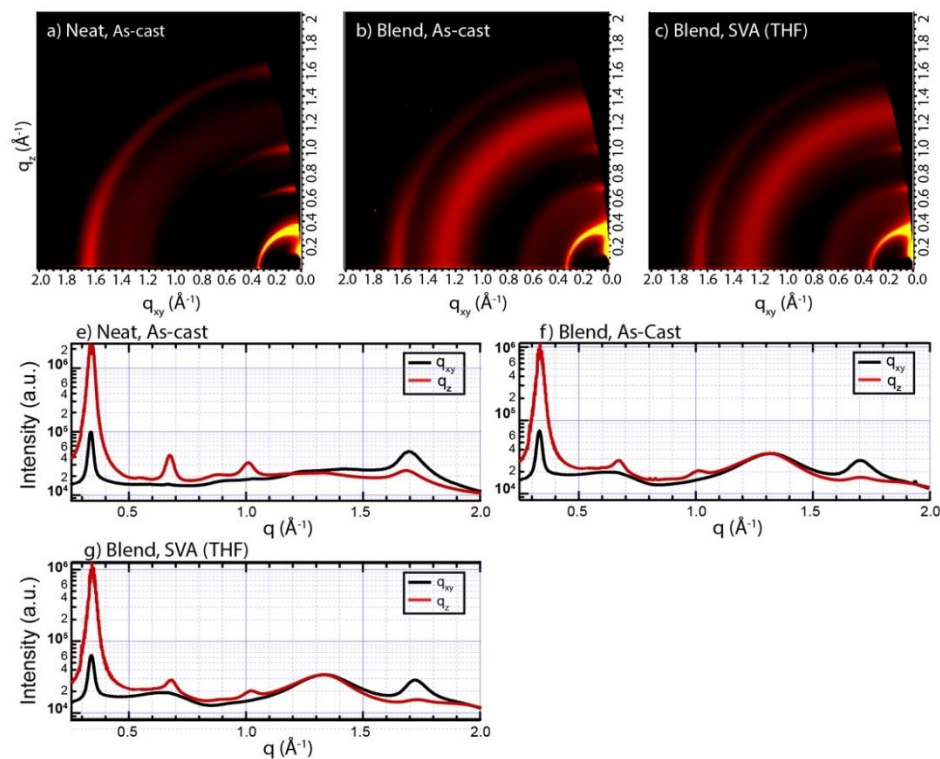


Figure 9. BTR-EH film GIWAXS scattering patterns that are: a) neat, as-cast; b) in a 1:1 fullerene blend, as-cast; c) in a 1:1 fullerene blend, solvent-vapor annealed with CHCl_3 for 20 seconds; and their respective sector profiles along the Q_{xy} and Q_z axes (d-f)

To summarize our findings, at the critical incident angle **BTR**, **BTR-TIPS** and **BTR-TE** all feature isotropic, ‘rolling log’ molecular orientations to some degree, whereas **BTR-H** and **BTR-EH** exhibit predominantly edge-on orientations with (100) and (020) reflections located primarily on the vertical and horizontal axes, respectively. Uniquely, upon SVA the **BTR-TIPS** analogue exhibits multiple off-axis reflections and polymorphism along with a large CCL of 23.9 nm, which we attribute to a relatively higher degree of crystalline structure. For all other analogues, as expected, solvent-vapor annealing results in increased crystallite correlation lengths and decreased lamellar *d*-spacing to varying degrees, due to the reorganization of kinetically-trapped structures from the spin-coating process into larger and more well-ordered domains.^[180]

Using this data we are able to observe a correlation between device morphology and performance. We find that our two high-performing materials with PCEs >9% (**BTR** and **BTR-TE**) both display isotropic, ‘rolling log’ orientations of their

conjugated backbones with respect to the substrate, while our two materials displaying edge-on orientations possess relatively worse performances. Several high-performance semiconductor materials also report similar ‘rolling log’ orientational distributions in thin films, and there is evidence to suggest that such orientations allow an extended three-dimensional network for enhanced charge transport.^[181] While **BTR-TIPS** is also seen to possess an isotropic orientation it also possesses highly offset π -stacked BDT cores and it is likely that other processes are affecting its performance. It is generally accepted that face-on orientation is beneficial for charge conduction in a vertically-stacked OSC device and so the fact that edge-on orientations are generally detrimental to OSC performance is not a novel one. However, we seek to shed some light on the source of the orientations of **BTR** and **BTR-TE**, as opposed to their edge-on counterparts **BTR-H** and **BTR-EH** and relate this to the molecular structure. For this, we turn to depth-profiling of the GIWAXS films.

Table 3. Summary of data calculated from GIWAXS scattering patterns of BTR analogues

Sample	Processing Conditions	S	CCL (100) (nm)	d (100) (nm)	d (020) (nm)
BTR	Neat, As-Cast	-0.13	29.5	1.88	0.38
BTR	Blend, As-Cast	-0.02	18.7	1.85	0.38
BTR	Blend, SVA (THF)	0.01	22.9	1.84	0.38
BTR	Blend, TA	-0.05	29.7	1.85	0.38
BTR-TIPS	Neat, As-Cast	-0.19	22.7	1.69	0.38
BTR-TIPS	Blend, As-Cast	0.02	12.6	1.72	0.38
BTR-TIPS	Blend, SVA (CHCl ₃)	0.64	23.9	1.31	0.38
BTR-TE	Neat, As-Cast	0.00	27.3	1.71	0.38
BTR-TE	Blend, As-Cast	-0.02	12.2	1.75	0.38
BTR-TE	Blend, SVA (THF)	0.05	19.3	1.68	0.38
BTR-H	Neat, As-Cast	0.47	19.3	1.84	0.37
BTR-H	Blend, As-Cast	0.25	18.4	1.84	0.37
BTR-H	Blend, SVA (THF)	0.24	20.5	1.85	0.37
BTR-EH	Neat, As-Cast	0.31	21.7	1.87	0.37
BTR-EH	Blend, As-Cast	0.16	21.6	1.86	0.37
BTR-EH	Blend, SVA (THF)	0.19	22.1	1.85	0.36

As previously mentioned, in GIWAXS measurements the choice of incident angle θ determines the region of the film that is analyzed. When the incident angle is smaller than the *critical angle* θ_c for total external reflection of the thin-film, the incident X-rays only penetrates into the sample as evanescent waves. These evanescent waves are surface-localized and penetrate up to ~5 nm (representing less than 2.5% of the 200 nm vertical thickness of our active-layer thin-films), and so are ideal for probing surface-layer structures.^[159, 182] At the critical angle, the penetration depths of the X-rays increase dramatically with a standing wave achieved, thus achieving the maximum scattering intensity. Angles above the critical angle similarly

probe the bulk of the film, with variations in scattering intensity due to wave-guiding effects.^[159, 183] Angle-dependent depth studies to differentiate between surface and bulk features have a strong precedence in the literature.^[159-160, 184] Our previously analyzed films (Figures 5-9) were recorded at θ_c , and so we look to incident angles above and below this to perform a qualitative analysis of the surface-to-bulk transition. We measured scattering patterns of our SVA-treated films for all analogues at incident angles at intervals of $0.01^\circ = \text{from } 0.02^\circ \text{ to } +0.01^\circ$ around the critical angle. Both out-of-plane (q_z) and in-plane (q_{xy}) line profiles as a function of these incident angles are shown in Figure 10. Here we show the line profile of **BTR**; the

line profiles for the other analogues can be found in the SI (Figure S11.1a-h). We can see that for scattering patterns of **BTR** taken at angles below the critical angle there is a roughly twofold greater peak intensity corresponding to the (020) π -stacking reflection pattern in the in-plane Q_{xy} axis (Figure 10b) relative to the Q_z axis (Figure 10a), whereas at and above the critical angle, the relative intensities for this peak are greater in the out-of-plane than the in-plane axis. The opposite phenomenon is observed for the first-order lamellar (100) reflection peak, i.e. that at $<\theta_c$ peak intensities from the in-plane axis are *weaker* than those in the out-of-plane axis.

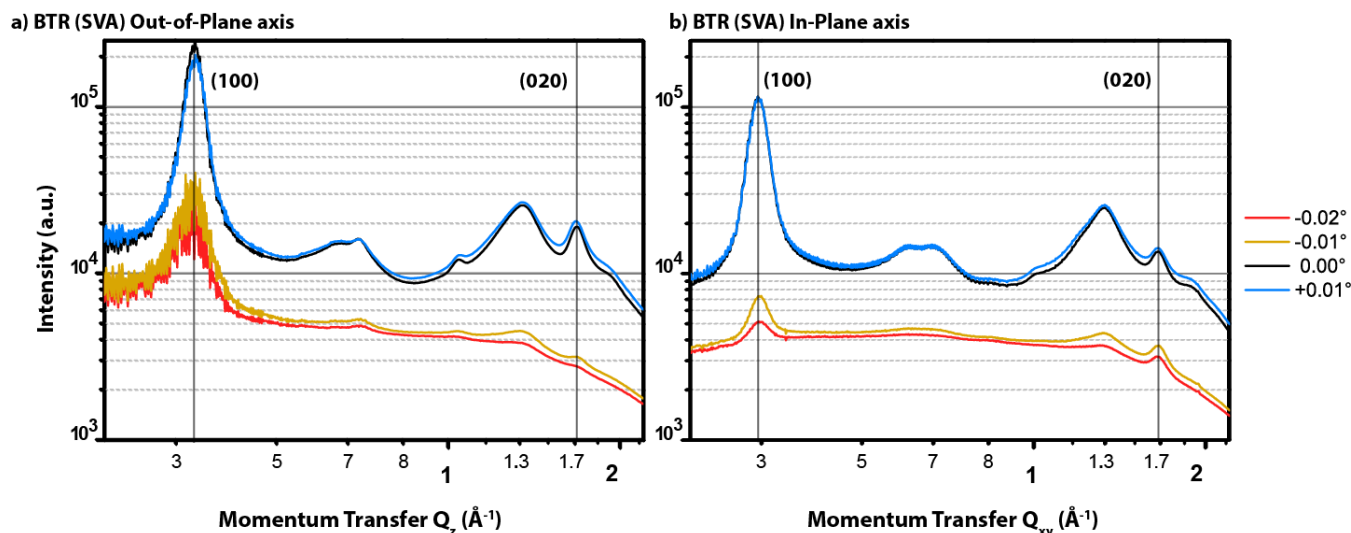


Figure 10. GIWAXS one-dimensional line profiles at incident angles relative to the critical angle (denoted as 0.0°) are shown in the out-of-plane (a) and in-plane directions (b) for **BTR**. Vertical lines are drawn to direct the eye to reflection peaks of interest, which are labelled with their unit cell indices.

To further investigate these depth-dependent findings we first plot peak intensity as a function of the polar angle χ for both the (100) and the (020) reflections for incident angles around the critical angle to determine their respective Hermans' orientation parameters (Figure S11.2), with this data found in Table 4. The potential discrepancies introduced by the 'rolling log' orientation are partially accounted for via the sinusoidal correction factor for peak intensity in the calculation of S .^[160a] We see that this highlights several of our key findings regarding our analogues' depth-dependence. The S (020) values measured from ($\theta_x < 0$) scattering patterns, representing surface-sensitive measurements, are all close to -0.5 indicating a more edge-on orientation for all our analogues, save for **BTR-TIPS**. At and above the critical angle (at $\theta_x \geq 0$) **BTR** and **BTR-TE** all exhibit much higher S (020) values of -0.12 to -0.15, indicating more isotropically orientations, while for **BTR-H** and **BTR-EH** S (020) values remain constant to those calculated below the critical angle, indicating a similar level of edge-on dominant orientations. These changes in orientation are qualitatively apparent from scattering patterns of **BTR** and **BTR-TE** taken at $\theta_x = -0.01, 0$ and 0.01° (Figures S11.4, 11.5) where a clear edge-on orientation can be observed from the sub-critical angle scattering patterns. Curiously the orientation parameters calculated from the (100) reflections of **BTR** and **BTR-TE** at incident angles $<\theta_c$ return values close to 0 indicating isotropic

We interpret these results to indicate that at a ~ 5 nm thick layer at the surface of the film (i.e. the air/BHJ blend interface) a greater portion of BTR crystallites are edge-on, while at depths probed at and beyond the critical angle of incidence, they are increasingly isotropic. A similar phenomenon can also be observed for the **BTR-TE** analogue at $\theta_x = -0.01$ to -0.03° . The **BTR-TIPS**, **BTR-H** and **BTR-EH** analogues do not display this behavior, where relative intensities for both the (100) and (020) reflections remain constant across the vertical and horizontal axes for incident angles below and above the critical angle, indicating that they maintain a constant orientation throughout the vertical depth of the thin film.

orientations, which disagree with the highly edge-on crystallites suggested by the S (020) values. While we are uncertain as to the cause of this, it is possible that these crystallites exhibit a lower degree of lamellar anisotropy at the film surface relative to π -stacking orientation and due to this uncertainty we utilize this reflection for our orientational analysis. This behavior is also apparent upon plotting the integrated intensity of the (100) and (020) reflections of our analogues along the q_{xy} and q_z axes against the incident angle (Figure S11.5) – while the relative intensities of the 100 reflections are constant across both axes, for **BTR** and **BTR-TE** there is an obvious increase in the $q_z:q_{xy}$ intensity ratio for the (020) reflection at the critical angle indicative of a transition from edge- to face-on. Ultimately, these findings are perhaps best illustrated by plotting the Hermans' orientation parameter of the (020) reflection against the incident angle (Figure 11), where the edge-on to face-on transition at the critical angle for **BTR** and **BTR-TE** is clear. From the available data we therefore propose that while most of our analogues are primarily edge-on oriented at the air/BHJ surface interface, **BTR**, **BTR-TE** and **BTR-TIPS** then transition towards orientations with an increased degree of isotropic, 'rolling log' arrangements in the bulk of the active-layer thin-film, while **BTR-H** and **BTR-EH** remain edge-on dominant throughout.

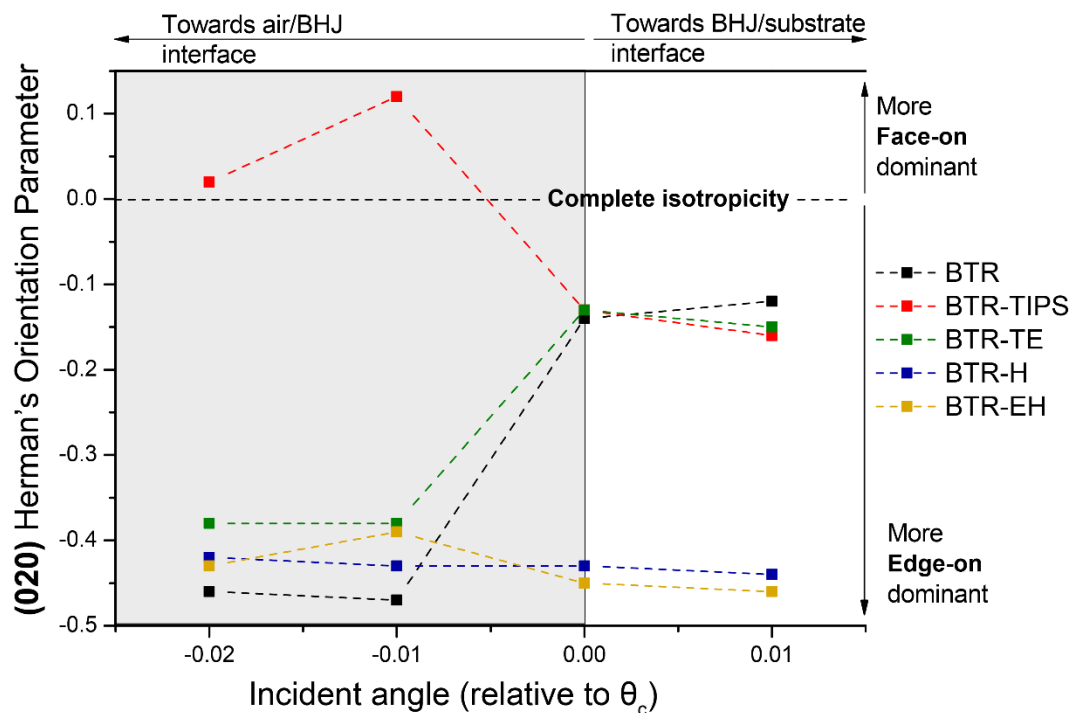


Figure 11. Measure of BTR analogue π -stacking orientation as a function of depth. Dashed lines between points are added to aid visualization.

Table 4. Summary of data calculated from GIWAXS scattering patterns of BTR analogues

Angle around θ_c	Hermans' orientation parameter S									
	BTR		BTR-TIPS		BTR-TE		BTR-H		BTR-EH	
	(100)	(020)	(100)	(020)	(100)	(020)	(100)	(020)	(100)	(020)
-0.02°	0.03	-0.46	0.24	0.02	0.08	-0.38	0.23	-0.42	0.19	-0.43
-0.01°	0.03	-0.47	0.47	0.12	0.07	-0.38	0.24	-0.43	0.20	-0.39
Critical Angle	0.01	-0.14	0.64	-0.13	0.05	-0.13	0.24	-0.43	0.19	-0.45
0.01°	0.00	-0.12	0.72	-0.16	0.05	-0.15	0.24	-0.44	0.18	-0.46

This edge-on dominance at the air interface is predicted in the literature, where it has been shown that for most spin-cast films of OSC semiconductors with BTR-type molecular architectures, crystallite nucleation tends to initiate from the air/BHJ interface as a primary site for solvent evaporation. Surface-energy effects at the air/BHJ interfaces dictate that edge-on crystallites are preferentially formed, due to the lower free energy of the alkyl sidechains relative to the conjugated backbone π -faces.^[184b, 185] The question then remaining to us is that of why there is a transition in the bulk away from edge-on crystallite orientations for some materials. While a definitive resolution to this is outside the scope of this work we propose a hypothesis by first considering the relative solubilities of our analogues in chloroform -the solvent from which they were deposited (**BTR-H** < **BTR-EH** < **BTR-TIPS** < **BTR-TE** < **BTR**,

in order of increasing solubility) and the effect that this has on the kinetics of films formation. **BTR** and **BTR-TE** possess higher solubilities than their counterpart analogues, and therefore would tend to form nucleates at later stages of the spin coating process. This delayed nucleation and reduced solution volume could then potentially allow crystallite formation to initiate not just at the air/film interface, but also in the film bulk, and therefore be exposed to orientational influences from other interfacial regions. This could then explain the spectrum of crystallite orientations seen for our more soluble and high-performing materials, due to co-existing top-down and bottom-up crystallization processes (Figure 12). The crystallite orientation for our less soluble and therefore faster-crystallizing analogues on the other hand would be predominantly influenced by the air/blend interface.

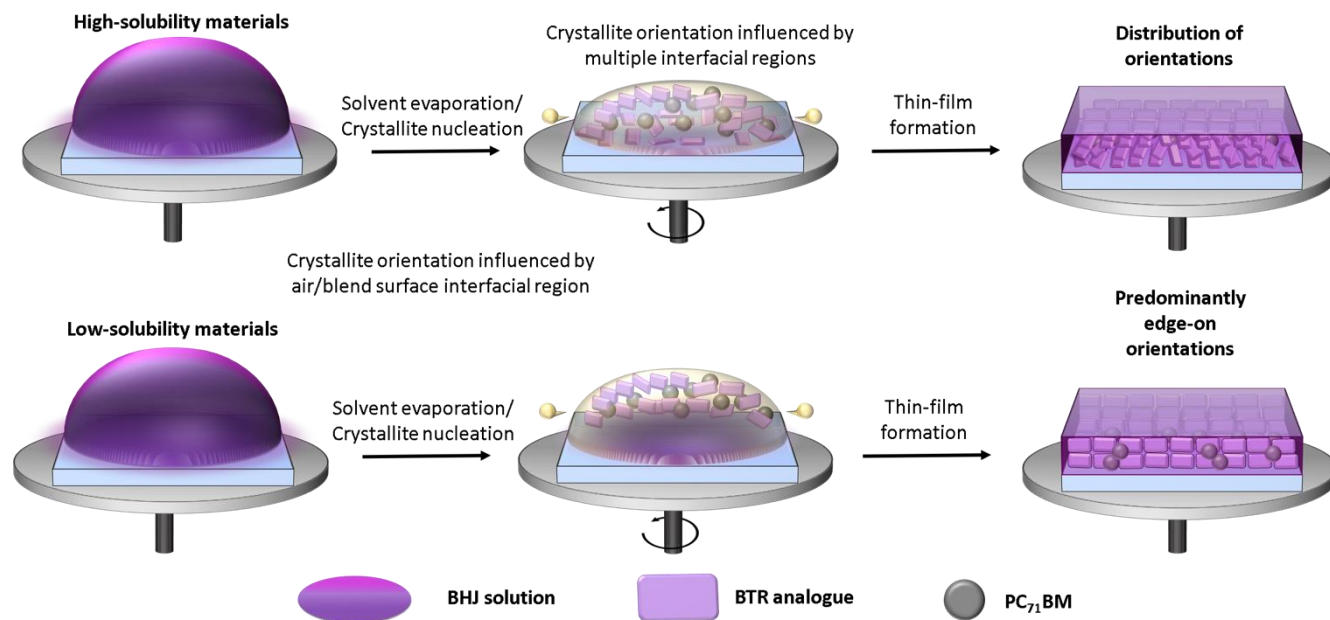


Figure 12. Formation of crystallite orientation during the spin-coating process as a function of solubility. Higher-solubility materials will nucleate at decreased solvent volumes than lower-solubility materials, and therefore crystallite orientations will be exposed to influences from both the air/blend and blend/substrate interfacial regions, resulting in a top-down transition from edge-on to isotropic crystallites.

CONCLUSION

We investigated the effect of 2D core-substituent structure on molecular solubility, thin-film morphology and performance. To do so we synthesized four novel BDT-based p-type OSC semiconductors, with the thioester-functionalized analogue **BTR-TE** possessing excellent PCEs of ~9%. Upon GIWAXS analysis of the thin-films we find a correlation between our highest-performing BDT-based materials with those that feature an isotropic distribution of crystallites with respect to the substrate, which have been shown to facilitate enhanced charge conduction through an extended π -network. GIWAXS depth-profiling revealed that these high-performing materials contained primarily edge-on oriented crystallites at the air/BHJ interface, which transitions towards an increasing isotropic orientation deeper into the film bulk. We hypothesize that this morphology could be due to the slower crystallization kinetics during the spin-coating process derived from the greater solubilizing properties of the dialkylthienyl and thioester core substituents of **BTR** and **BTR-TE**. While further work needs to be carried out to verify this, nonetheless we believe these results to be a valuable structure-property analysis contributing to the understanding of sidechain engineering and its potential impact on bulk morphology and OSC performances.

ASSOCIATED CONTENT

Supporting Information. Full experimental details - materials and methods, synthesis and physical/thermal/electrochemical characterization of compounds, device fabrication, GIWAXS film preparation and depth profiles, AFM images, crystallographic information and supporting references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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All authors have given approval to the final version of the manuscript.

Notes

This research was undertaken on the SAXS/WAXS and MX1 beamlines at the Australian Synchrotron, part of ANSTO, and via the Collaborative Access Program (proposal number 13618b).^[141, 144]

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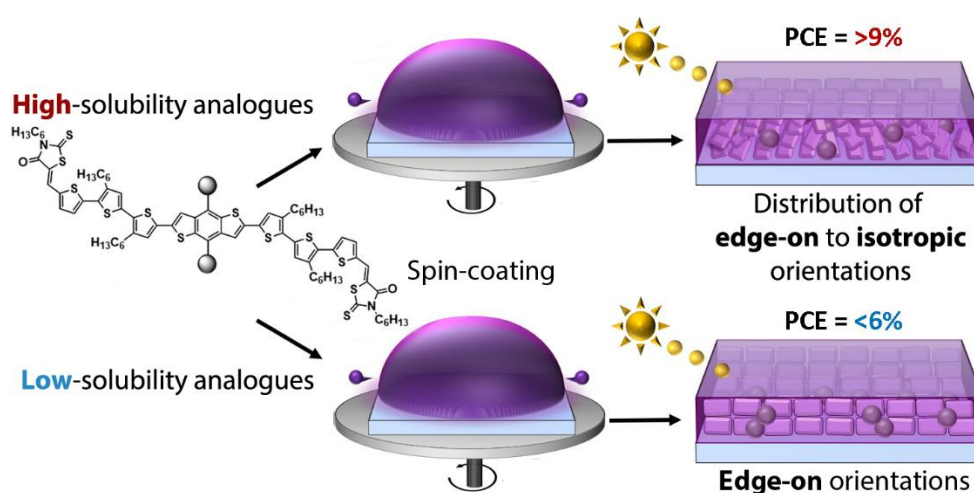
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Table of contents graphical abstract



3.6 Chapter conclusion

Here four novel p-type small molecular semiconductors based on the high-performance **BTR** molecule were designed and synthesized with core substituents of varying steric bulk. Of these, the **BTR-TE** analogue produced a notable PCE of >9%. Though one of the primary goals underlying the study -analysing the degree of π -stacking offset- was not able to be achieved due to the lack of single-crystal structures, GIWAXS analysis revealed different π -stacking behaviours from each of the four molecules, which could be correlated with OPV performance. Further analysis using depth-dependant studies revealed the underlying cause behind this relationship, establishing a link between high material solubility, material crystallization and an optimal π -stacking orientation as a function of the vertical depth of the film. This work serves as a reminder that small structural changes can have far-reaching impact upon bulk properties, and reinforces the critical role that sidechain-conferred solubility can play towards achieving optimal film morphologies.

3.7 Published supplementary information

Solubilizing core modifications on high-performing benzodithiophene-based molecular semiconductors and their influences on thin-film nanostructure and photovoltaic performance

Calvin J. Lee, Valerie D. Mitchell, Jonathan White, Xuechen Jiao, Christopher R. McNeill, Jegadesan Subbiah and David J. Jones *

S1 Materials and Methods

Unless noted, all materials were reagent grade and used as received without further purification. Anhydrous solvents were prepared by drying HPLC grade solvents using freshly activated molecular sieves. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick).

IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-Vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. ^1H NMR and ^{13}C NMR spectra were carried out on a 400 MHz or 600 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet). MALDI-TOF mass spectrometry was performed on a Bruker microflex instrument, using chloroform as solvent and DCTB or terthiophene as the assisted matrix.

Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE-440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC at a ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mV/s. CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/Ag^+ pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in CH_3CN . The solutions were deoxygenated by sparging with argon prior to

each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the polymer was drop-casted on the electrode from chlorobenzene solution to form a film. Ferrocene/ferrocenium redox couple was used as the internal standard.

CCDC 1864646 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S1.1 Device fabrication and characterization:

Organic photovoltaic devices were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. The conventional devices were fabricated with a device geometry of ITO/PEDOT:PSS/BTR-X:PC₇₁BM-(1:1)/Ca/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone and isopropyl alcohol for 15 minutes each and subsequently treated in UV–Ozone for 15 minutes. A thin layer of PEDOT:PSS was spin-coated onto the ITO surface. After being baked at 150 °C for 10 minutes, the substrates were transferred into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated from blend chloroform solutions (32 mg/mL) with weight ratio of BTR analogue and PC₇₁BM at 1:1 and the active layer thicknesses of all films were measured as 210–260 nm. Then, the substrates were placed in a glass Petri dish containing 1 mL THF or CHCl₃ for solvent vapour annealing (SVA), as specified in the main body of the text. After SVA treatment, the films were transferred to a metal evaporation chamber and a bilayer cathode consisted of Ca (30 nm) capped with Al (100 nm) was deposited through a shadow mask (active area was 0.1 cm²) at approximately 1 × 10⁻⁶ Torr.

S1.2 Thin-film fabrication and characterization:

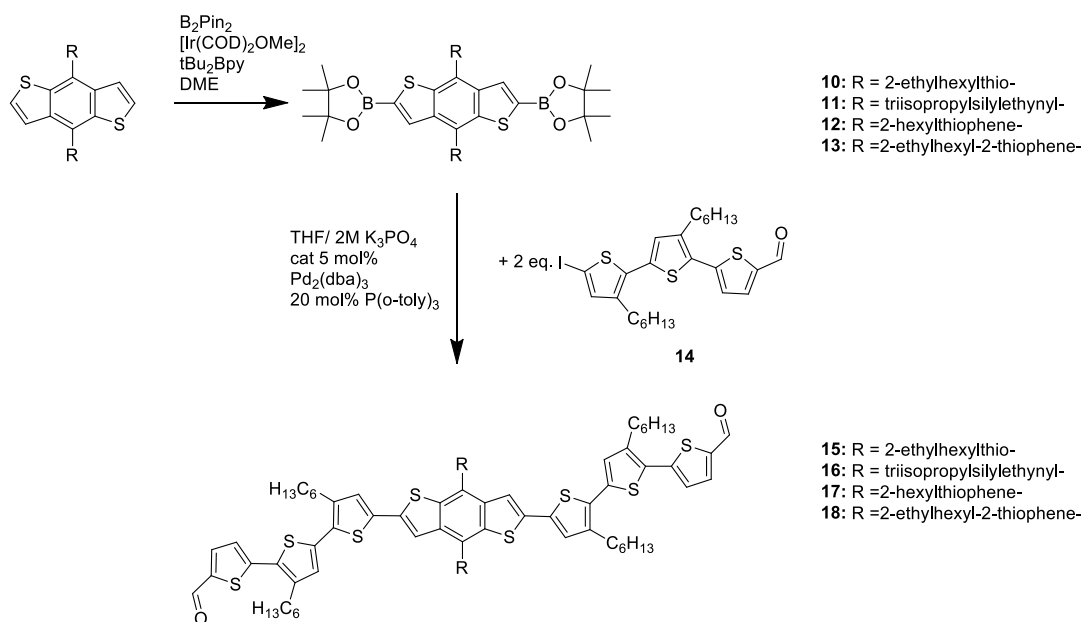
Samples were prepared for GIWAXS by spin-coating solutions of BTR analogue blends onto PEDOT:PSS coated Si substrates using the same deposition condition and annealing conditions as for the photovoltaic devices. The Si wafers had been sonicated in acetone and isopropanol for 30 minutes each followed by 15 minutes of UV/Ozone treatment. GIWAXS experiments were performed at the Australian Synchrotron on the SAXS/WAXS beamline under ambient conditions. A Pilatus 200K detector was used for 2D diffraction pattern collection. The energy of the incident beam was 11 keV at a range of incident angles from $\theta = 0.02 - 0.20^\circ$.

The sample-to-detector range was 28 cm. Data from GIWAXS experiments was gathered from the SAXS/WAXS beamline of the Australian Synchrotron and analysed using a customized version of NIKA 2D based in IgorPro.^[144] Single-crystal data was gathered from the MX1 beamline at the Australian Synchrotron^[141, 152] Atomic force microscopy images were acquired using an Asylum Research Cypher scanning probe microscope operated in tapping mode.

S2 Synthesis

The synthesis of the thioester-functionalized BDT core (compounds **1-6**),^[186] the triisopropylsilylethynyl-functionalized BDT core (compound **7**)^[187], the 2-hexylthienyl functionalized BDT core (compound **8**)^[188] and the 2-(2'-ethylhexyl)thienyl functionalized BDT core (compound **9**)^[189] have all previously been reported in the literature. Synthesis of the terthiophene π -bridge (compound **14**) and the n-hexyl rhodanine acceptor (compound **19**) has been reported in our earlier work.^[39a]

2.1 General synthesis of BTR-Dialdehyde cores

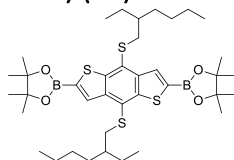


General procedure for the diborylated BDT cores

To a Schlenk flask was added the corresponding BDT core (1 g), B_2Pin_2 (1.5 eq.), bis-*tert*-butylbipyridine (0.06 eq.) and $[Ir(COD)OMe]_2$ (0.02 eq.) and the flask heated under vacuum for 1 hour at 60°C. Dry, degassed DME (2 mL) was added and the temperature raised to 85 °C. The reaction was stirred for 2 hours under N_2 after

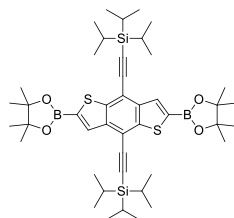
which the reaction vessel was cooled to RT. The crude mixture was precipitated in IPA and the product collected via filtration, and after drying under vacuum, yielded analytically pure material.

2.1.1 2,2'-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10)



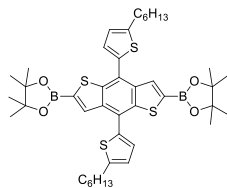
Product formed light brown crystals. Yield = 1.3 g (1.78 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.28 (s, 2H), 3.00 (d, J = 4.9 Hz, 4H), 1.55 (s, CH_3 , 12H), 1.47-1.15 (m, 18H), 0.82 (m, 12H). ^{13}C NMR (125 MHz), CDCl_3) δ 148.00, 142.03, 134.25, 124.59, 84.56, 40.28, 39.99, 32.10, 28.77, 25.48, 24.81, 22.90, 14.06, 10.75. IR (Neat): ν = 2958, 2923, 2856, 2298, 2160, 1536, 1321, 1134, 848, 662 cm^{-1} . MS(MALDI $^+$) m/z calculated for $\text{C}_{38}\text{H}_{60}\text{B}_2\text{O}_4\text{S}_4[\text{M}^+]$: 730.36, found: 730.47. Elemental analysis calculated for $\text{C}_{38}\text{H}_{60}\text{B}_2\text{O}_4\text{S}_4$: C, 62.46; H, 8.28; B, 2.96; O, 8.76; S, 17.55. Found; C, 62.39; H, 8.47; N: 0.00

2.1.2 ((2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (11)



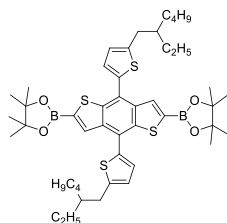
Product formed bright yellow crystals. Yield = 1.03 g, (1.29 mmol, 71%). ^1H NMR (600 MHz, CDCl_3) δ 8.11 (s, 2H), 1.39 (s, 24H), 1.23 (s, 36H). ^{13}C NMR (125 MHz), CDCl_3) δ 144.26, 140.16, 133.50, 112.66, 102.46, 102.12, 84.57, 24.80, 18.82, 11.34, 11.30. IR (Neat): ν = 2940, 2889, 2863, 2229, 2065, 1460, 880, 662 cm^{-1} . MS(MALDI $^+$) m/z calculated for $\text{C}_{44}\text{H}_{68}\text{B}_2\text{O}_4\text{S}_2\text{Si}_2[\text{M}^+]$: 802.43, found: 802.56. Elemental analysis calculated for $\text{C}_{44}\text{H}_{68}\text{B}_2\text{O}_4\text{S}_2\text{Si}_2$: C:65.82; H, 8.54; B, 2.69; O, 7.97; S, 7.99; Si, 7.00. Found; C:65.69; H, 8.26; N: 0.00

2.1.3 2,2'-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**12**)



Product formed bright yellow crystals. Yield = 1.14 g, (1.47 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 2H), 7.26 (d, J = 3.0 Hz, 2H), 6.87 (d, J = 3.4 Hz, 2H), 2.90 (t, J = 7.7 Hz, 4H), 1.84 – 1.69 (m, 4H), 1.46 (s, 4H), 1.35 (s, 24H), 0.94 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz), CDCl_3) δ 147.20, 142.60, 138.31, 136.59, 133.61, 128.09, 124.80, 124.25, 84.50, 31.60, 30.25, 28.96, 24.77, 22.60, 14.11. IR (Neat): ν = 2929, 2854, 2029, 1533, 1424, 1328, 1137, 849, 665 cm^{-1} . MS(MALDI $^+$) m/z calculated for $\text{C}_{42}\text{H}_{56}\text{B}_2\text{O}_4\text{S}_4$ [M^+]: 774.77, found: 774.49. Elemental analysis calculated for $\text{C}_{42}\text{H}_{56}\text{B}_2\text{O}_4\text{S}_4$: C, 65.11; H, 7.29; B, 2.79; O, 8.26; S, 16.55. Found; C:66.08; H, 7.47; N: 0.00

2.1.4 2,2'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**13**)

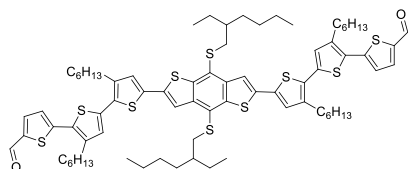


Product formed bright yellow crystals. Yield = 1.16 g (1.40 mmol, 81%). ^1H NMR (600 MHz, CDCl_3) δ 8.14 (s, 2H), 7.28 (d, J = 3.4 Hz, 2H), 6.85 (d, J = 3.5 Hz, 2H), 2.84 (d, J = 6.7 Hz, 4H), 1.67 (d, J = 6.3 Hz, 2H), 1.35 (s, 40H), 1.01 – 0.82 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 145.80, 142.56, 138.25, 136.86, 133.64, 128.02, 125.32, 124.78, 84.48, 41.38, 34.25, 32.46, 30.89, 28.93, 25.66, 24.75, 23.01, 14.16, 10.84. IR (Neat): ν = 2929, 2854, 2029, 1533, 1424, 1328, 1137, 849, 665 cm^{-1} . MS(MALDI $^+$) m/z calculated for $\text{C}_{46}\text{H}_{64}\text{B}_2\text{O}_4\text{S}_4$ [M^+]: 830.39, found: 830.61. Elemental analysis calculated for $\text{C}_{46}\text{H}_{64}\text{B}_2\text{O}_4\text{S}_4$: 66.49; H, 7.76; B, 2.60; O, 7.70; S, 15.44. Found; C:66.25; H, 7.71; N: 0.00

General procedure for the BTR dialdehydes

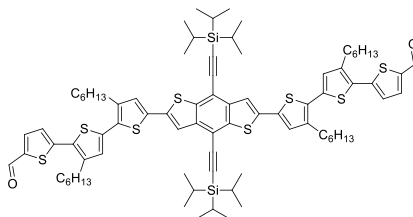
A mixture of the borylated BDT core (0.5 g), 3',3''-dibutyl-5''-iodo-[2,2':5',2''-terthiophene]-5-carbaldehyde **14** (2.2 eq.), THF (30 mL) and 2.0 M K₃PO₄ (15 mL) was degassed by bubbling dinitrogen through for 30 minutes. The catalyst, Pd₂(dba)₃ (5 mol%) and P(*o*-tol)₃ (20 mol%) was added and the reaction mixture was stirred at 60°C for 12 h. The reaction mixture was filtered through celite filter aid and the THF removed under vacuum. Diethyl ether (40 mL) was added and the organic phase separated, washed with water (2 x 20 mL) and dried over MgSO₄ and filtered. After removing the solvent the crude product was purified by silica gel column chromatography (petroleum spirit: dichloromethane = 1:1) to give the pure product.

2.1.5 Synthesis of 5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (**15**)



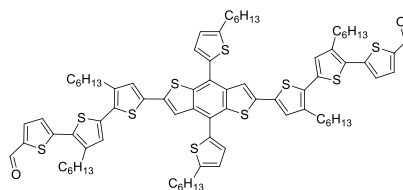
Product formed a red powder. Yield = 0.69 g, (0.51 mmol, 74%). *R*_f = 0.20 (PS:DCM = 1:1) ¹H NMR (600 MHz, CDCl₃) δ 9.89 (s, 2H), 7.71 (d, *J* = 1.5 Hz, 2H), 7.71 (s, 2H), 7.24 (d, *J* = 3.9 Hz, 2H), 7.18 (s, 2H), 7.04 (s, 2H), 3.00 (d, *J* = 3.2 Hz, 4H), 2.94 – 2.66 (m, 8H), 1.71 (s, 8H), 1.54 – 1.16 (m, 42H), 1.03 – 0.78 (m, 24H). ¹³C NMR (125 MHz), CDCl₃) δ 146.00, 144.59, 142.55, 142.20, 141.22, 141.12, 138.11, 136.81, 135.88, 135.50, 130.69, 129.60, 129.11, 128.56, 125.87, 122.63, 119.42. IR (Neat): ν = 2956, 2923, 2855, (C=O) 1659, 1523, 1424, 1379, 1344, 1226, 1136, 1055, 848, 814, 671 cm⁻¹. MS(MALDI⁺) *m/z* calculated for C₇₆H₉₈O₂S₁₀ [M+H⁺]: 1363.49, found: 1363.63. Elemental analysis calculated for C₇₆H₉₈O₂S₁₀: C, 66.91; H, 7.24; O, 2.35; S, 23.50. Found; C:66.74; H, 7.23; N: 0.00

2.1.6 Synthesis of 5'',5''''-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (16)



Product formed a red powder. Yield = 0.74 g, (0.52 mmol, 74%). R_f = 0.30 (PS:DCM = 1:1) ^1H NMR (600 MHz, CDCl_3) δ 9.90 (s, 2H), 7.72 (d, J = 3.9 Hz, 2H), 7.61 (s, 2H), 7.26 (d, J = 3.6 Hz, 2H), 7.17 (s, 2H), 7.05 (s, 2H), 2.90 – 2.77 (m, 8H), 1.72 (t, J = 7.7 Hz, 8H), 1.49 – 1.19 (m, 66H), 0.95 – 0.86 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 182.56, 145.99, 142.56, 142.26, 141.36, 140.15, 139.39, 138.20, 136.82, 135.77, 135.34, 130.82, 129.74, 129.36, 128.71, 125.97, 118.95, 111.24, 102.34, 102.20, 31.64, 30.41, 30.23, 29.75, 29.55, 29.21, 22.62, 22.59, 18.82, 14.09, 14.07, 11.35. IR (Neat): ν = 2940, 2863, 2196, 2065, 1460, 1375, 1203, 881, 657 cm^{-1} . MS(MALDI $^+$) m/z calculated for $\text{C}_{82}\text{H}_{106}\text{O}_2\text{S}_8\text{Si}_2$ [M^+]: 1436.41, found: 1436.787. Elemental analysis calculated for $\text{C}_{82}\text{H}_{106}\text{O}_2\text{S}_8\text{Si}_2$: C, 68.57; H, 7.44; O, 2.23; S, 17.86; Si, 3.91. Found; C:67.15; H, 7.24; N: 0.00

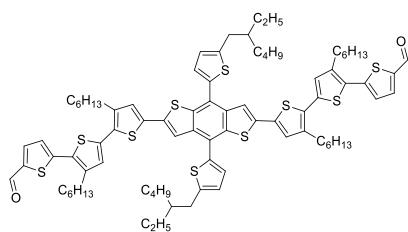
2.1.7 Synthesis of 5'',5''''-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (17)



Product formed a red powder. Yield = 0.78 g (0.56 mmol, 86%). R_f = 0.25 (PS:DCM = 1:1) ^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 2H), 7.70 (d, J = 3.9 Hz, 2H), 7.61 (s, 2H), 7.31 (d, J = 3.5 Hz, 2H), 7.22 (d, J = 3.9 Hz, 2H), 7.11 (s, 2H), 7.01 (s, 2H), 6.96 (d, J = 3.4 Hz, 2H), 2.96 (t, J = 7.7 Hz, 4H), 2.84 – 2.78 (m, 4H), 2.77 – 2.72 (m, 4H), 1.86 – 1.80 (m, 4H), 1.72 – 1.64 (m, 8H), 1.53 – 1.47 (m, 4H), 1.46 – 1.29 (m, 32H), 0.97 – 0.88 (m, 18H). ^{13}C NMR (125 MHz, CDCl_3) δ 182.50, 147.43, 146.02, 142.52, 142.16, 141.13, 138.72, 137.44, 137.36, 136.79, 136.48, 135.95, 135.51, 130.33, 129.47, 129.03, 128.39, 127.89, 125.82, 124.38, 123.37, 119.13, 31.62, 31.59, 31.51, 30.33, 30.30, 30.19, 29.76, 29.63, 29.24, 29.22, 28.96, 22.61, 22.57, 14.10, 14.06, 14.04. IR (Neat): ν =

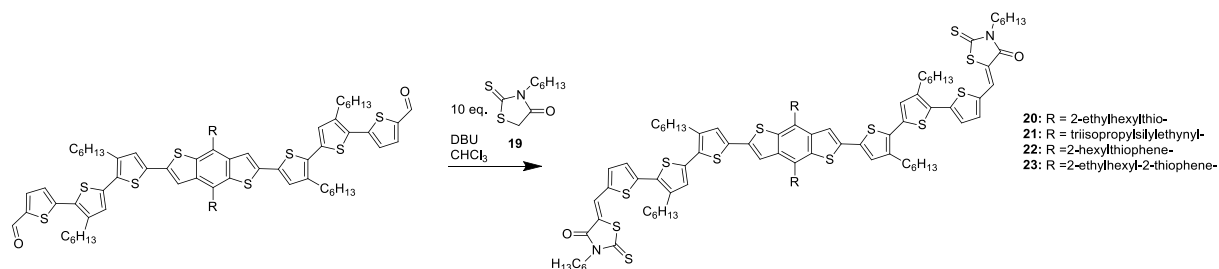
2954, 2924, 2855, 1741, (C=O) 1661, 1454, 1377, 1223, 1057, 1019, 802, 670 cm^{-1} . MS(MALDI⁺) m/z calculated for $\text{C}_{80}\text{H}_{94}\text{O}_2\text{S}_{10}$ [$\text{M}+\text{H}^+$]: 1407.46, found: 1407.693. Elemental analysis calculated for $\text{C}_{80}\text{H}_{94}\text{O}_2\text{S}_{10}$: C, 68.23; H, 6.73; O, 2.27; S, 22.77. Found; C:68.15; H, 6.72; N: 0.00

2.1.8 Synthesis of 5'',5''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (18)



Product formed a red powder. Yield = 0.78 g (0.54 mmol, 89%). ¹H NMR (600 MHz, CDCl_3) δ 9.89 (s, 2H), 7.71 (d, J = 3.9 Hz, 2H), 7.63 (s, 2H), 7.31 (d, J = 3.5 Hz, 2H), 7.23 (d, J = 4.0 Hz, 2H), 7.12 (s, 2H), 7.02 (s, 2H), 6.94 (d, J = 3.5 Hz, 2H), 2.90 (dd, J = 6.9, 3.7 Hz, 2H), 2.79 (dt, J = 20.8, 7.9 Hz, 8H), 1.77 – 1.63 (m, 8H), 1.53 – 1.23 (m, 44H), 1.05 – 0.81 (m, 24H). ¹³C NMR (125 MHz, CDCl_3) δ 182.52, 146.07, 146.03, 142.52, 142.19, 141.17, 138.71, 137.44, 137.35, 136.80, 136.70, 135.94, 135.56, 130.34, 129.49, 129.07, 128.38, 127.79, 125.86, 125.47, 123.40, 119.20, 41.47, 34.34, 32.49, 31.62, 31.60, 30.35, 30.19, 29.75, 29.61, 29.22, 29.21, 28.93, 25.83, 23.03, 22.56, 14.18, 14.05, 14.04, 10.96. IR (Neat): ν = 2955, 2922, 2853, 1741, (C=O) 1657, 1454, 1377, 1223, 1051, 1019, 800, 671 cm^{-1} . MS(MALDI⁺) m/z calculated for $\text{C}_{84}\text{H}_{102}\text{O}_2\text{S}_{10}$ [M^+]: 1463.51, found: 1463.08. Elemental analysis calculated for $\text{C}_{84}\text{H}_{102}\text{O}_2\text{S}_{10}$: C, 68.90; H, 7.02; O, 2.19; S, 21.90. Found; C:70.08; H, 6.91; N: 0.00

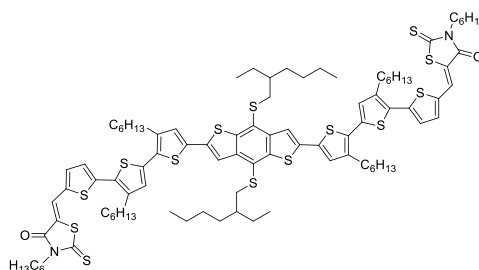
2.2 General synthesis of BTR Analogue Molecules



General procedure for the Knoevenagel condensation

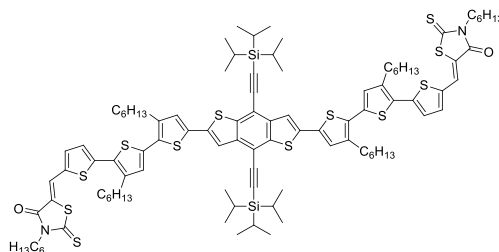
The corresponding BTR-dialdehyde core (200 mg) and n-hexyl rhodanine (10 eq.) were dissolved in chloroform (5 mL). Catalytic DBU (5 drops) was added to this solution, which was then stirred for 2 hours. The solvent was then removed under reduced pressure, and the crude mixture purified via column chromatography (silica, 1:1 petroleum spirits: chloroform unless otherwise noted) and size-exclusion chromatography (toluene, Biobeads) and precipitated in methanol to yield the product.

2.2.1 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl))bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5'-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**20**, BTR-TE)



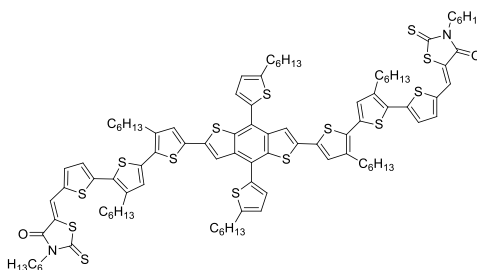
Product formed a purple powder. Yield = 0.21 g (0.12 mmol, 82%). R_f = 0.80 (PS:CHCl₃ = 1:1) ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.65 (d, J = 1.8 Hz, 2H), 7.34 (d, J = 3.9 Hz, 2H), 7.20 (d, J = 3.9 Hz, 2H), 7.15 (s, 2H), 7.01 (s, 2H), 4.19 – 4.01 (t, 4H), 2.99 (d, J = 3.6 Hz, 4H), 2.81 (dt, J = 16.8, 8.0 Hz, 10H), 1.72 (ddd, J = 9.5, 7.5, 3.7 Hz, 14H), 1.60 – 1.18 (m, 52H), 1.03 – 0.80 (m, 30H). ¹³C NMR (125 MHz, CDCl₃) δ 192.10, 167.43, 144.53, 144.24, 141.88, 141.07, 140.98, 138.01, 137.00, 135.53, 135.33, 134.58, 130.84, 129.75, 128.97, 128.49, 126.40, 124.89, 122.50, 120.15, 119.31. IR (Neat): ν = 2955, 2923, 2856, 1698, 1578, 1424, 1181, 820 cm⁻¹. MS(MALDI) m/z calculated for C₉₄H₁₂₄N₂O₂S₁₄ [M+H⁺]: 1762.56, found: 1762.34. Elemental analysis calculated for C₉₄H₁₂₄N₂O₂S₁₄: C, 64.04; H, 7.09; N, 1.59; O, 1.82; S, 25.46. Found: C, 64.10; H, 7.12; N, 1.48; S, 25.17

2.2.2 (5*Z*,5'*Z*)-5,5'-((5'',5''''-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl))bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**21**, BTR-TIPS)



Product formed a purple powder. Yield = 0.20 g (0.11nmol, 79%). R_f = 0.80 (PS:CHCl₃ = 3:2)¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.50 (s, 2H), 7.34 (s, 2H), 7.21 (s, 2H), 7.08 (s, 2H), 6.98 (s, 2H), 4.05 (dd, J = 8.8, 6.8 Hz, 4H), 2.81 (dt, J = 19.0, 7.9 Hz, 8H), 1.71 (dt, J = 12.2, 5.8 Hz, 12H), 1.53 – 1.19 (m, 778H), 0.99 – 0.90 (m, 12H), 0.93 – 0.85 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 192.11, 167.42, 144.18, 141.83, 140.98, 140.02, 139.35, 138.11, 137.00, 135.30, 135.03, 134.56, 131.03, 129.83, 129.13, 128.58, 126.42, 124.95, 120.06, 118.72, 111.05, 102.34, 102.17. IR (Neat): ν = 2940, 2889, 2863, 2196, 2065, 1460, 1375, 1203, 881, 657 cm⁻¹. MS(MALDI) m/z calculated for C₁₀₀H₁₃₂N₂O₂S₁₂Si₂ [M+H⁺]: 1834.66, found: 1834.45 . Elemental analysis calculated for C₁₀₀H₁₃₂N₂O₂S₁₂Si₂: C, 65.45; H, 7.25; N, 1.53; O, 1.74; S, 20.97; Si, 3.06. Found: C, 65.46; H, 7.32; N, 1.47; S, 21.04

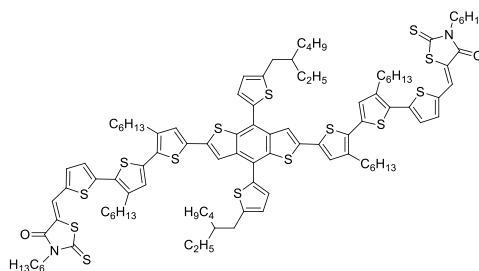
2.2.3 (5*Z*,5'*Z*)-5,5'-((5'',5''''-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl))bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**22**, BTR-H)



Product formed a purple powder. Yield = 0.18 g (0.10 mmol, 70%). R_f = 0.75 (PS:CHCl₃ = 2:1)¹H NMR (400 MHz, CDCl₃) 7.82 (s, 2H), 7.58 (s, 2H), 7.34 (d, J = 3.9 Hz, 2H), 7.31 (d, J = 3.8 Hz, 2H), 7.19 (d, J = 4.9 Hz, 2H), 7.09

(s, 2H), 6.99 (s, 2H), 6.96 (d, $J = 2.6$ Hz, 2H), 4.14 – 4.05 (m, 4H), 2.97 (t, $J = 7.8$ Hz, 4H), 2.81 (t, $J = 7.9$ Hz, 4H), 2.75 (t, $J = 8.0$ Hz, 4H), 1.94 – 1.79 (m, 4H), 1.80 – 1.64 (m, 12H), 1.53 – 1.22 (m, 48H), 1.02 – 0.80 (m, 24H). ^{13}C NMR (125 MHz), CDCl_3) δ 147.40, 144.24, 141.90, 140.99, 138.68, 137.42, 137.34, 137.04, 136.51, 135.61, 135.40, 134.61, 130.47, 129.66, 129.02, 128.38, 127.90, 126.49, 124.94, 124.38, 123.31, 120.20, 119.08. IR (Neat): $\nu = 2954, 2924, 2853, 1699, 1578, 1424, 1184, 1066, 802, 670\text{ cm}^{-1}$. MS(MALDI) m/z calculated for $\text{C}_{98}\text{H}_{120}\text{N}_2\text{O}_2\text{S}_{14}$ [$\text{M}+\text{H}^+$]: 1806.56, found: 1806.28. Elemental analysis calculated for $\text{C}_{98}\text{H}_{120}\text{N}_2\text{O}_2\text{S}_{14}$: C, 65.14; H, 6.69; N, 1.55; O, 1.77; S, 24.84. Found: C, 64.57; H, 6.66; N, 1.85; S, 25.34

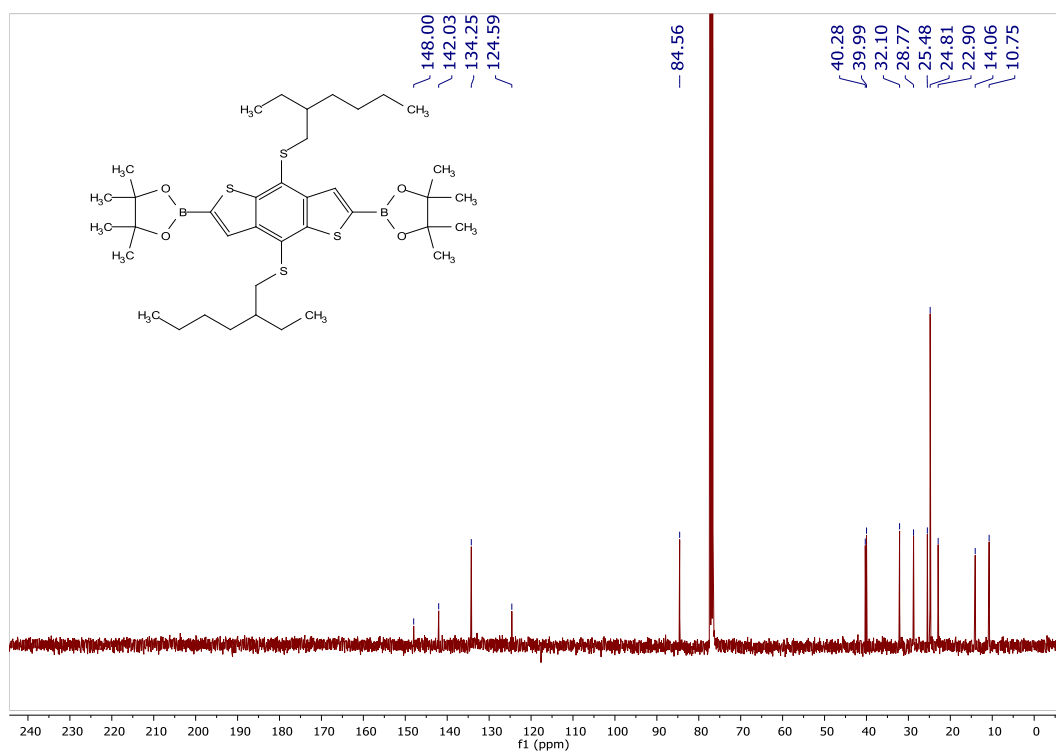
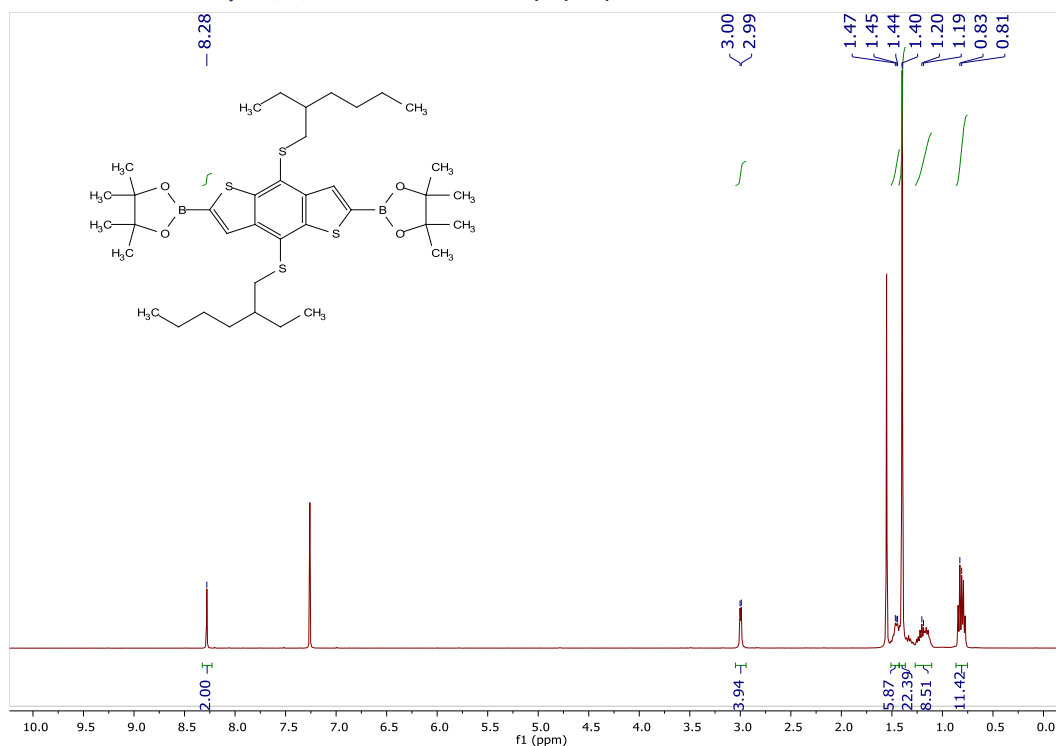
(5*Z*,5'*Z*)-5,5'-((5'',5''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**23**, BTR-EH)



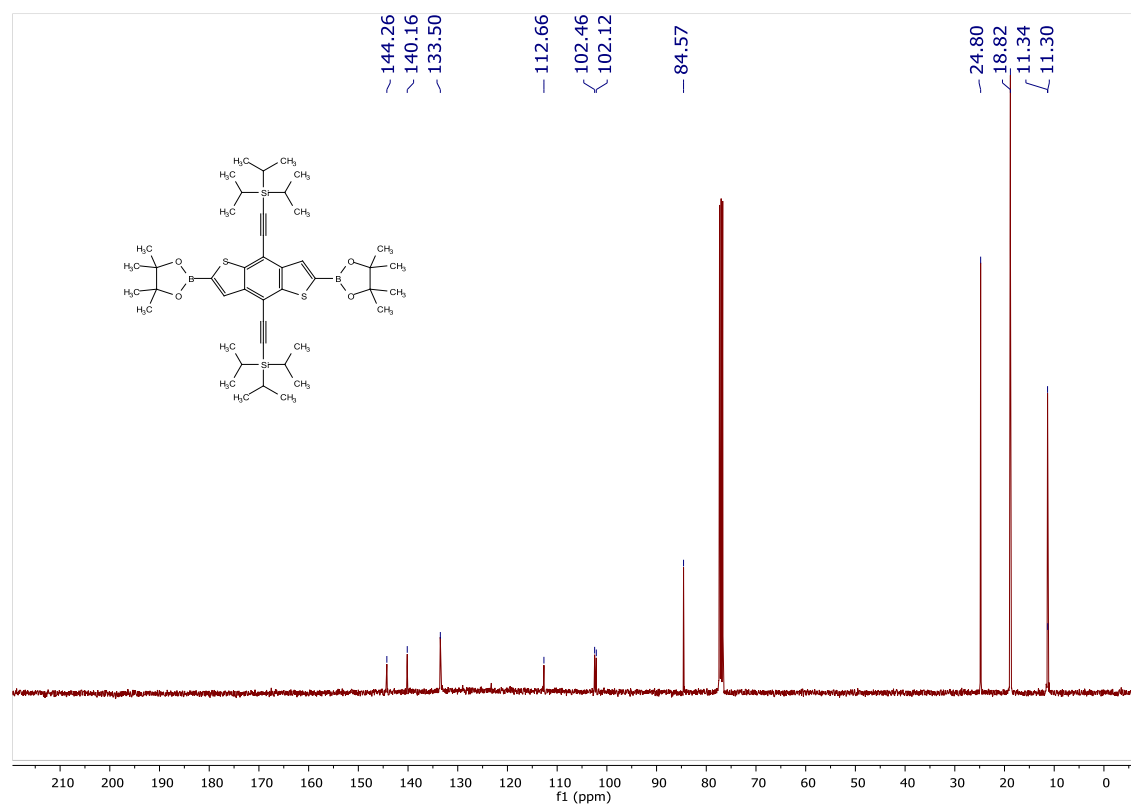
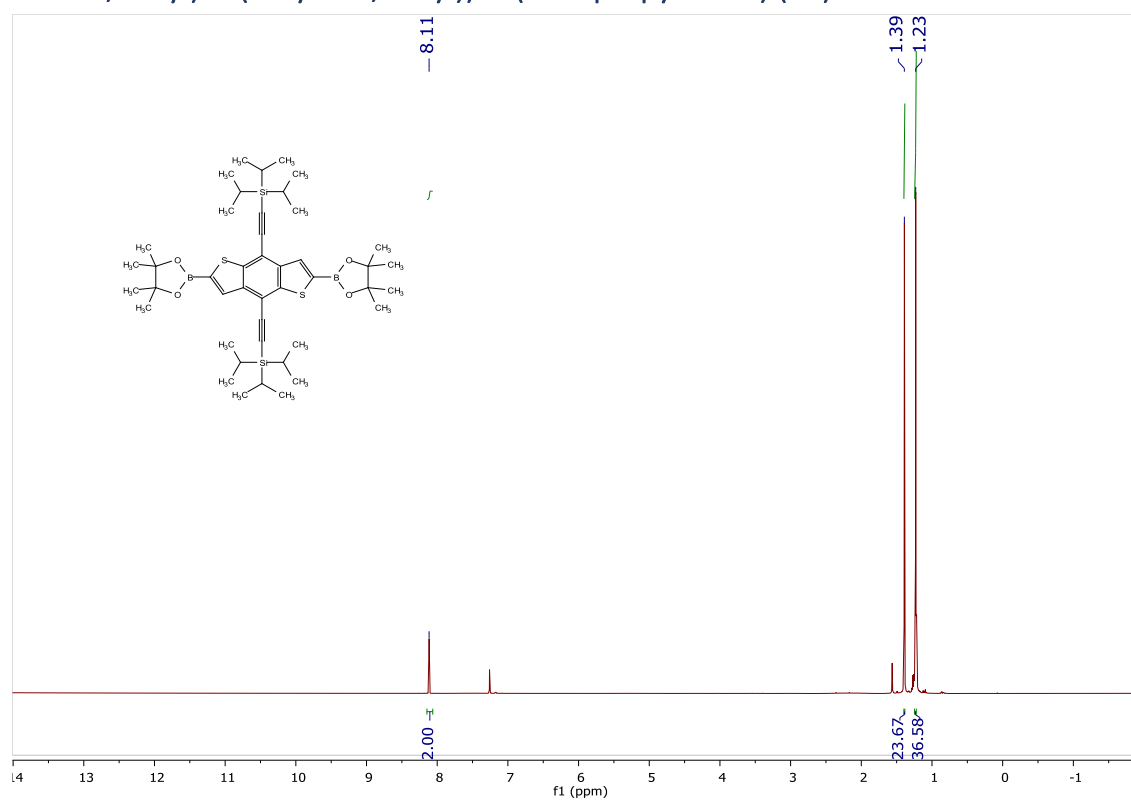
Product formed a purple powder. Yield = 0.16 g (0.09 mmol, 68%). $R_f = 0.75$ (PS:DCM = 1:1) ^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 2H), 7.60 (s, 2H), 7.35 (d, $J = 4.0$ Hz, 2H), 7.32 (d, $J = 3.4$ Hz, 2H), 7.19 (d, $J = 4.0$ Hz, 2H), 7.09 (s, 2H), 6.99 (s, 2H), 6.94 (d, $J = 3.4$ Hz, 2H), 4.13 – 4.05 (m, 4H), 2.91 (t, $J = 6.6$ Hz, 4H), 2.78 (dt, $J = 30.0, 8.0$ Hz, 4H), 1.74 – 1.64 (m, 16H), 1.52 – 1.29 (m, 54H), 1.02 – 0.86 (m, 30H). ^{13}C NMR (125 MHz), CDCl_3) δ 192.11, 167.44, 145.97, 144.24, 141.86, 140.94, 138.62, 137.35, 137.29, 136.99, 136.77, 135.60, 135.39, 134.58, 130.47, 129.64, 128.95, 128.31, 127.80, 126.42, 125.45, 124.91, 123.26, 120.14, 119.09, 44.83, 41.48, 34.36, 32.51, 31.68, 31.64, 31.30, 30.28, 30.25, 29.84, 29.69, 29.67, 29.30, 29.27, 29.24, 28.95, 26.90, 26.42, 25.84, 23.06, 22.64, 22.60, 22.48, 14.21, 14.10, 13.97, 10.98. IR (Neat): $\nu = 2956, 2921, 2851, 1699, 1579, 1424, 1184, 1066, 802, 670\text{ cm}^{-1}$. MS(MALDI) m/z calculated for $\text{C}_{102}\text{H}_{128}\text{N}_2\text{O}_2\text{S}_{14}$ [$\text{M}+\text{H}^+$]: 1862.62, found: 1862.45. Elemental analysis calculated for $\text{C}_{102}\text{H}_{128}\text{N}_2\text{O}_2\text{S}_{14}$: C, 65.76; H, 6.93; N, 1.50; O, 1.72; S, 24.10. Found: C, 65.72; H, 6.85; N, 1.62; S, 23.98

S3 ^1H and ^{13}C NMR Spectra

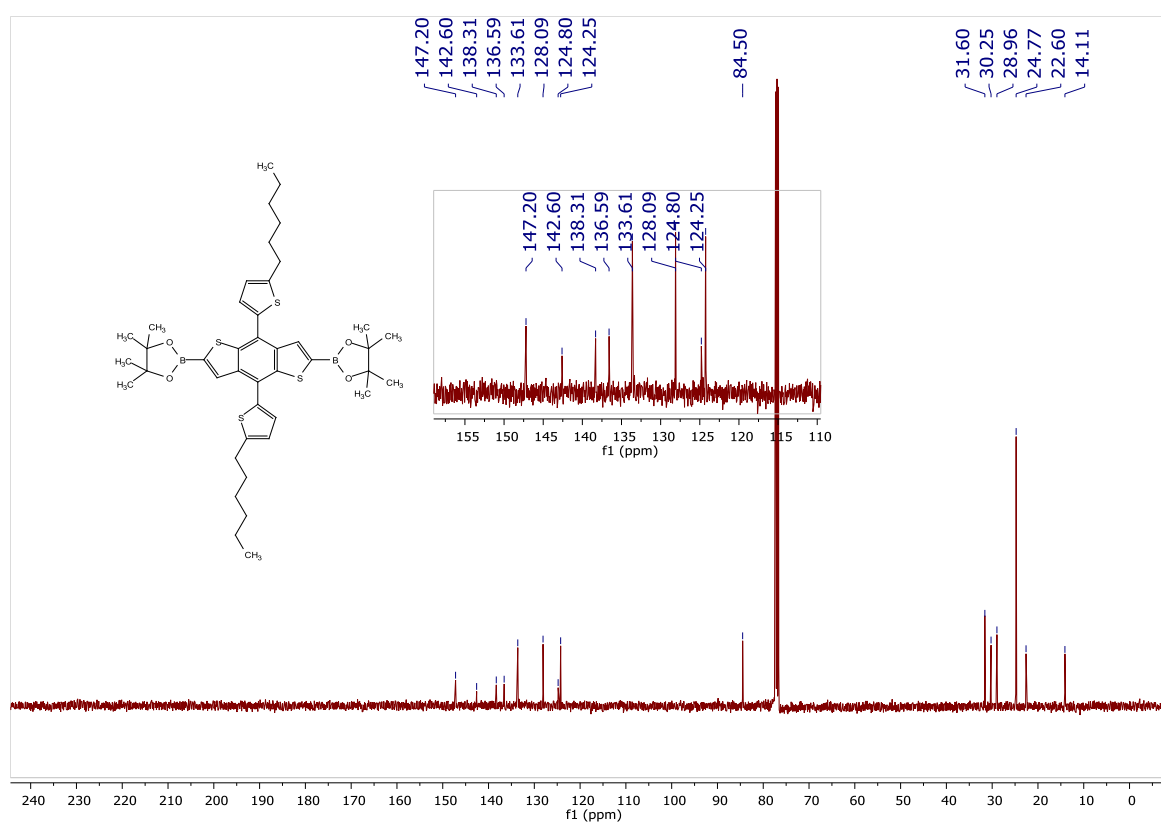
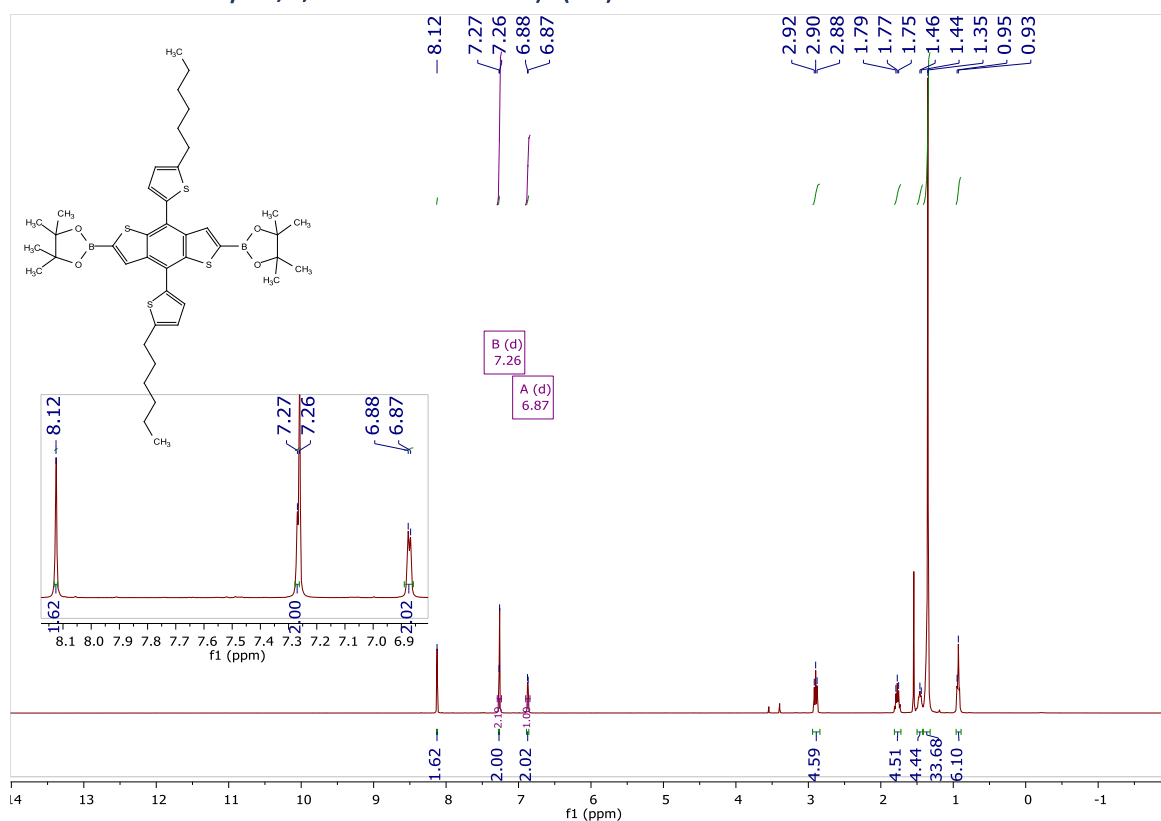
3.1 2,2'-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10)



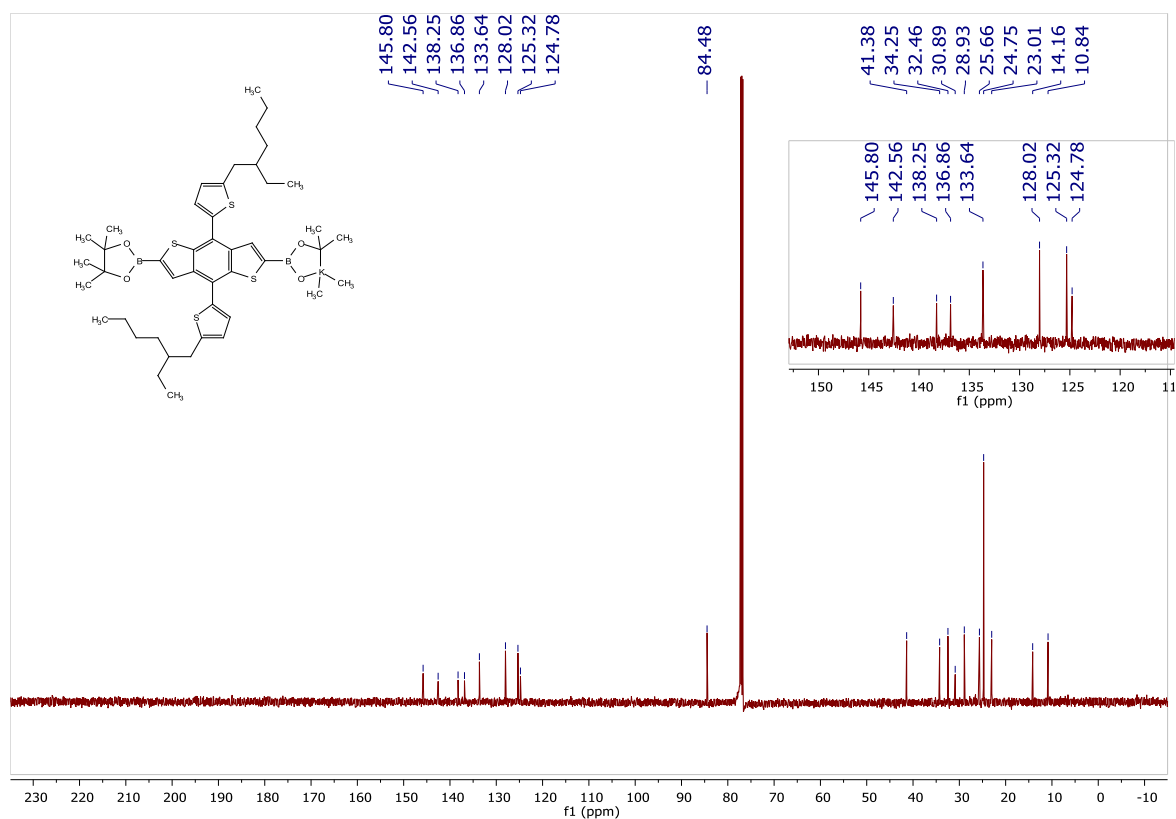
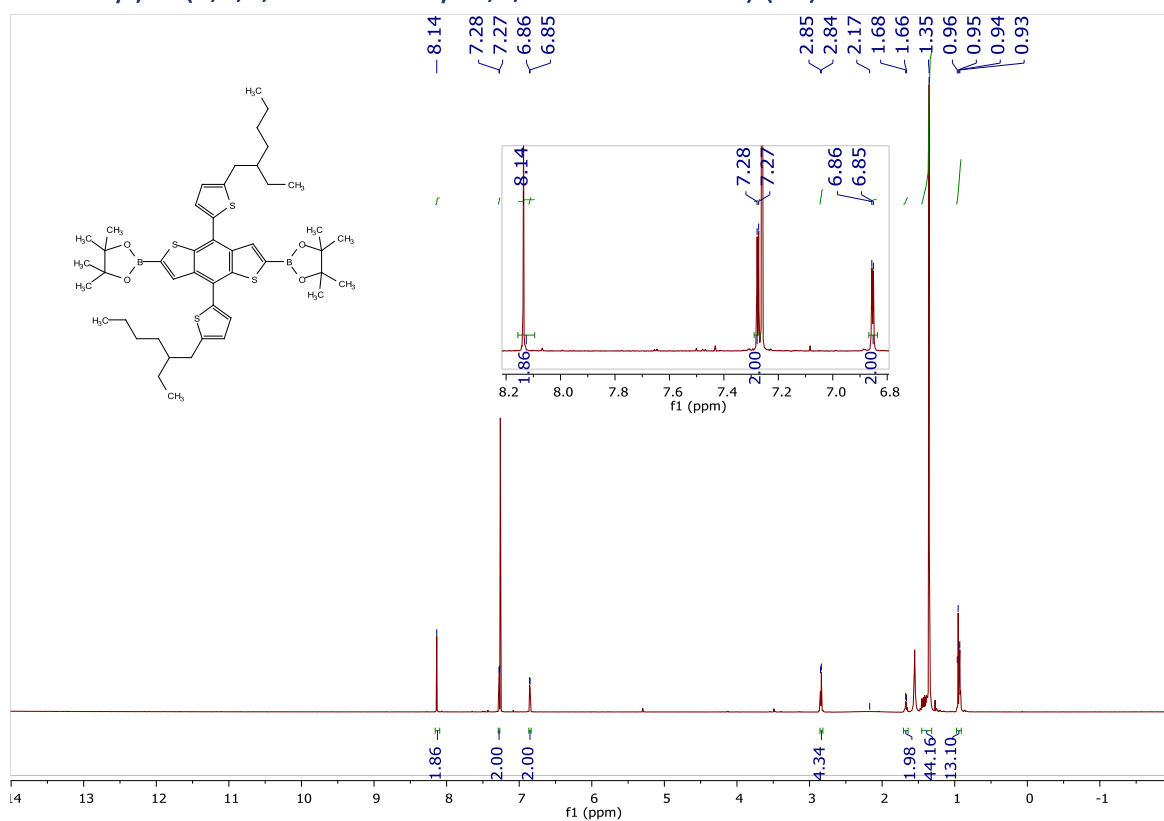
3.2 ((2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (11)



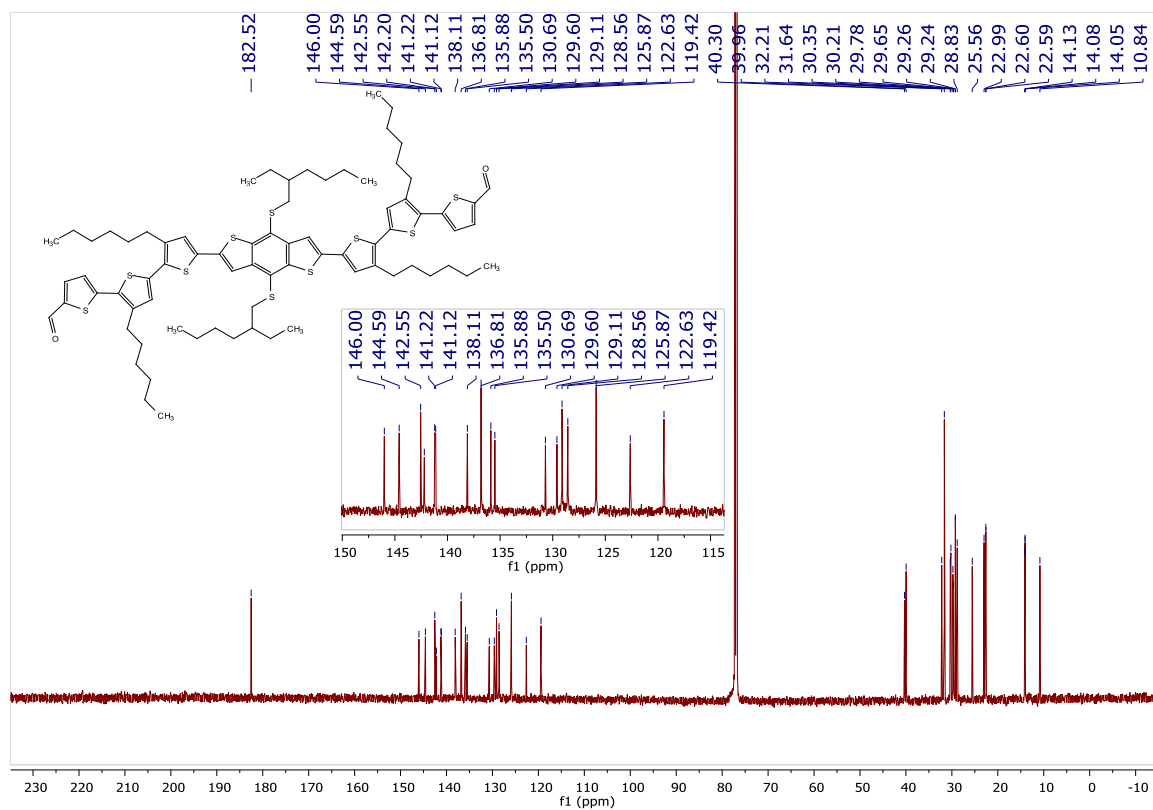
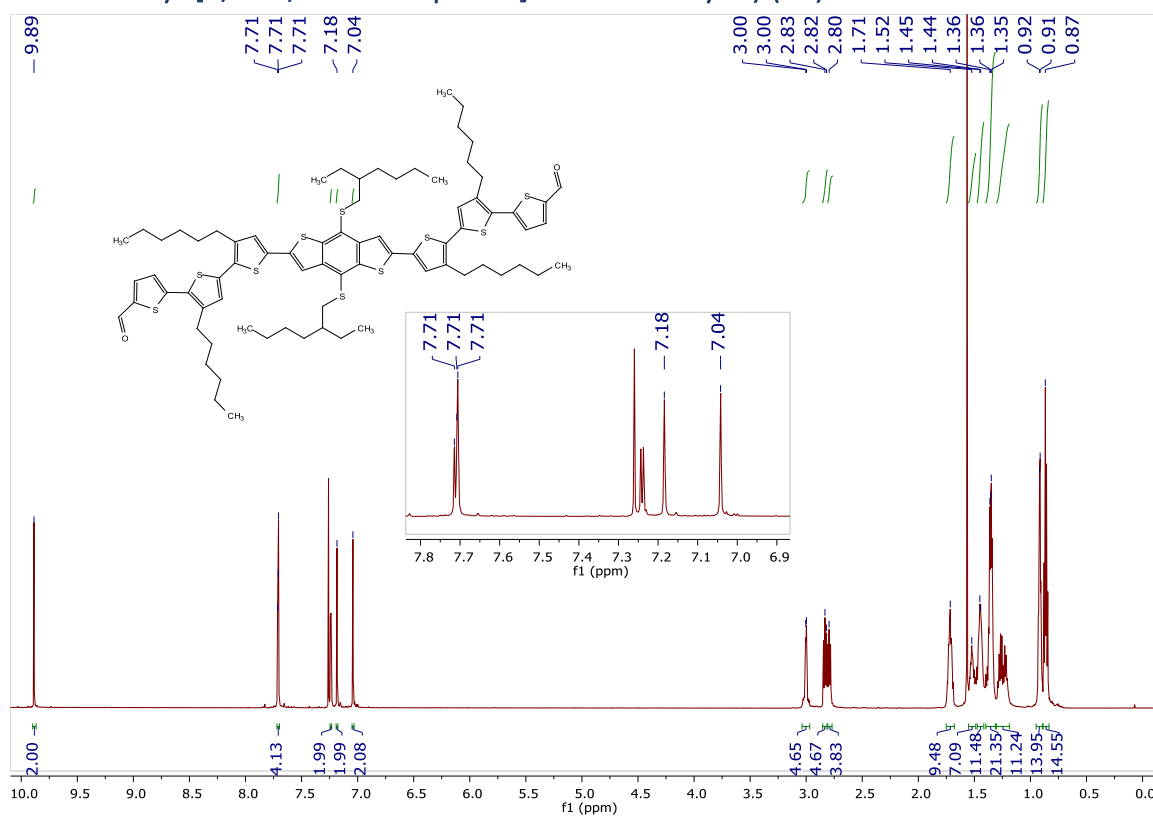
3.3 2,2'-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12)



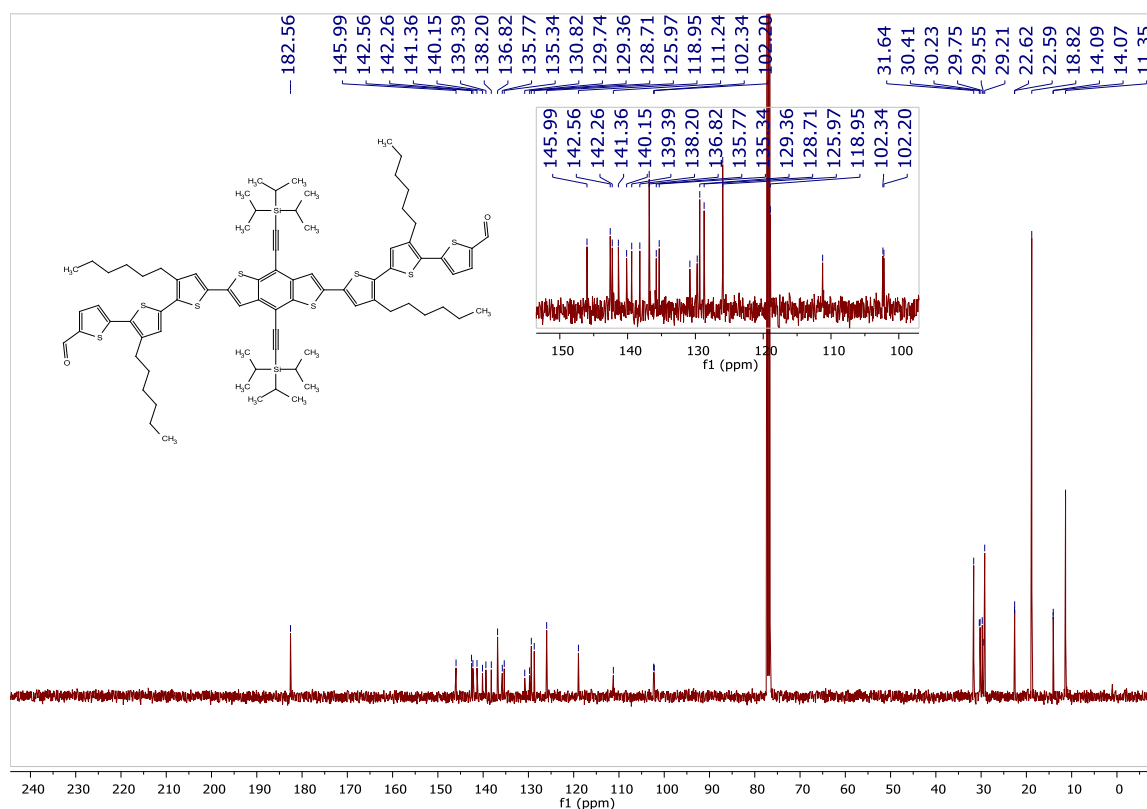
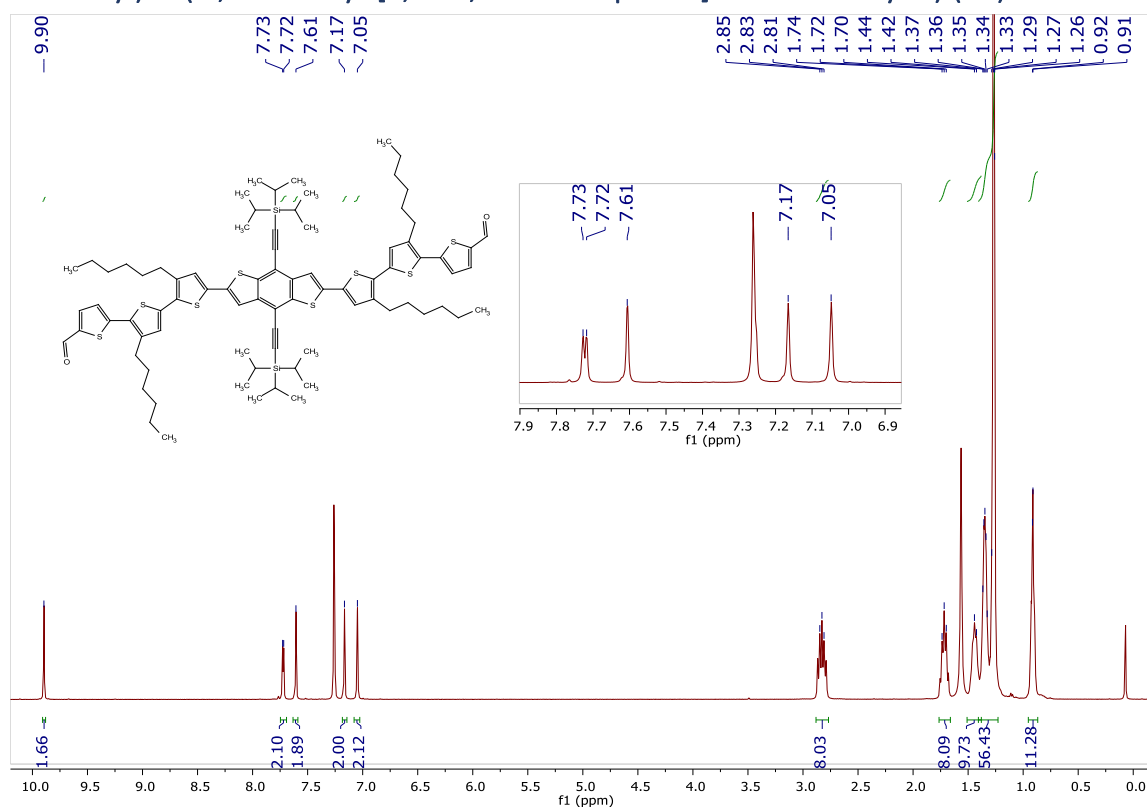
3.4 2,2'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13)



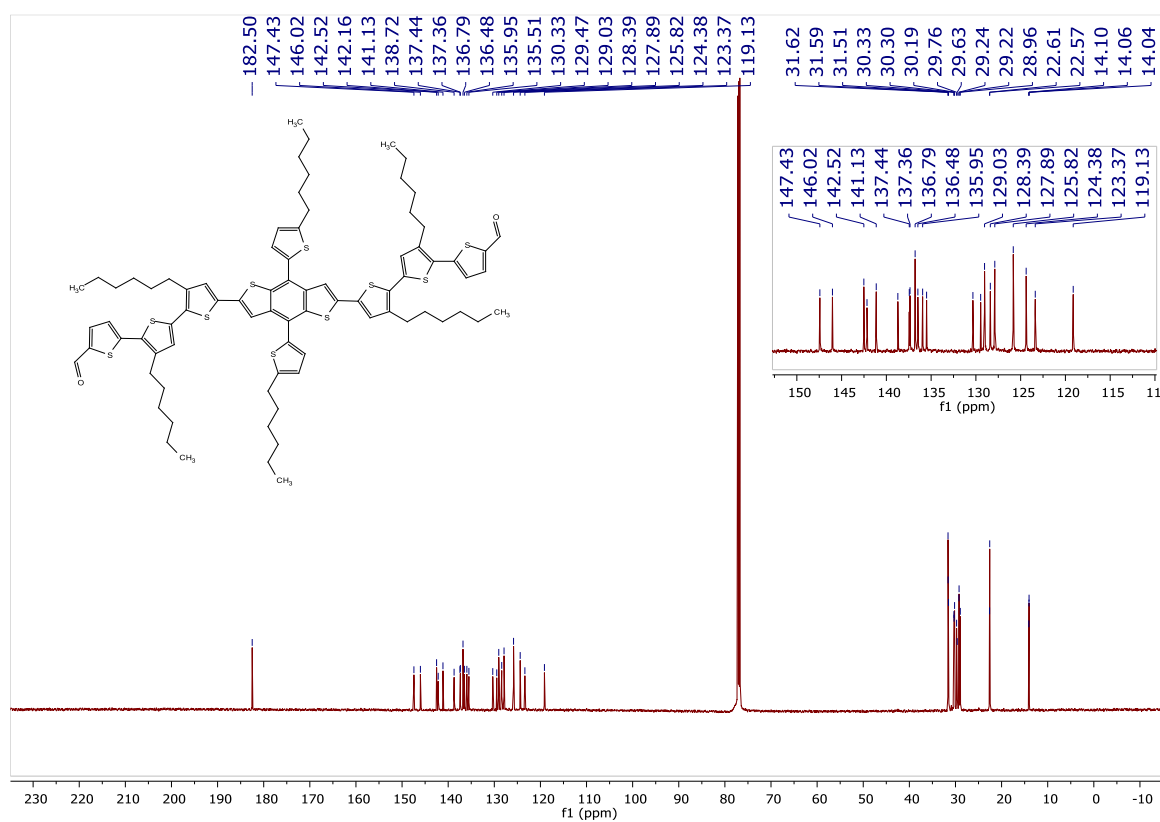
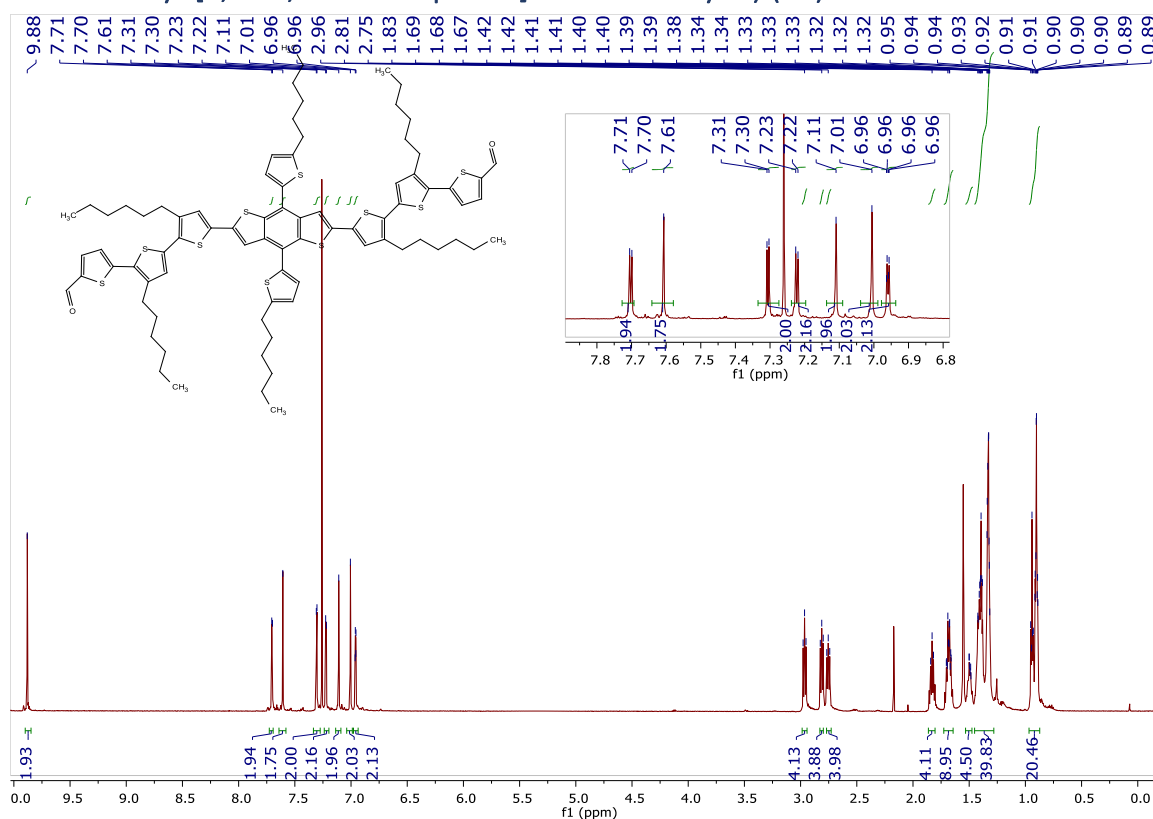
3.5 5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (15)



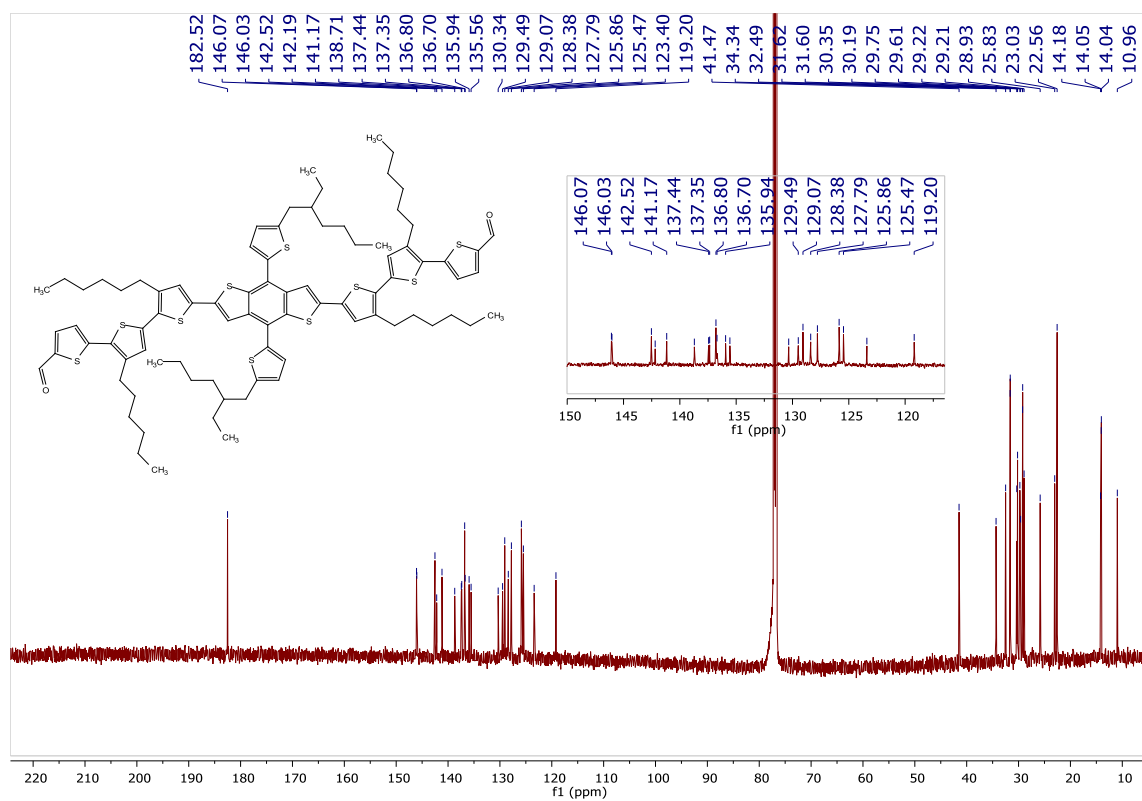
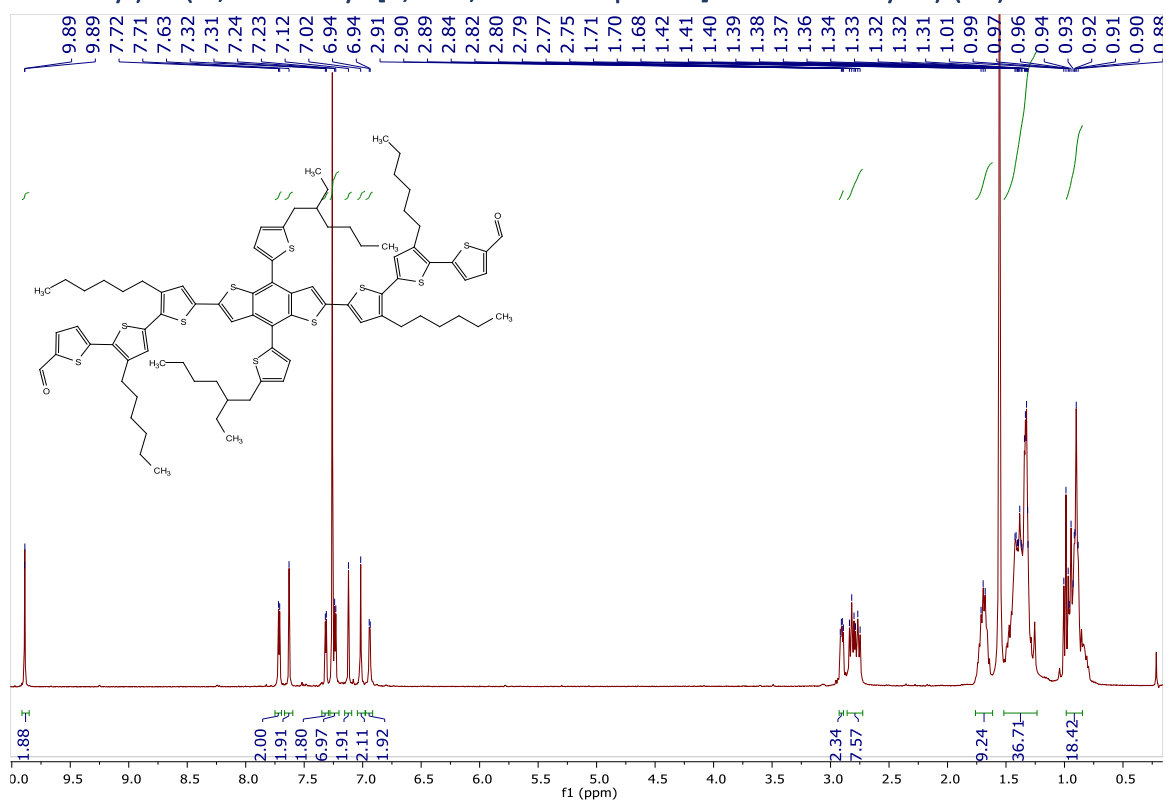
3.6 5'',5''''-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (16)



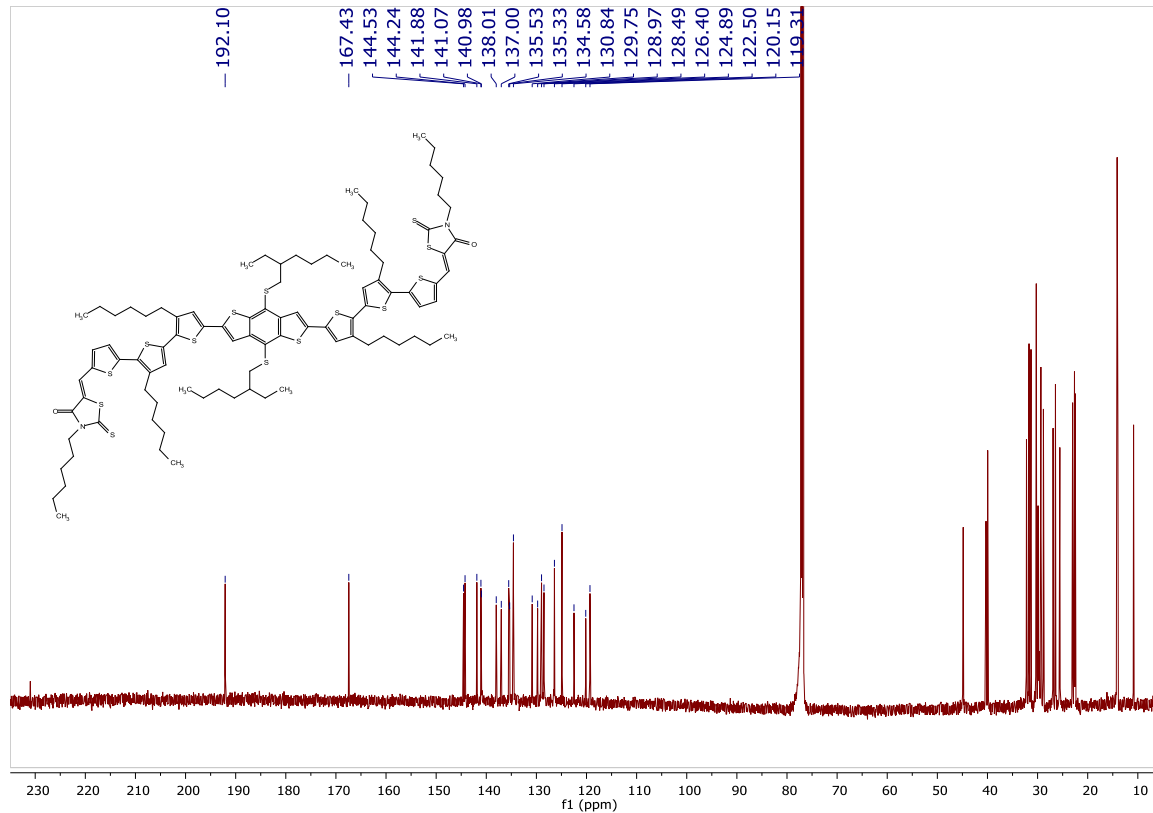
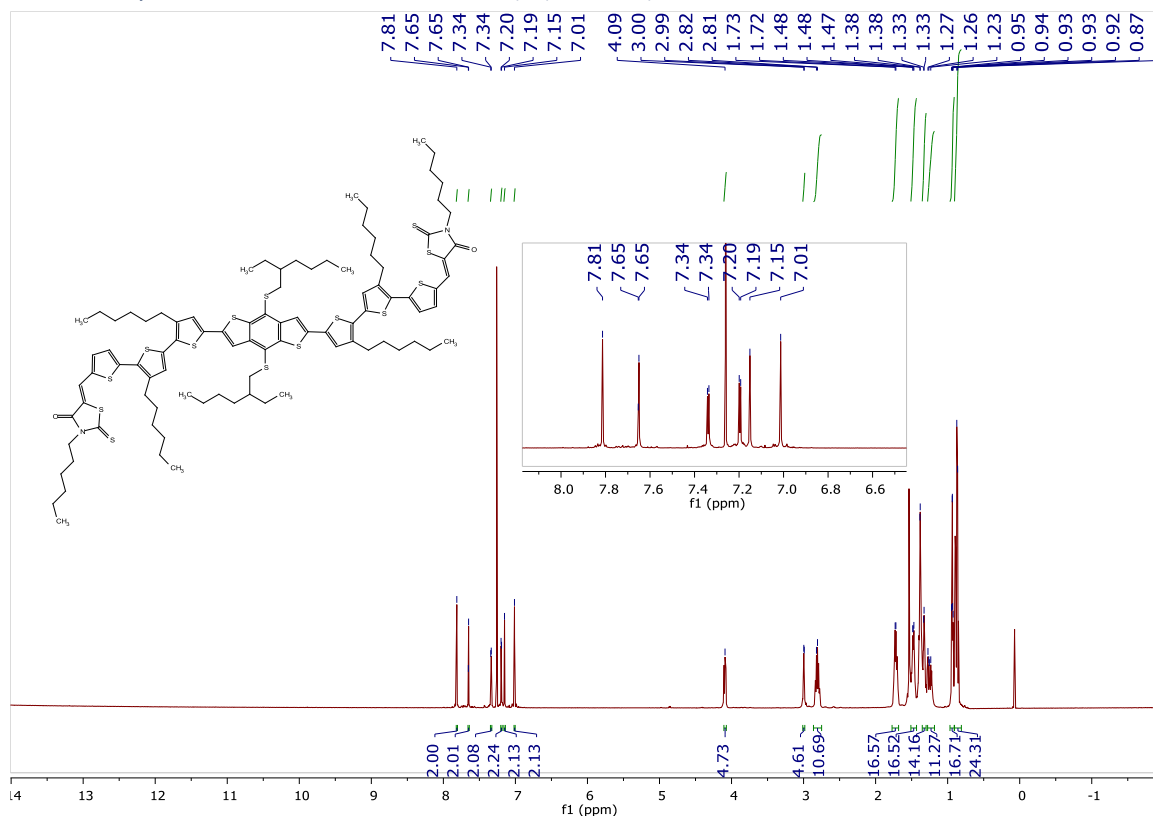
3.7 5'',5'''-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (17)



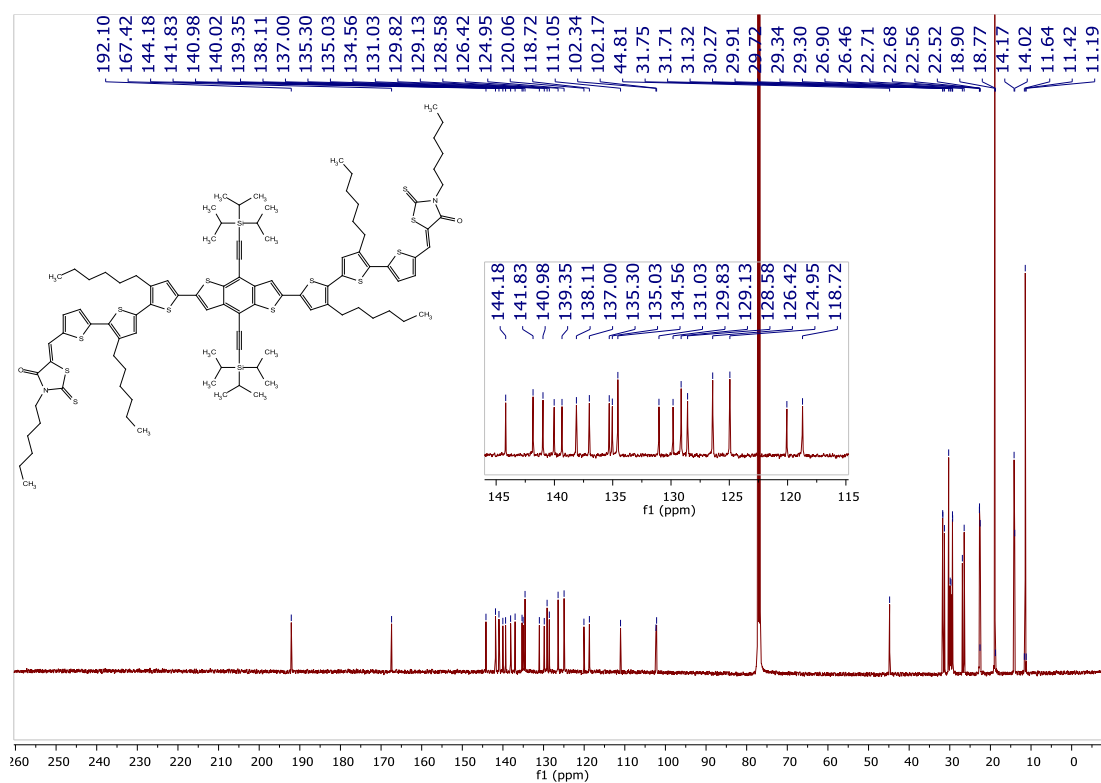
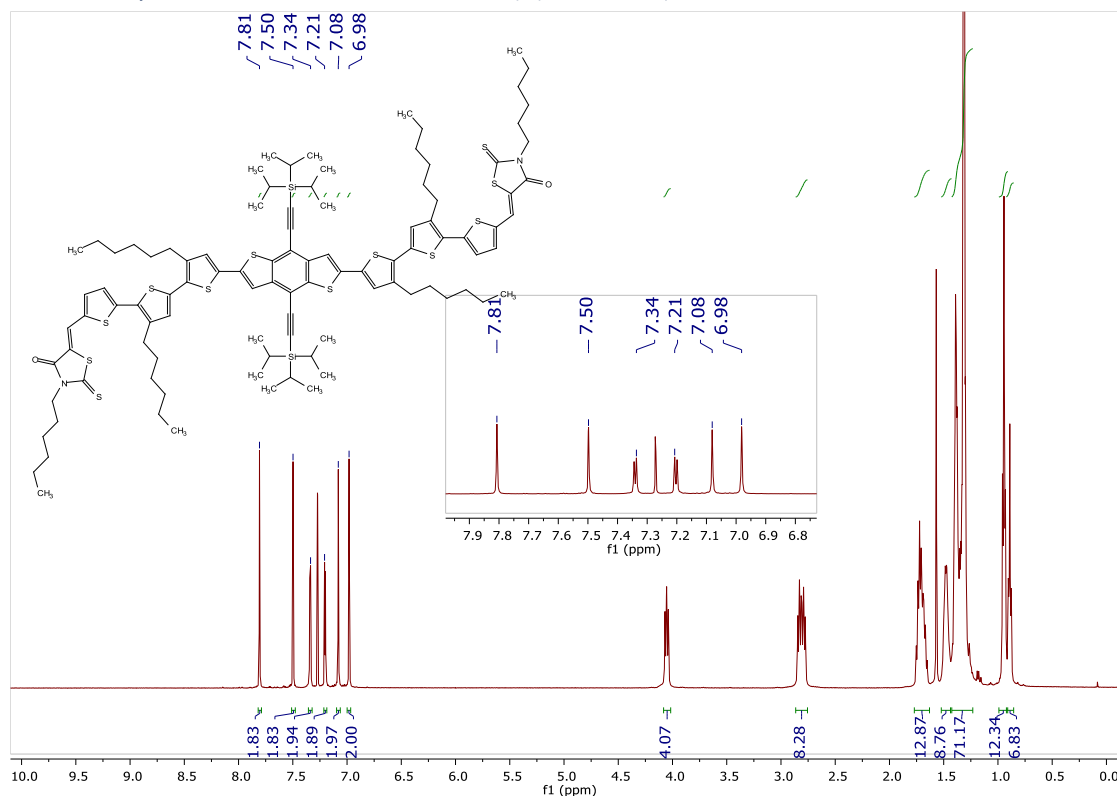
3.8 5'',5''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-diethyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (18)



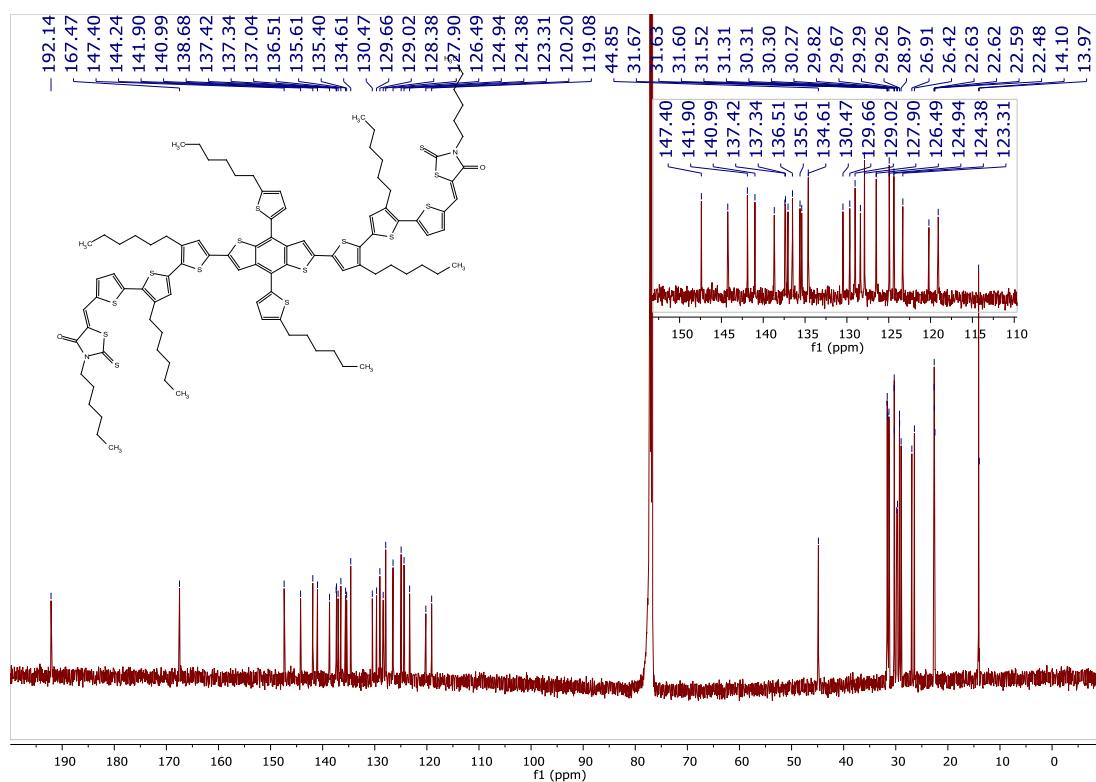
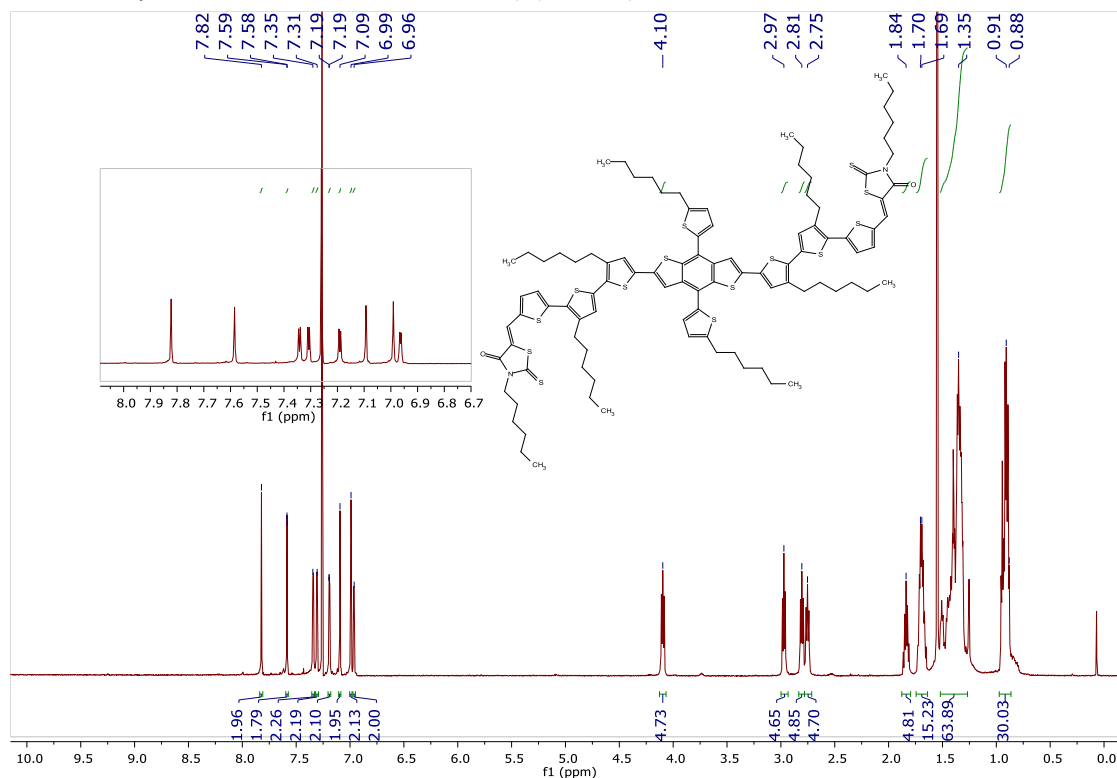
3.9 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-TE)



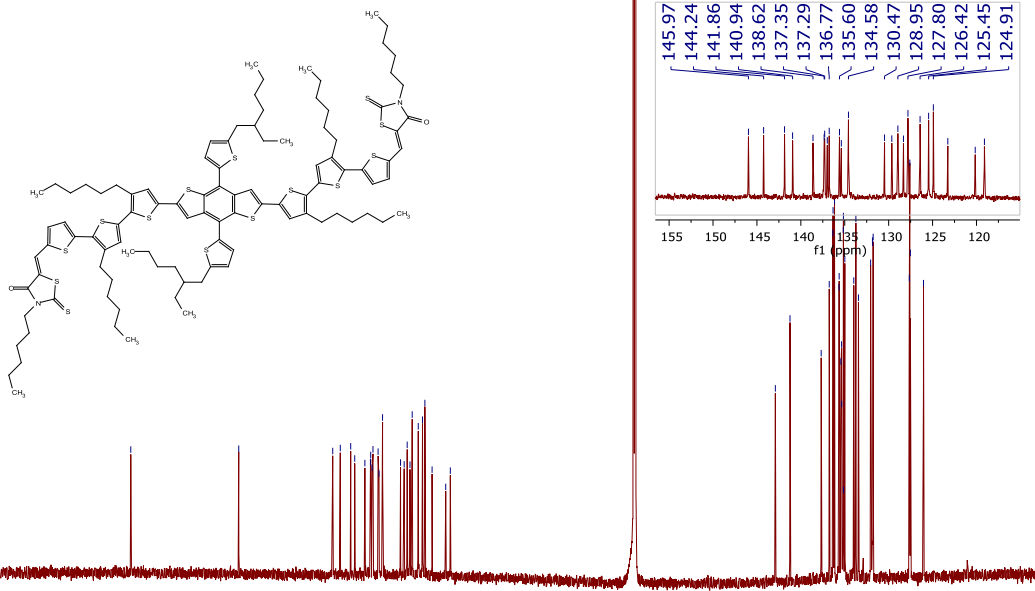
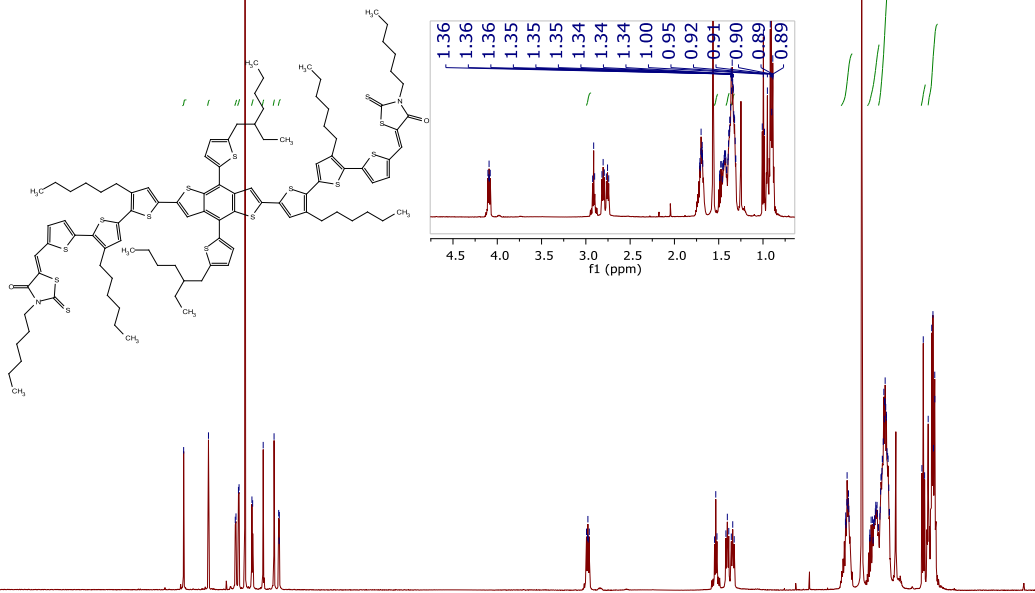
3.10 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5'-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-TIPS)



3.11 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-H)

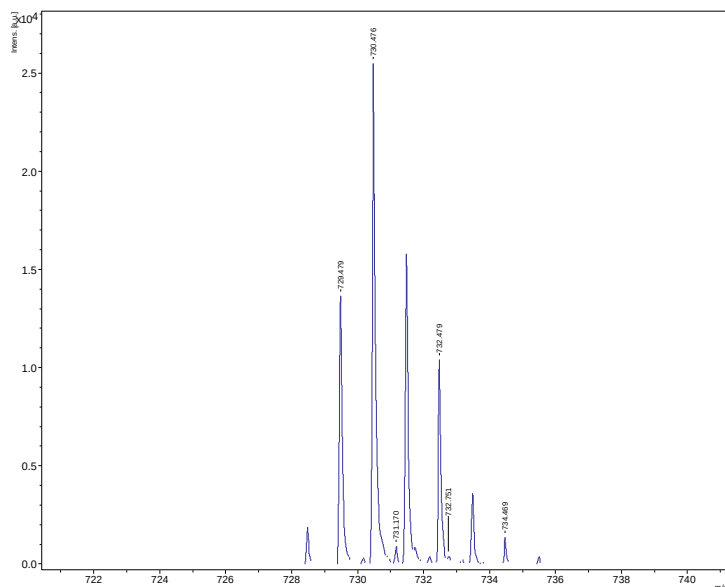


diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-EH)

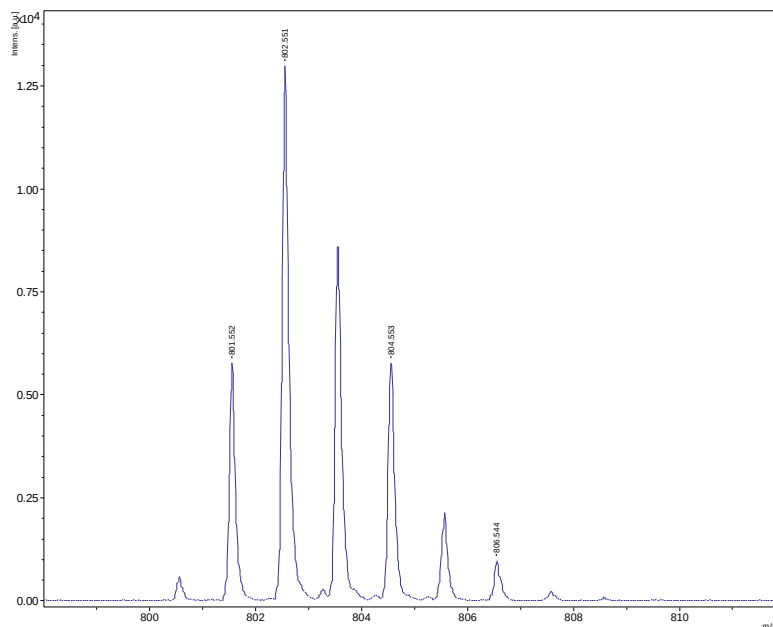


S4 MALDI spectra for the BTR-dialdehyde and BTR-analogue materials

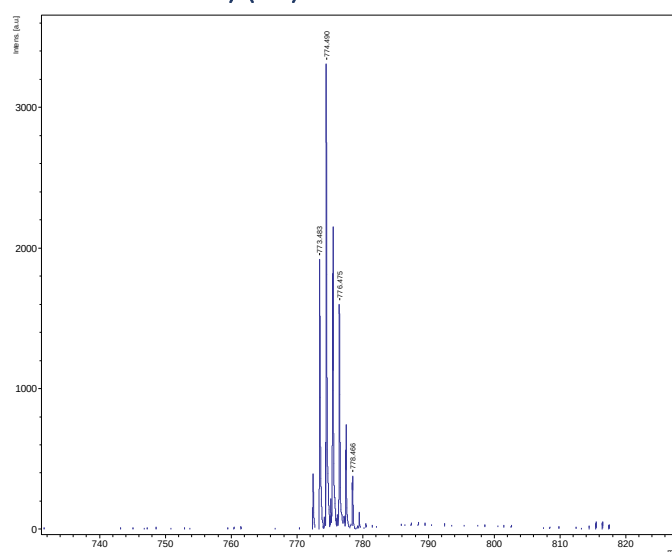
4.1 2,2'-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



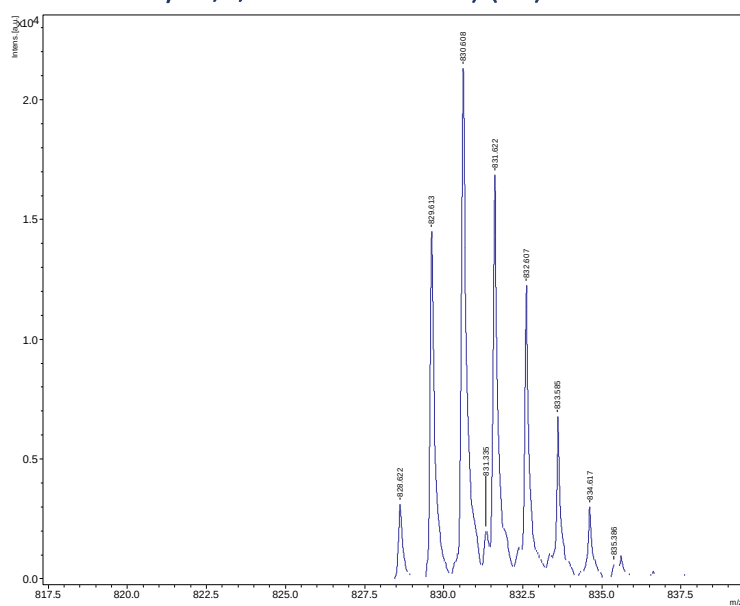
4.2 ((2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (11)



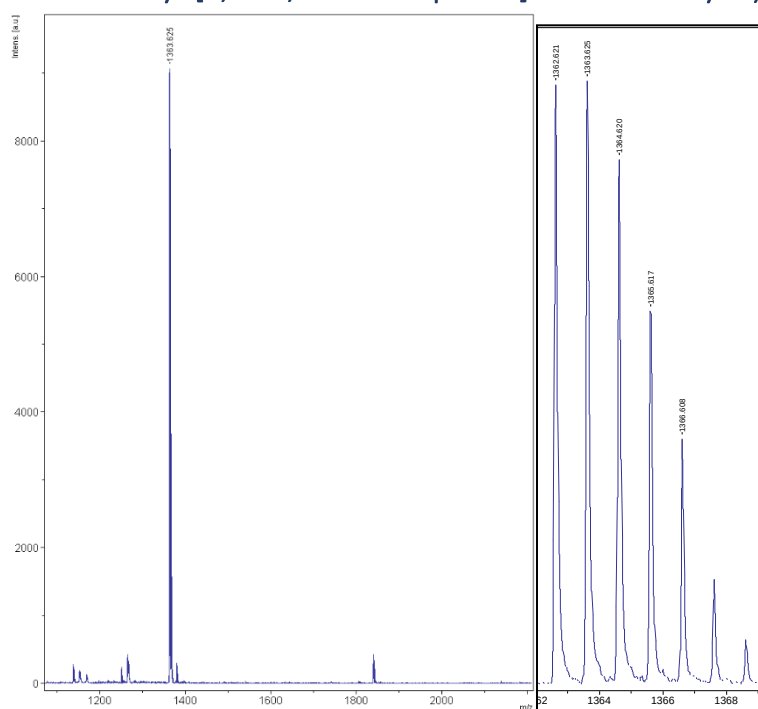
4.3 2,2'-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12)



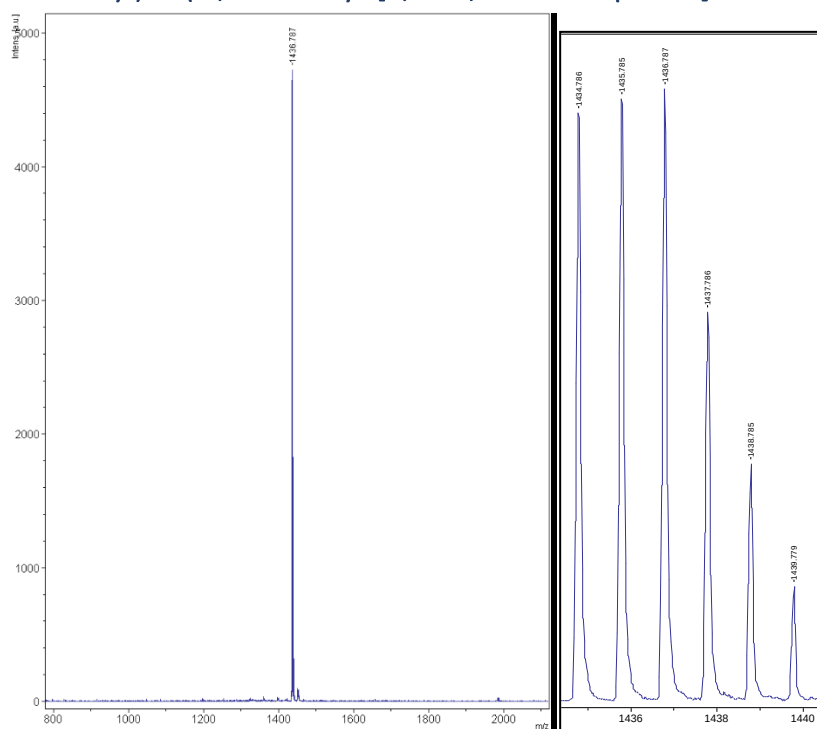
4.4 2,2'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13)



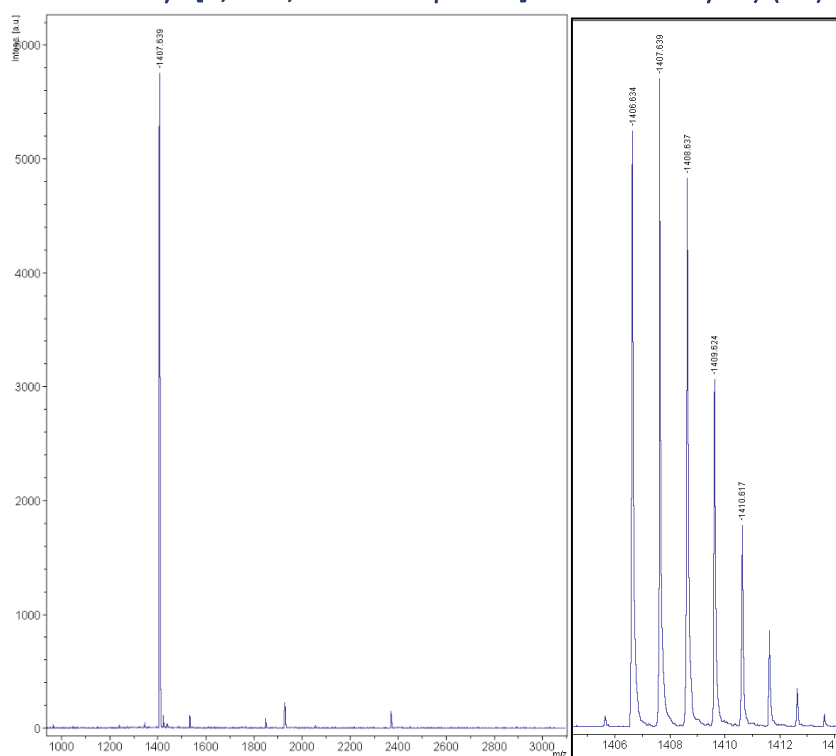
4.5 5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (15)



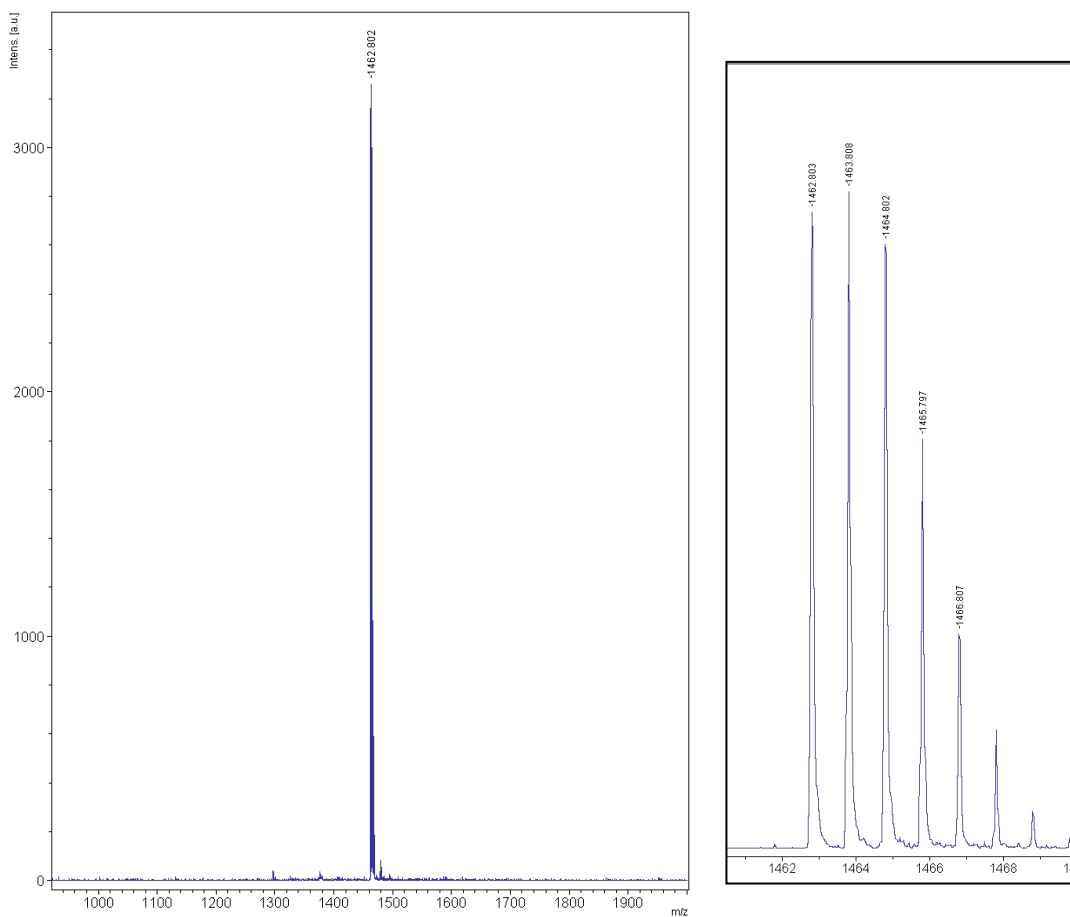
4.6 5'',5''''-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (16)



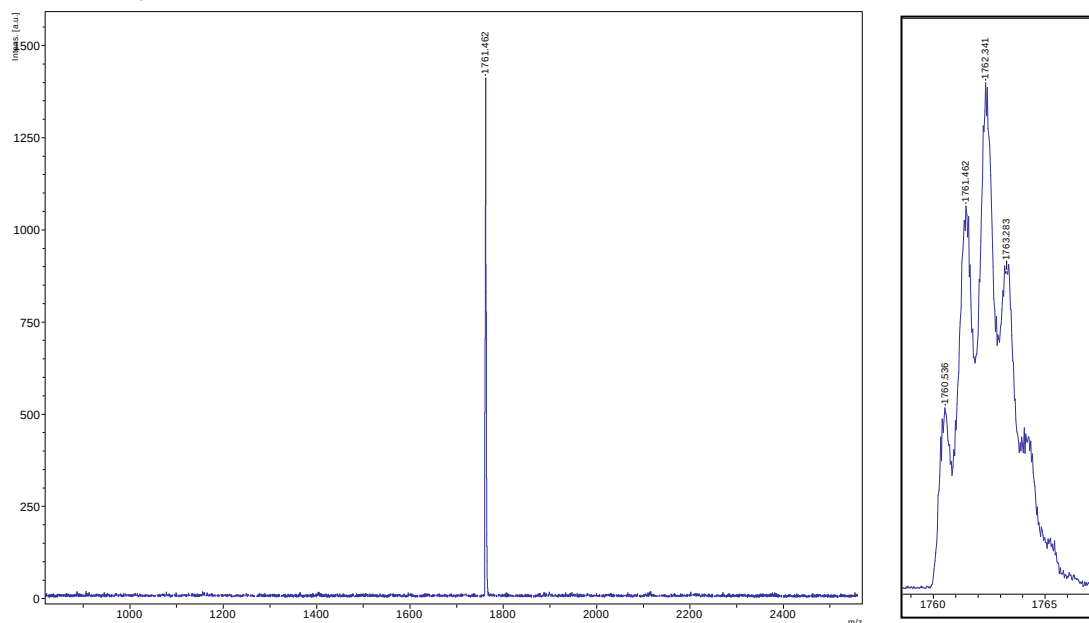
4.7 5'',5''''-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (17)



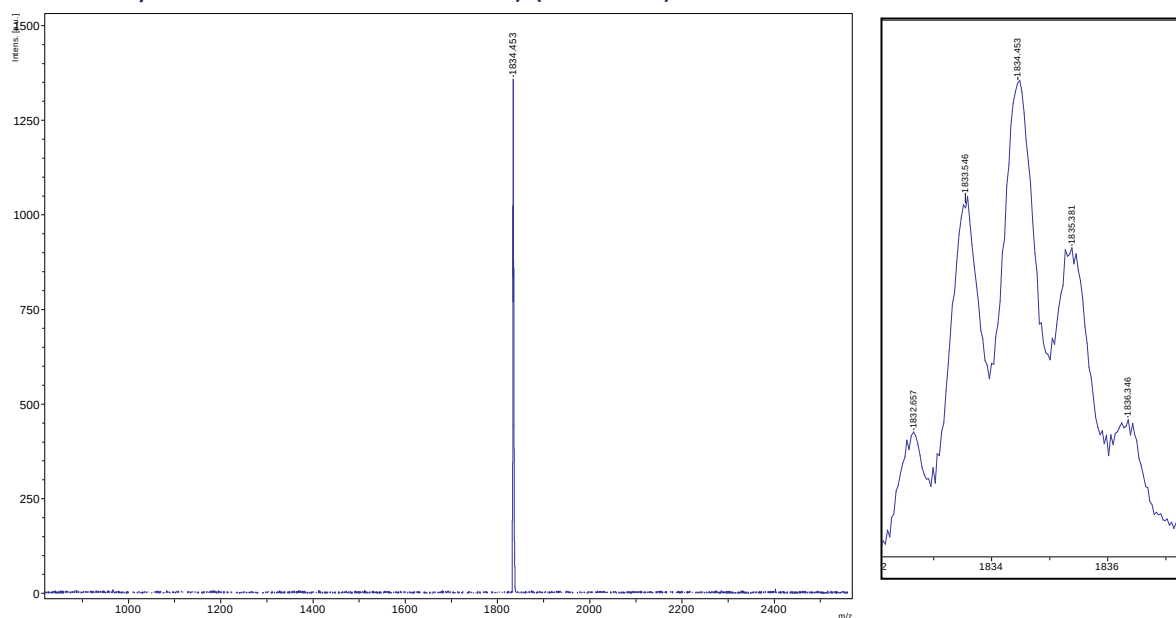
4.8 5'',5''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (18)



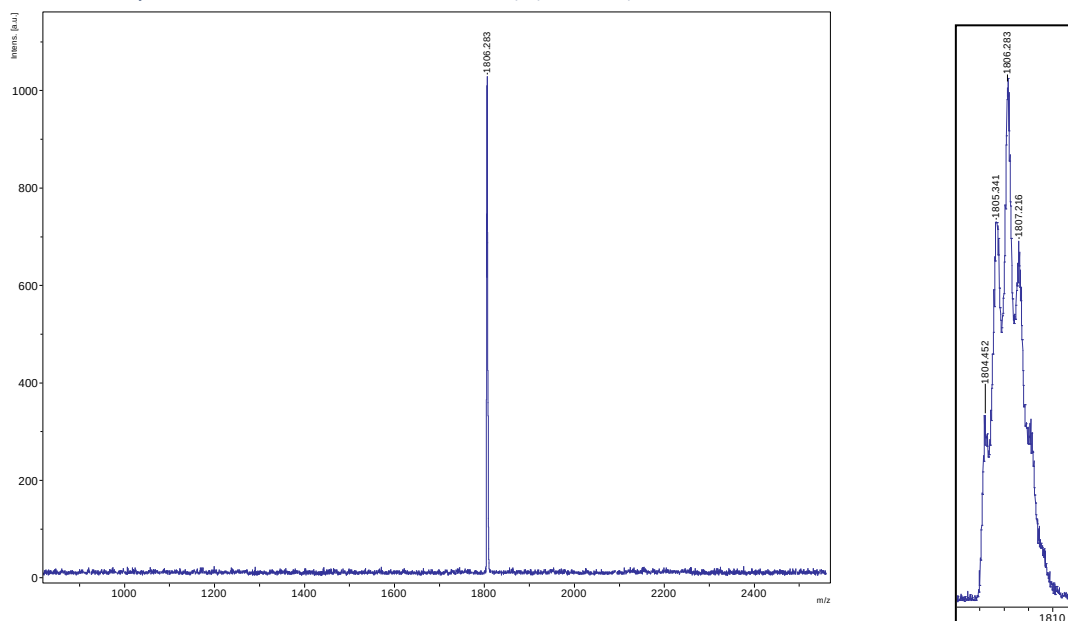
4.9 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis((2-ethylhexyl)thio)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-TE)



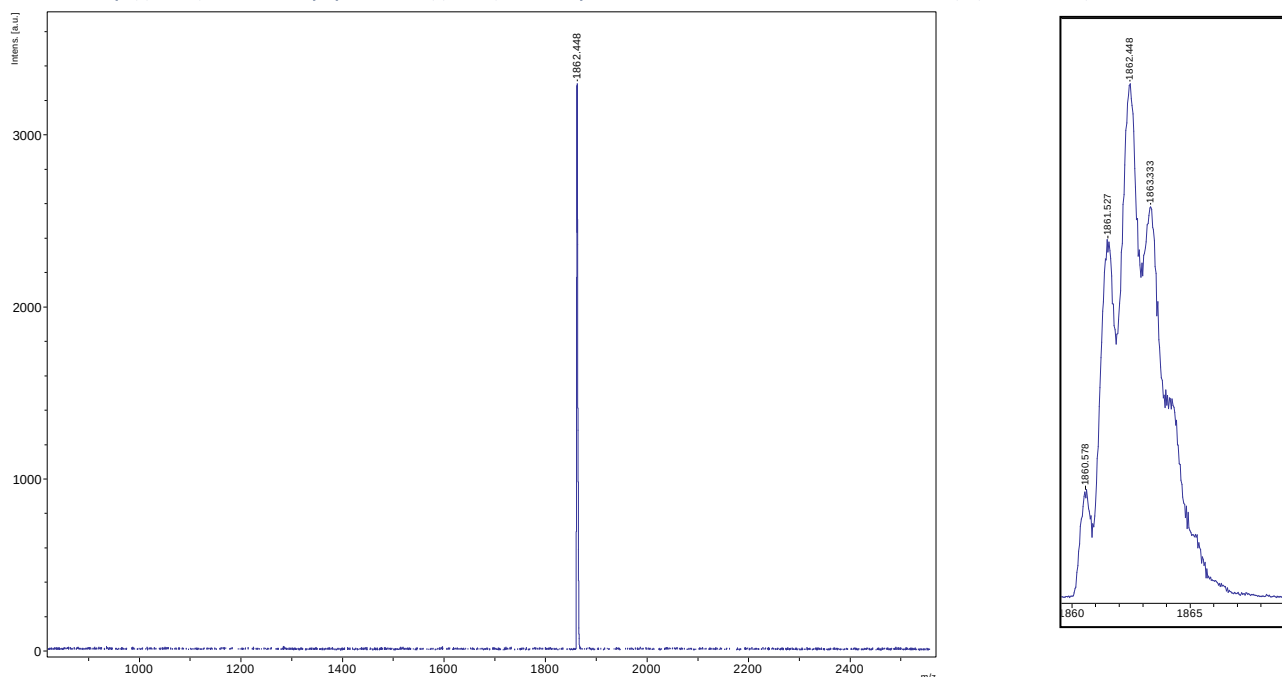
4.10 (5Z,5'Z)-5,5'-((5'',5''''-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-TIPS)



4.11 (5Z,5'Z)-5,5'-((5'',5'''-(4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-H)



4.12 (5Z,5'Z)-5,5'-((5'',5'''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (BTR-EH)



S5 Thermogravimetric Thermograms

Analysis

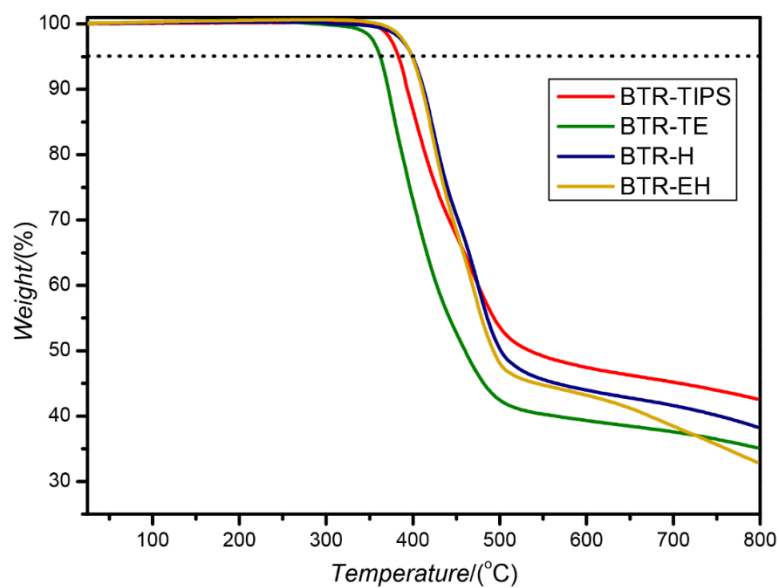


Figure S5.1. TGA thermogram for the BTR analogue materials

S6 DSC thermograms

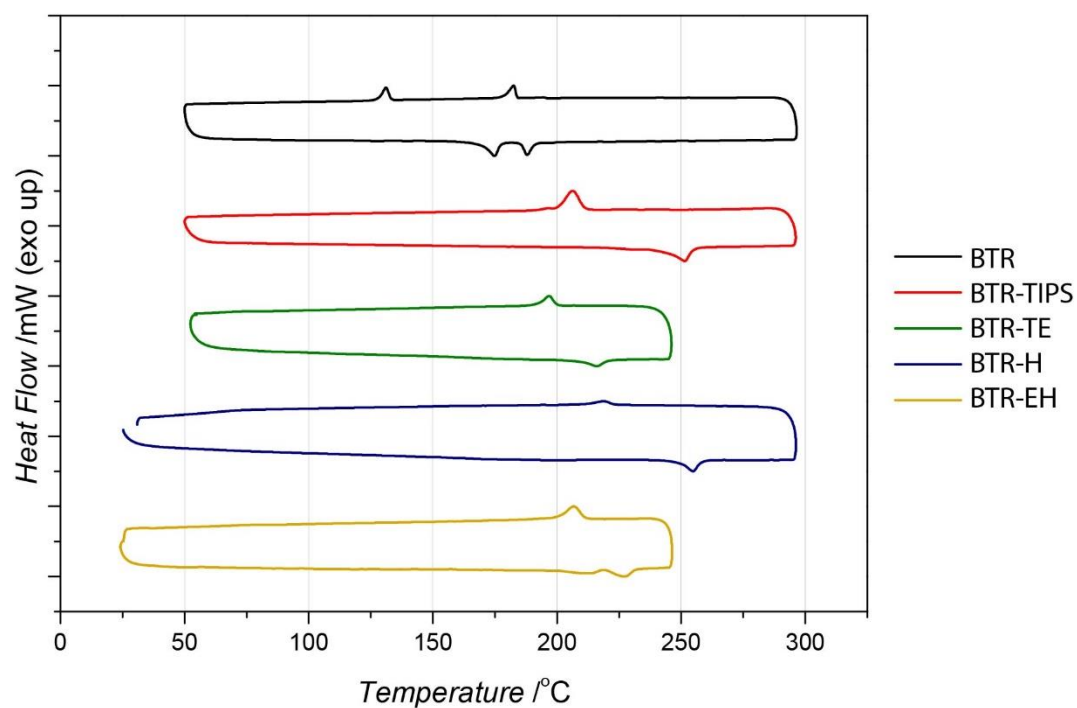


Figure S6.1. Normalized DSC thermograms for the BTR analogues.

S7 Solubility measurements

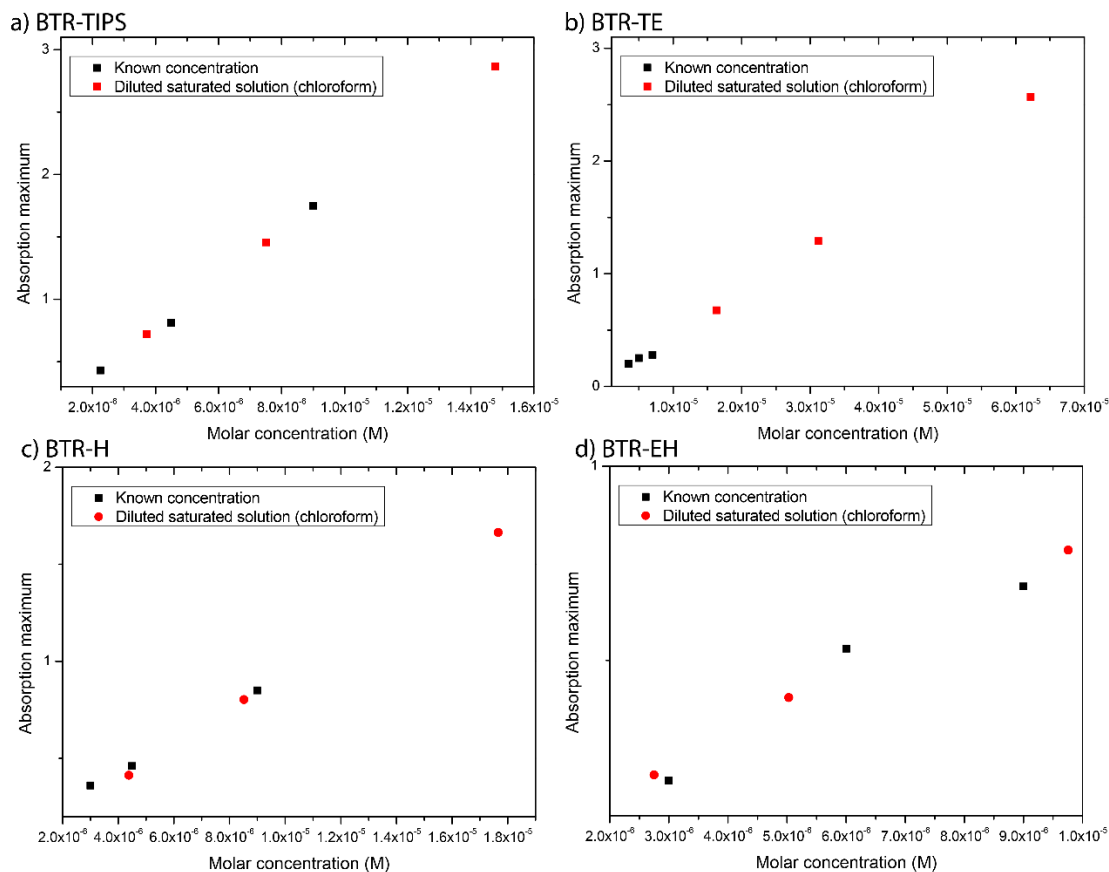


Figure S7.1. Plot of absorption maximum vs. solution concentration for a) BTR-TIPS, b) BTR-TE, c) BTR-H and d) BTR-EH analogues, allowing the derivation of solubility of the analogues in chloroform. Saturated solutions were made up, diluted by a known factor and had their absorption measured. This was compared to the maxima of solutions of known concentration.

S8 Photoluminescence spectra

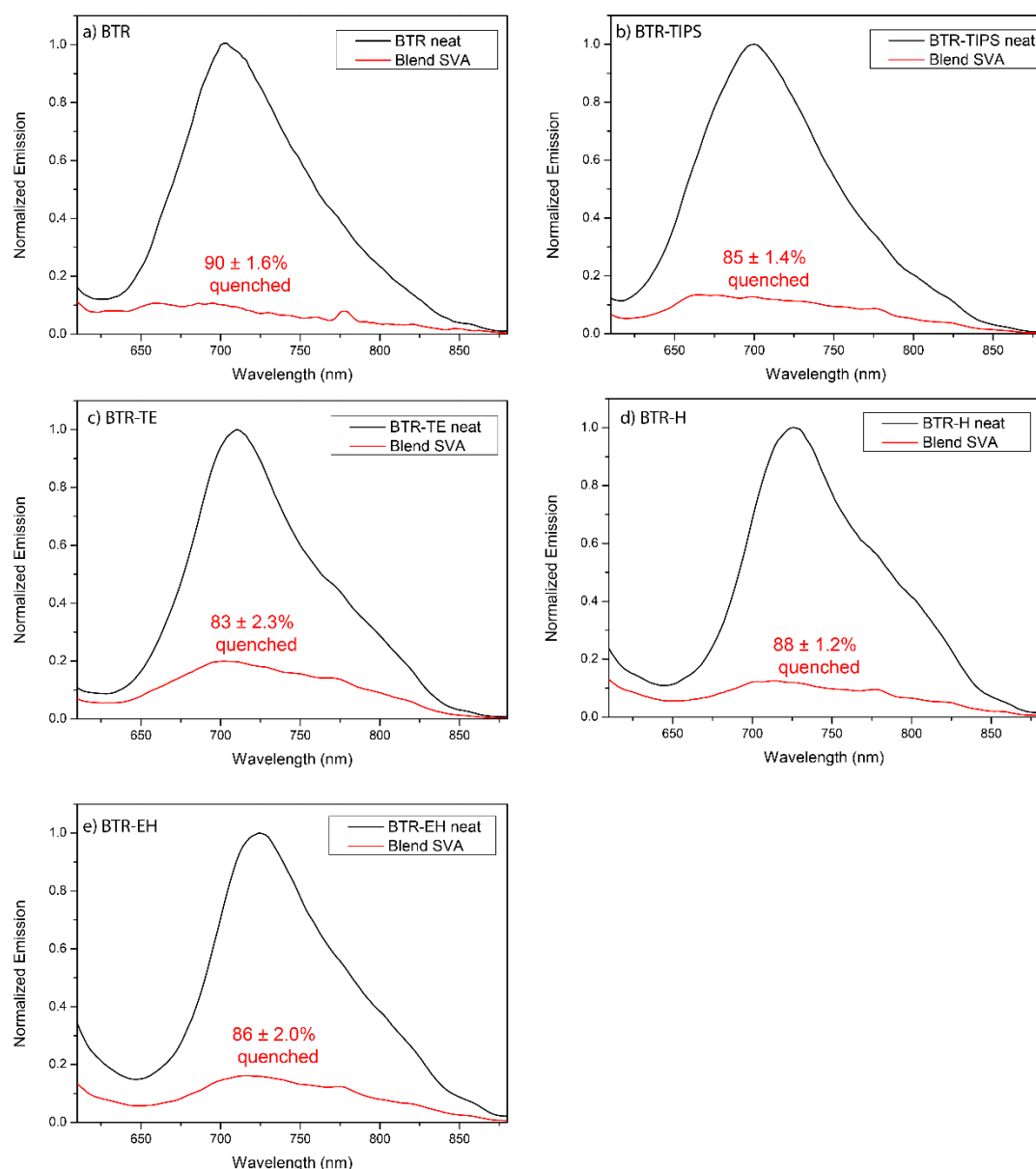


Figure S8.1. Photoluminescence spectra of a) BTR, b) BTR-TIPS, c) BTR-TE, d) BTR-H and e) BTR-EH neat films (black) and the solvent-vapor annealed blends (reds) to show quenching of emission with the introduction of PC₇₁BM. Films were excited at 580 nm and four measurements were conducted by rotating the measured film by 90° each time to gain an average intensity spectra. The fluorescence intensities are corrected for the relative absorbance at 580 nm (Abs) by dividing the emission spectra by (1×10^{-Abs}). The fluorescence quenching efficiencies are as labelled.

S9 Cyclic Voltammograms

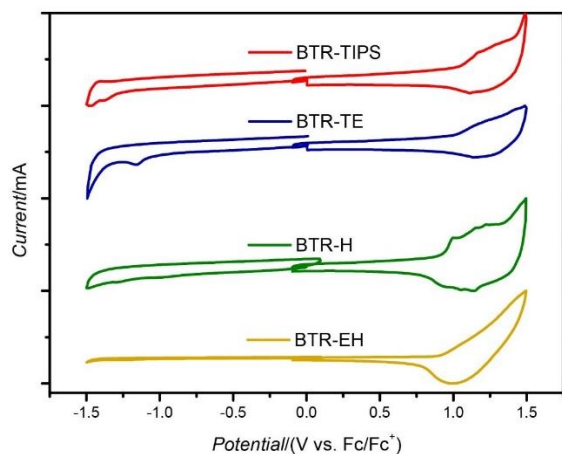


Figure S9.1. Normalized thin film cyclic voltammograms for the BTR analogues.

S10 AFM Images

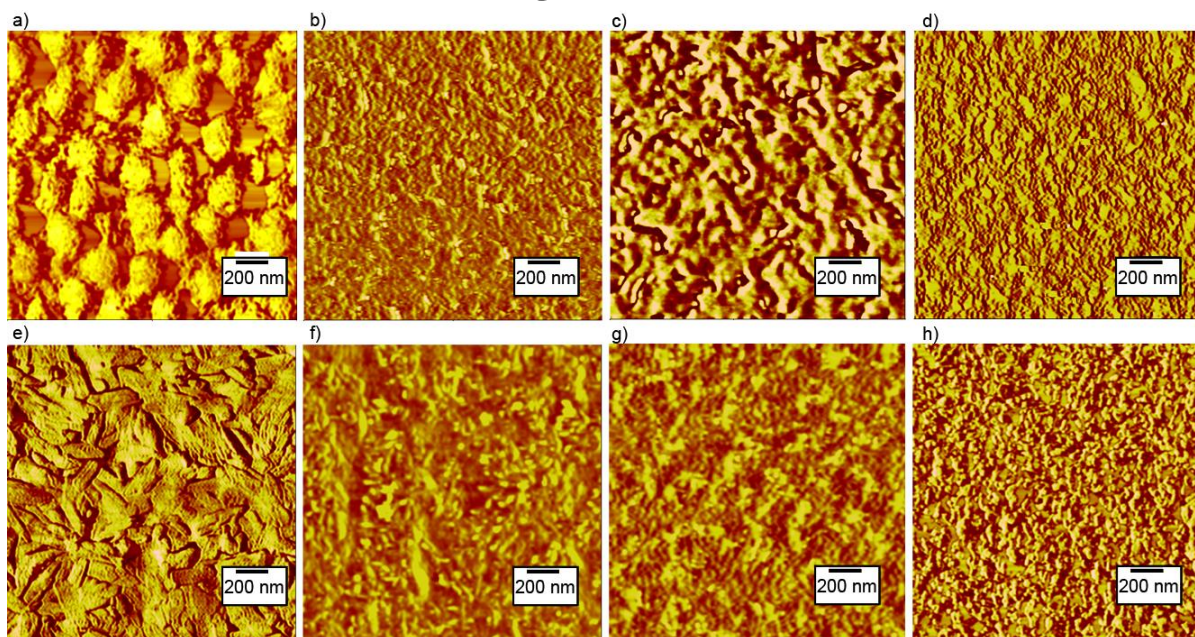
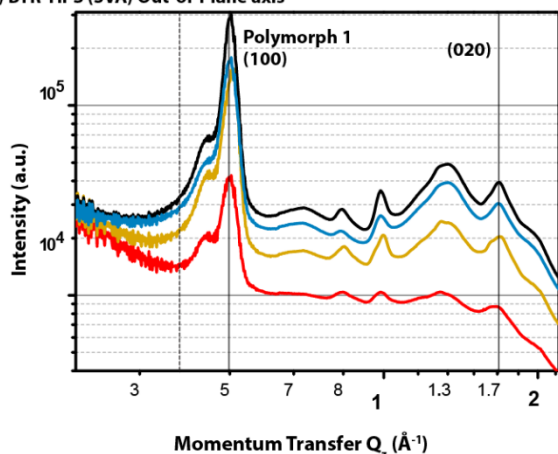


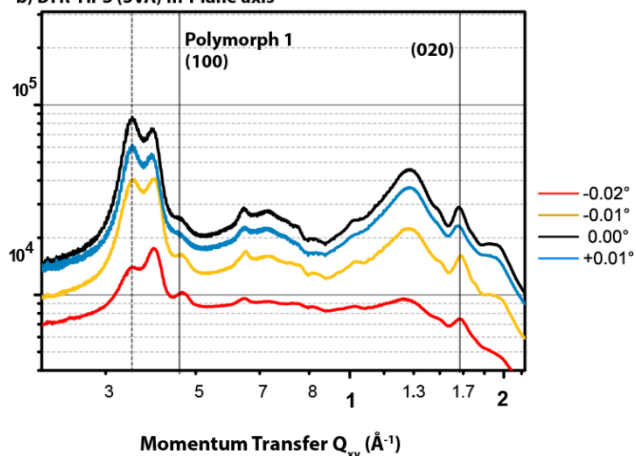
Figure S10.1. AFM images show the phase topography of an as-cast film of a 1:1 weight ratio blend of PC₇₁BM with a) BTR-TIPS, b) BTR-TE, c) BTR-H, d) BTR-EH; and solvent vapor annealed films of the same blend with e) BTR-TIPS, f) BTR-TE, g) BTR-H and h) BTR-EH.

S11 GIWAXS Depth Profiles

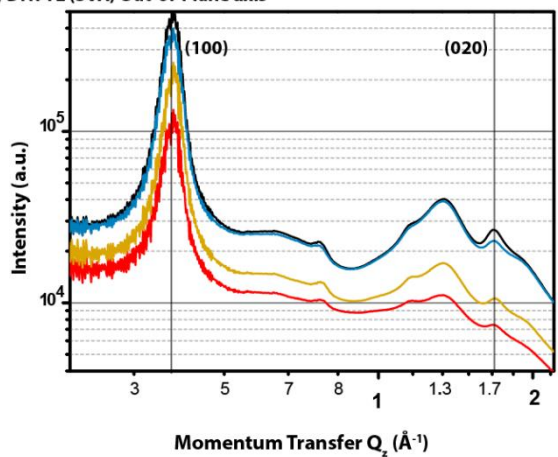
a) BTR-TIPS (SVA) Out-of-Plane axis



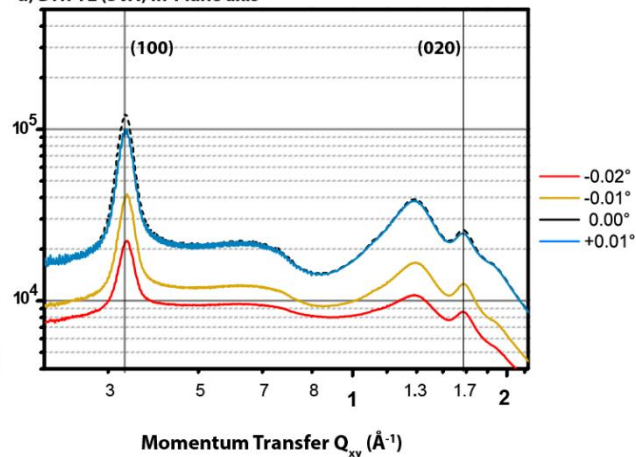
b) BTR-TIPS (SVA) In-Plane axis



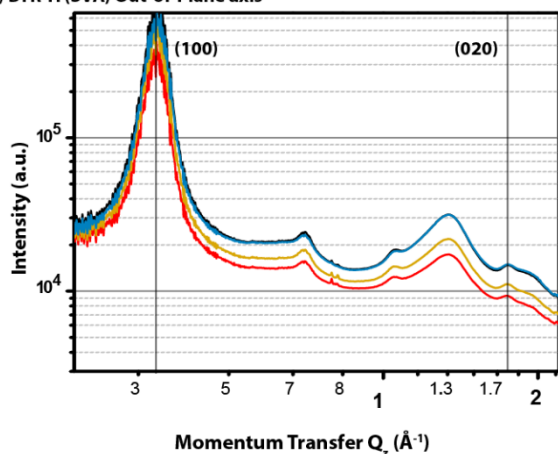
c) BTR-TE (SVA) Out-of-Plane axis



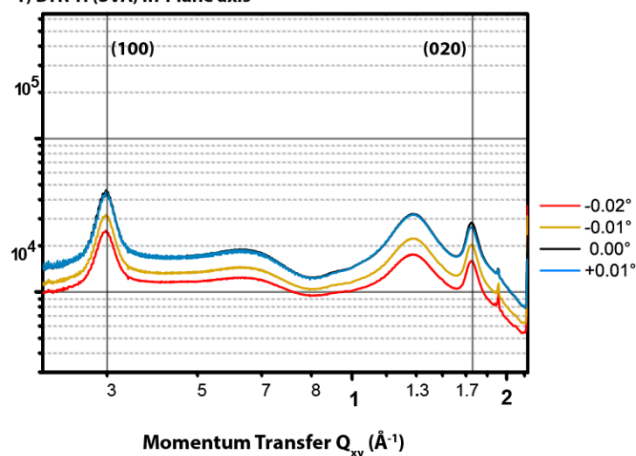
d) BTR-TE (SVA) In-Plane axis



e) BTR-H (SVA) Out-of-Plane axis



f) BTR-H (SVA) In-Plane axis



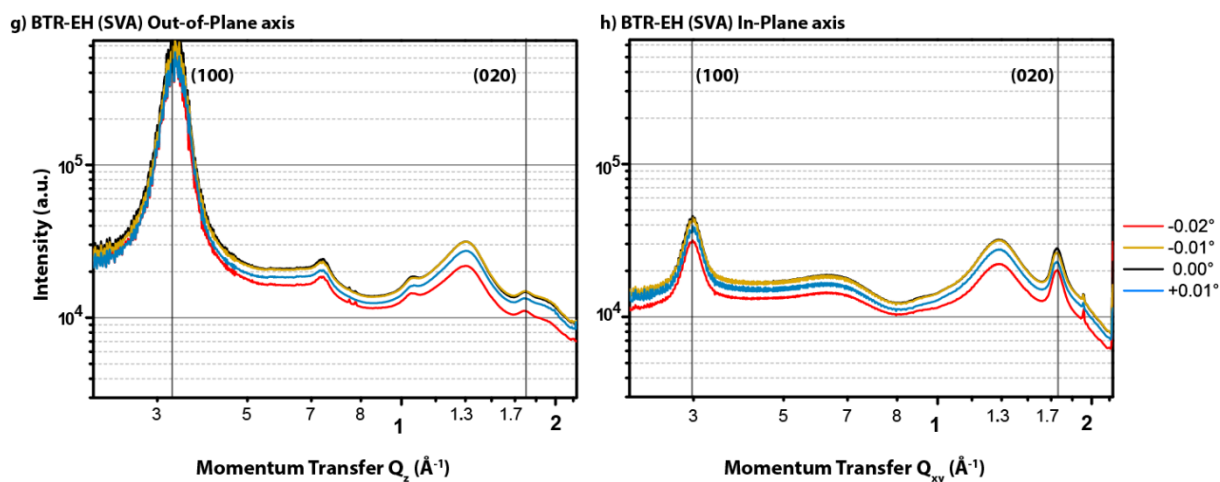
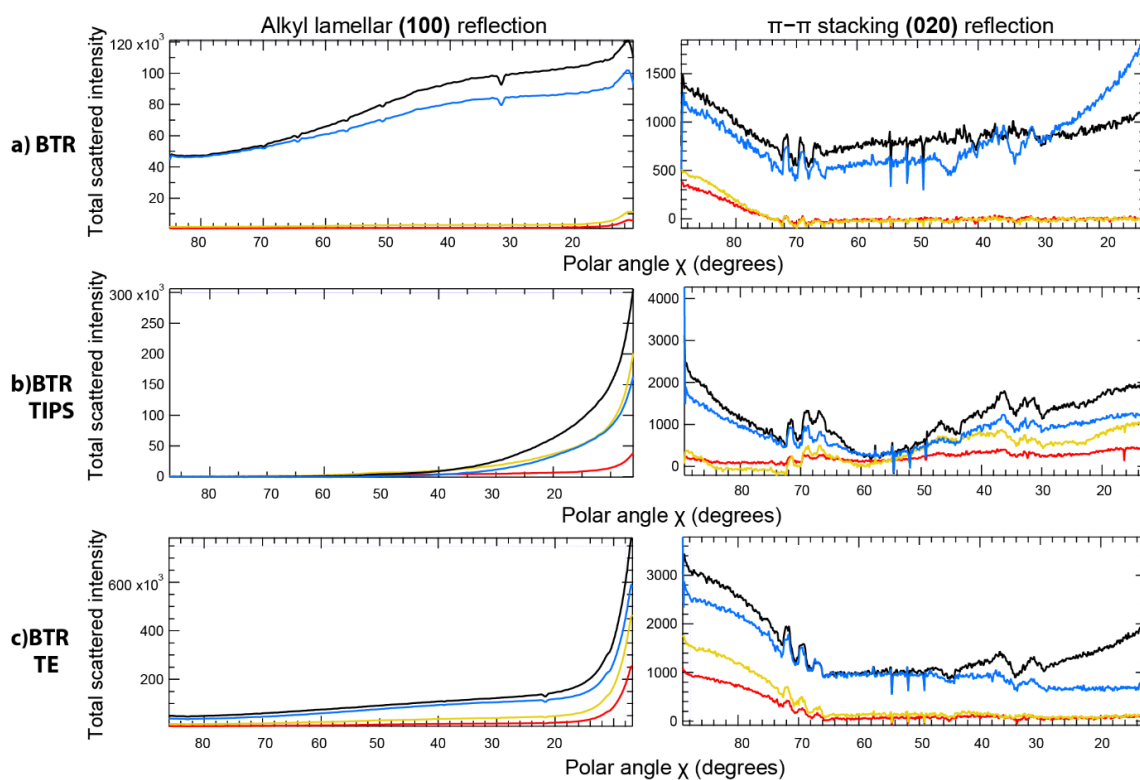


Figure S11.1. GIWAXS one-dimensional line profiles at incident angles relative to the critical angle (denoted as 0.0°) are shown in the out-of-plane and in-plane directions for BTR-TIPS (a-b), BTR-TE (c-d), BTR-H (e-f) and BTR-EH (g-h). Vertical lines are drawn to direct the eye to reflection peaks of interest, which are labelled with their unit cell indices. The dashed vertical lines for Figure S9.1a-b indicate the (100) reflection of polymorph 2 (see main text).



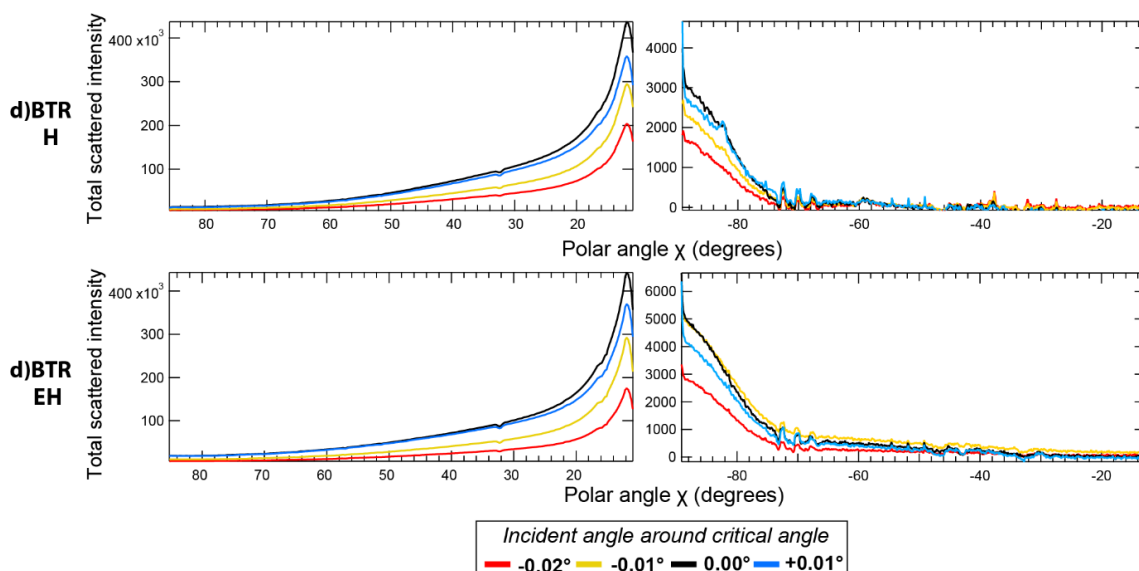


Figure S11.2. Line profiles of total scattered intensity at each polar angle of the (100) and (020) reflections taken from GIWAXS scattering patterns of a) BTR, b) BTR-TIPS, c) BTR-TE, d) BTR-H and e) BTR-EH at various incident angles around the critical angle. X values of 10° and 90° refer to the vertical and horizontal axes of the scattering pattern, respectively.

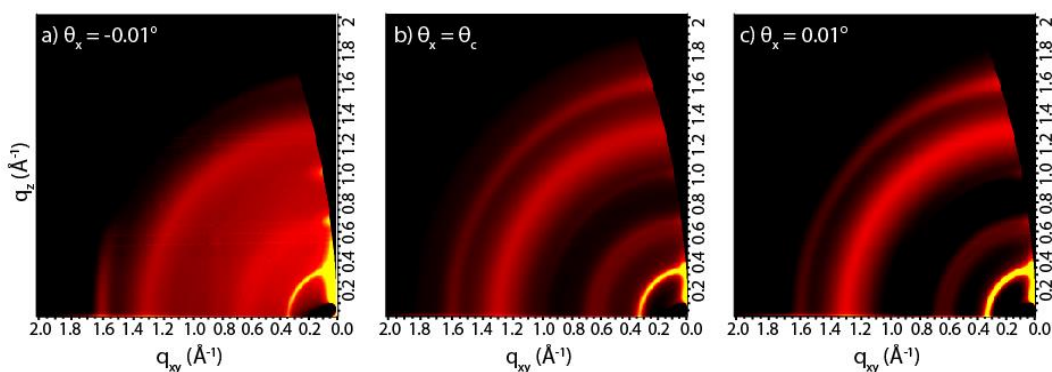


Figure S11.3. GIWAXS scattering patterns of the SVA-treated BTR:fullerene blend taken at various incident angles θ_x around the critical angle. Note the change in the (020) π -stacking reflection at $q = 1.62$ Å⁻¹.

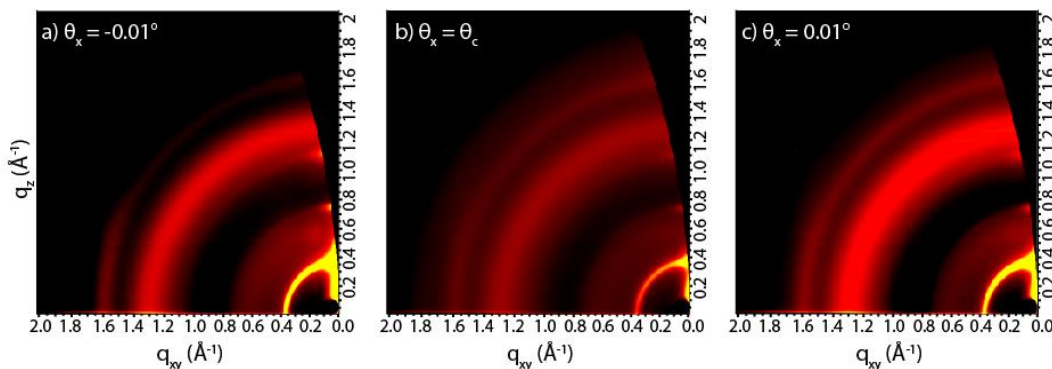
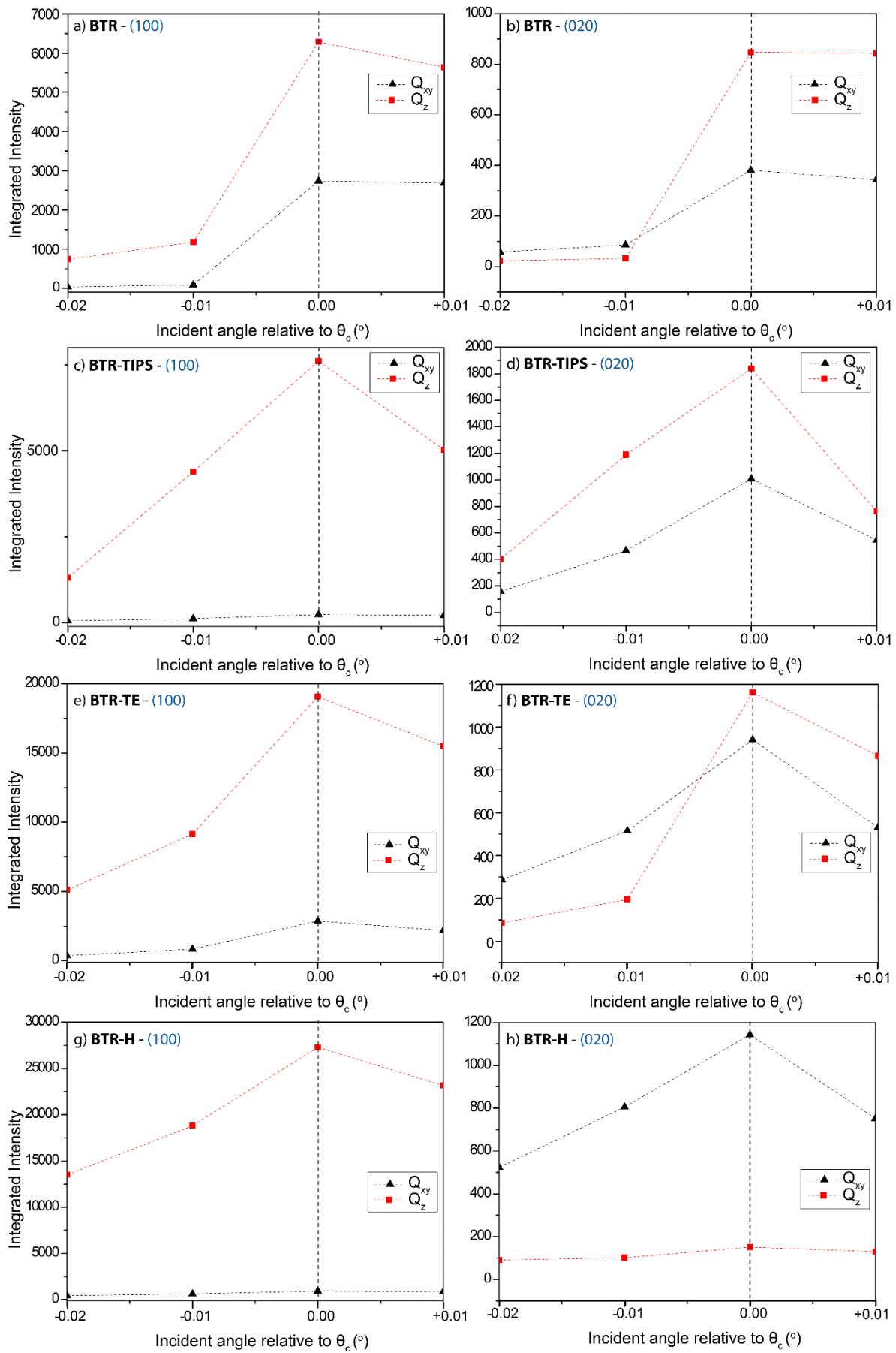


Figure S11.4. GIWAXS scattering patterns of the SVA-treated BTR-TE:fullerene blend taken at various incident angles θ_x around the critical angle. Note the change in the (020) π -stacking reflection at $q = 1.62$ Å⁻¹.



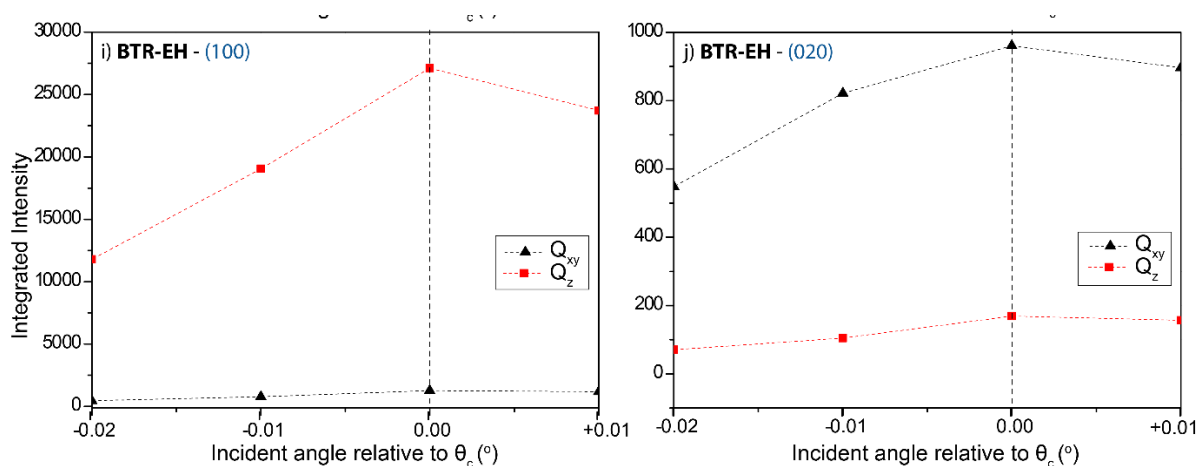
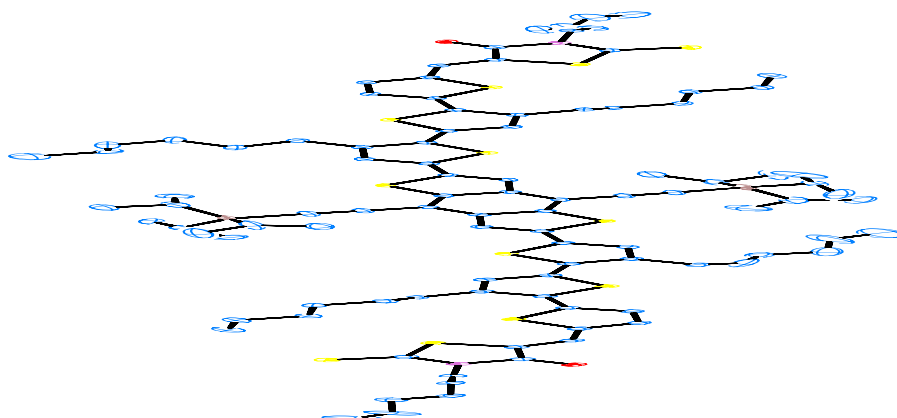


Figure S11.5. Integrated intensities of peaks corresponding to the (100) and the (020) reflections along the q_{xy} (black) and q_z (red) axes of: a-b) BTR, c-d) BTR-TIPS, e-f) BTR-TE, g-h) BTR-H and i-j) BTR-EH, against the incident angle. Peaks were determined via a Gaussian fit. Red and black dashed lines are intended to aid visualization.

S12 Crystallography



Crystal data for **BTR-TIPS**. $C_{100}H_{127}N_2O_2Si_{12}Si_2$ $M = 1829.93$, $T = 100.0(2)$ K, $\lambda = 0.710920$ Å, Triclinic, space group $P-1$, $a = 15.075(3)$, $b = 17.897(4)$, $c = 20.430(4)$ Å, $\alpha = 67.14(3)^\circ$, $\beta = 81.00(3)^\circ$, $\gamma = 77.91(3)^\circ$, $V = 4949(2)$ Å³, $Z = 2$, $D_c = 1.228$ Mg M⁻³, $\mu = 0.337$ mm⁻¹, $F(000) = 1954$, crystal size 0.07 x 0.03 x 0.005 mm. $\theta_{max} = 31.79^\circ$, 83760 reflections measured, 22426 independent reflections ($R_{int} = 0.048$) the final $R = 0.0936$ [$I > 2\sigma(I)$, 15002 data] and $wR(F^2) = 0.2895$ (all data) GOOF = 1.039. CCDC code: 1864646.

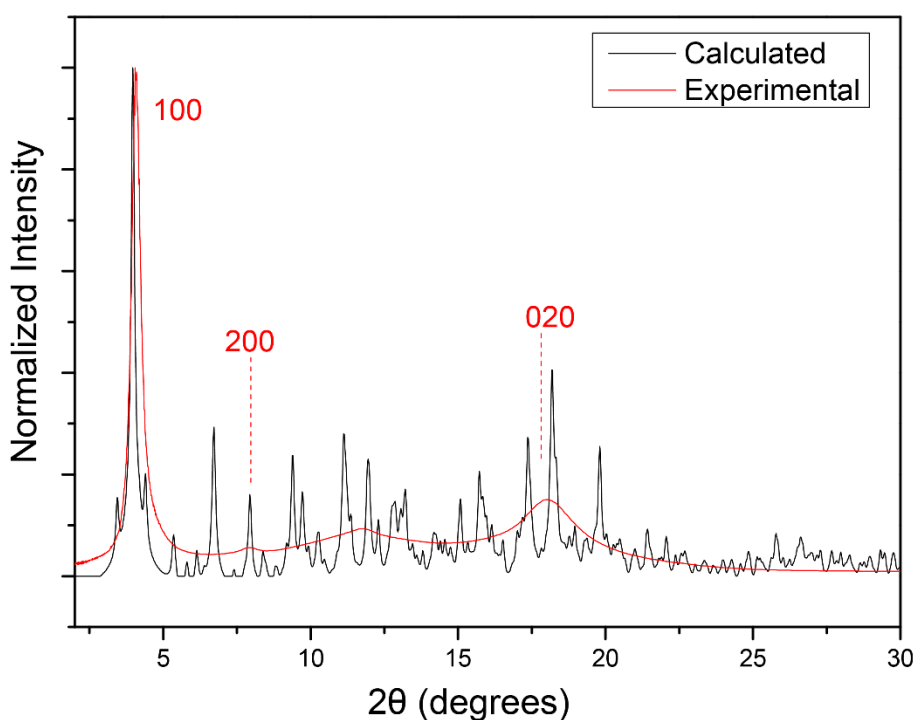


Figure S12.1. Simulated (black line) powder diffraction pattern for the BTR-TIPS structure derived from the single-crystal (CCDCs code: 1864646) and experimentally-determined GIWAXS linecut (red line) of a neat, as-cast film. Wavelength used for calculations: 1.12713 Å

S13 References

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- [2] a) N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjekar, J. R. Price, A. Riboldi-Tunncliffe, R. Williamson, T. Caradoc-Davies, *J. Synchrotron Radiat* **2014**, 22, 187; b) E. Gann, X. Gao, C.-a. Di, C. R. McNeill, *Adv. Funct. Mater.* **2014**, 24, 7211.
- [3] Y. Huang, F. Wu, M. Zhang, S. Mei, P. Shen, S. Tan, *Dyes and Pigments* **2015**, 115, 58.
- [4] H. G. Kim, S. B. Jo, C. Shim, J. Lee, J. Shin, E. C. Cho, S.-G. Ihn, Y. S. Choi, Y. Kim, K. Cho, *Journal of Materials Chemistry* **2012**, 22, 17709.
- [5] Y. Zhang, L. Gao, C. He, Q. Sun, Y. Li, *Polymer Chemistry* **2013**, 4, 1474.
- [6] B. Achala, E. M. D., E. Moneim, M. J. F., T. Brian, C. Sumit, J. E. Malika, *Journal of Polymer Science Part A: Polymer Chemistry* **2016**, 54, 316.
- [7] P. B. Geraghty, C. Lee, J. Subbiah, W. W. H. Wong, J. L. Banal, M. A. Jameel, T. A. Smith, D. J. Jones, *Beilstein J. Org. Chem* **2016**, 12, 2298.

Chapter 4

Regioregular alkyl sidechains on A-D-A oligothiophenes and their effect on morphology

4.1 Chapter introduction

With the beneficial impacts of sidechain engineering on the OPV performance of **BTR** established,^[119] the next logical step was to assess whether the application of these proven techniques on similar high-performance semiconducting materials would also confer the same benefits. As discussed in Chapter 2, the repositioning of the oligothiophene π -bridge sidechains of **BTR** into a regioregular orientation with the sidechains directed away from the benzodithiophene core was one such technique, and was theorized to confer improved π - π stacking interactions (with the observed increased intermolecular charge transport mobilities resulting from this) through the minimization of steric bulk around the core moiety.

The work in this chapter sought to apply this sidechain engineering technique to a series of oligothiophene-based semiconductors. These type of materials have been the subject of significant interest in the literature, having first been investigated as early as the 1980s for organic field-effect transistor applications,^[190] and with the advent of push-pull architectures they have also gained popularity as electron-rich cores end-capped by electron-poor moieties as acceptor-donor-acceptor (A-D-A) structured OPV p-type materials.^[191] Over this time they have demonstrated good charge transport properties, high degrees of polarizability and are known to offer facile tunability of their optical and electrochemical properties.^[165d, 191c, 192] Oligothiophene-based materials also possess a high degree of industrial relevancy as they are synthetically and structurally simple molecules, relative to other high-performance OPV materials in the literature. The majority of these more complex materials are generally comprised of a combination of multiple electron-rich and electron-poor moieties to create push-pull type architectures, frequently resulting in atomic masses of >2000.

In 2015 Chen et al. reported a series of A-D-A oligothiophenes (Figure 4-1), amongst which was the first p-type small molecular material (**DRCN5T**) to feature a BHJ PCE of >10% when combined with PC₇₁BM,^[118] which has since been incorporated in all-small-molecular OPV devices with an indacenodithiophene acceptor to exhibit PCEs of >8%.^[193] The original study examined oligothiophenes end-capped by electron-poor 2-(1,1-dicyanomethylene)rhodanine (**CHR**) moieties, and varied the oligothiophene conjugation length from 4-9 thiophene units. An odd-even correlation was observed between the conjugation length and the OPV device performance, with the odd-numbered, axisymmetric oligothiophenes found to possess higher J_{SC}s and hole

mobilities than their even-numbered, centrosymmetric counterparts. This was attributed to the large dipole moment change upon excitation exhibited by the odd-numbered oligothiophenes relative to the even-numbered, which was expected to facilitate intramolecular charge disassociation. Morphologically speaking, the even-numbered oligothiophenes were observed by transmission electron microscopy to possess smaller domains (~20 nm) in films of the SVA-treated blend with a higher degree of interpenetration, whereas the odd-numbered possessed larger domains (~40 nm) unfavourable for exciton diffusion and disassociation. This difference suggested a correlation between the degree of crystallinity of the bulk material and the nature of the oligothiophene molecular symmetry. In addition to this, all the oligothiophene devices exhibited high FF values (0.68) except those incorporating **DRCN6T** (0.58), which reflected the fact that among all the DFT-calculated structures only it possessed a nonplanar structure.

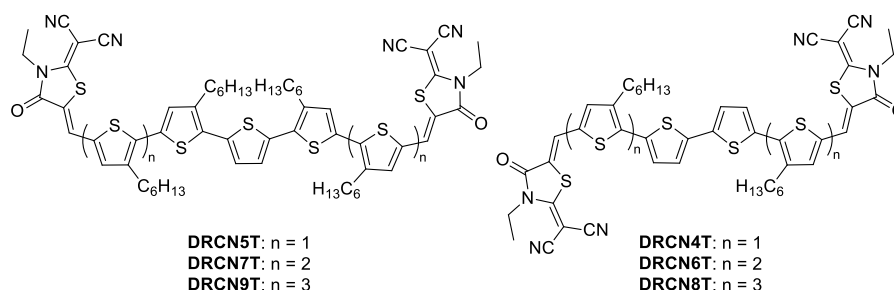


Figure 4-1: Chemical structures of the oligothiophenes studied by Chen et al. discussed in the text

The motivation behind the work in this chapter stemmed from the observation that the materials designed by Chen et al. all featured sidechains oriented towards the centre of the molecule, with the hypothesis that if these sidechains were instead oriented to point outwards away from the centre in a regioregular manner (as with **BTR**), this could potentially alleviate any steric interference and increase intermolecular charge transport by improving π - π interactions. It is worthwhile to mention that though studies by Wessendorf et al. have shown that the use of outwards-facing sidechains appended to oligothiophenes have indeed improved π -stacking interactions,^[137a, 194] these modifications have nonetheless resulted in overall lowered OPV efficiencies relative to analogues with inwards-facing sidechains.^[137a, 194-195] As shown from comparing the performances of the analogues pre- and post-annealing, this trade-off is believed to result from the inwards-facing sidechains conferring a larger diffusive motion of the molecules during the process of solvent vapor annealing. This facilitates molecular rearrangement and allows the kinetically-trapped morphology formed from the spin-coating deposition process to move towards a thermodynamically-favoured morphology optimized for light-harvesting. Furthermore, results have suggested that a *lower* degree of planarization in the conjugated backbone could confer increased solvation during the SVA process, with correspondingly improved morphologies and performances resulting from this.

In order to have the best of both worlds, in this chapter it was hypothesized that the potential decreased molecular diffusion during the SVA process conferred by the outwards-facing sidechains could be offset while still maintaining an increased π -stacking interaction. This was to be done by introducing sidechains of different lengths (namely, hexyl and octyl sidechains) onto the oligothiophene analogues, with increased molecular diffusion shown to be conferred by longer sidechains on polymeric thiophenes.^[56, 58] To assess these sidechain engineering effects across multiple molecular substrates of relevance to the literature, three end-group acceptors of varying electron affinities commonly paired with oligothiophenes to tune the relevant energy levels are studied. In addition to the **CHR-** moiety used by Chen et al., in this work a malononitrile (**MN**) and hexyl rhodanine (**HR**) moiety are included.^[196] These alterations are made on both the axisymmetric pentathiophene and a centrosymmetric hexathiophene substrate, in order to determine the effectiveness of the sidechain engineering efforts on not only the best-performing oligothiophene substrate (as shown by the aforementioned study), but also to assess whether the sidechain repositioning can planarize the previously-observed twisted nature of the hexathiophene backbone. These efforts resulted in the design of the twelve p-type oligothiophene based materials in Figure 4-2.

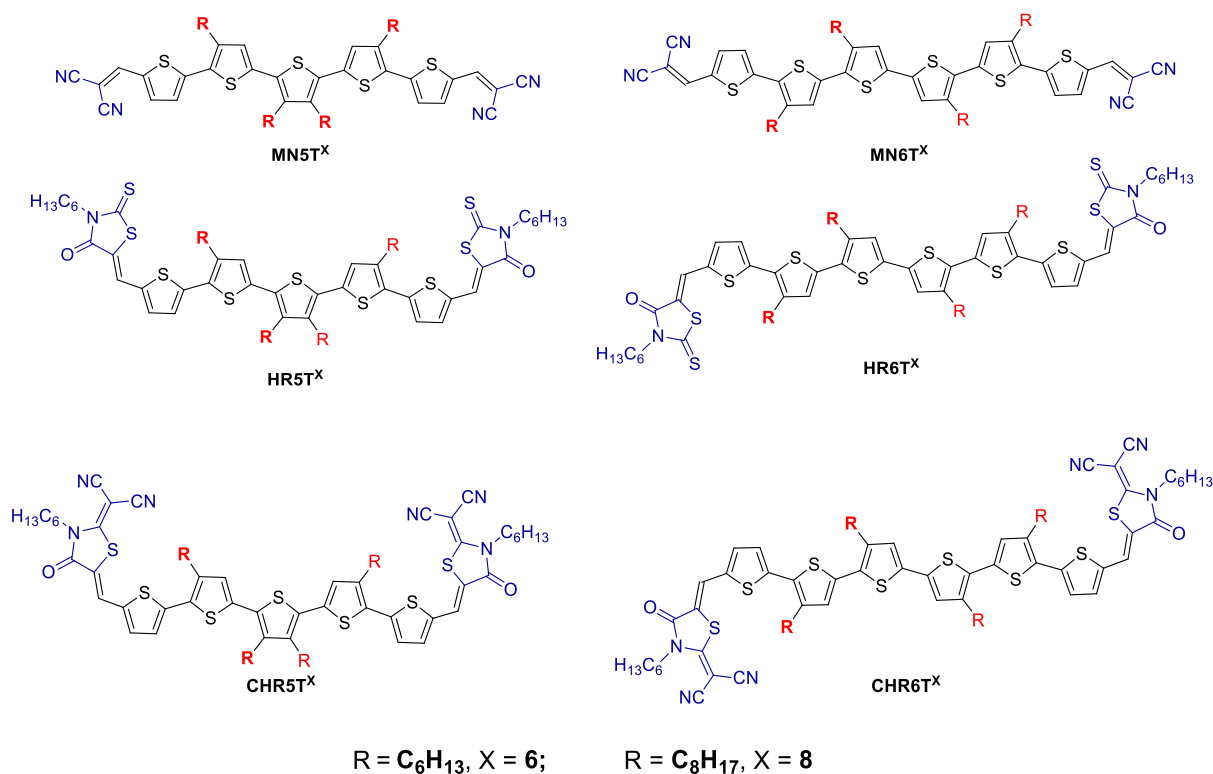


Figure 4-2: Chemical structures of the oligothiophenes designed and studied in this chapter

The investigations in this chapter focus on furthering efforts in the prediction of bulk properties from molecular structure, with such a predictive structure-morphology paradigm have eluded the OPV field so far. This was carried out by assessing the 1) annealing conditions that would result in optimal thin-film morphologies for blends of our oligothiophenes with PC₇₁BM in OPV devices, and 2) morphological impacts on the bulk material as a function of the sidechain engineering efforts performed on the oligothiophene

molecules. From these studies it was shown that OPV performances are maximized when different end-group moieties are matched with different oligothiophene conjugation lengths, with the highest PCEs recorded when **MN** and **CHR** end-groups are matched with pentathiophene substrates, and when **HR** end-groups are paired with hexathiophenes. A slight but consistent increase in performance was also observed for the octyl-functionalized materials relative to the hexyl analogues. An in-depth GIWAXS analysis was carried out on both the neat and blend films, and it was found that a majority of the oligothiophene films possessed scattering patterns with complex crystallinities. Of these films an increase in the degree of crystallinity was correlated to analogues with longer sidechains, suggesting that it was indeed possible for these lengthened sidechains to have conferred a greater molecular mobility during the annealing process, therefore resulting in larger, crystallized domains.

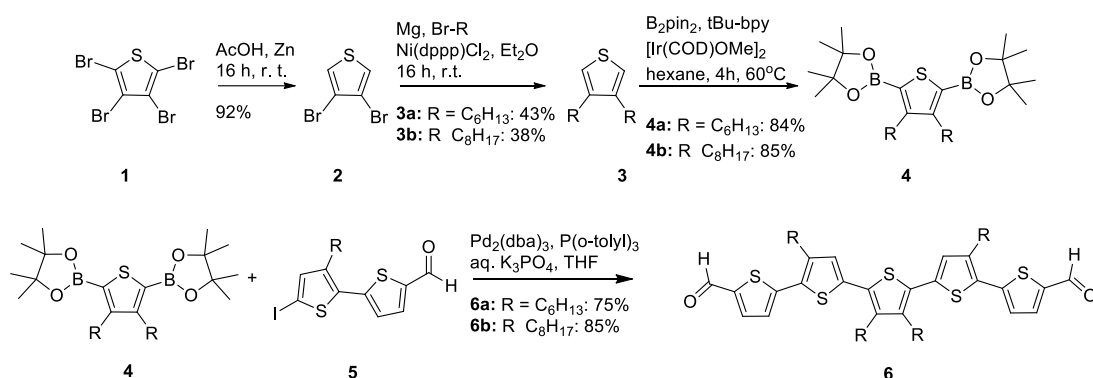
4.2 Contribution from the candidate

Except where noted in this paragraph, the candidate was responsible for the synthesis, purification and full characterization of all the octyl-functionalized materials described in this study. Following the initial synthesis of limited quantities of all hexyl-functionalized materials by Dr. Fadi Jradi of the Marder Group (Georgia Institute of Technology), the candidate was responsible for synthesis and purification of larger quantities of all materials, as well as their full characterization. Sample preparation, data collection/processing and interpretation of the GIWAXS measurements was performed by the candidate, with Dr. Valerie Mitchell and Prof. Christopher McNeill providing feedback on the interpretations of this data. Professor Jonathan White was responsible for obtaining the single-crystal structures discussed in this chapter, and Dr. Jegadesan Subbiah was responsible for AFM studies, OPV device fabrication and device characterization.

4.3 Oligothiophene synthesis

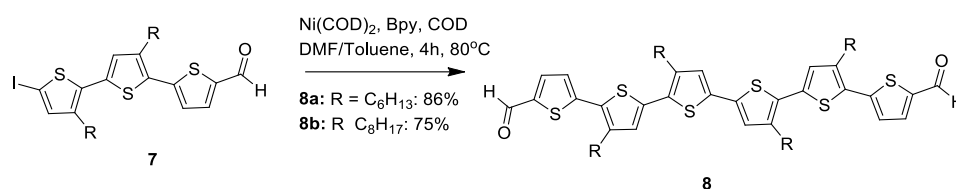
Full experimental details for the synthesis of the twelve oligothiophene analogues and their precursors are given in Section 4.8.2. In summary, this synthesis proceeded in two parts: forming the oligothiophene dialdehydes, and then coupling them to their end-group acceptors. The route to these dialdehydes utilized 3-alkylated oligothiophene components previously synthesized for the BT^xR analogue synthesis in Chapter 2, and synthetic details for these precursors can be found in that chapter

To form the alkylated pentathiophenes the iodinated 3-alkyl bithiophenes **5a** and **5b** are cross-coupled via a Suzuki reaction to the central bis-borylated dialkylated thiophene core **4a** and **4b**, in order to form the hexyl and octyl-functionalized pentathiophene dialdehydes **6a** and **6b** respectively (Scheme 4-1). These cores were themselves synthesized according to a procedure in the literature,^[197] where tetrabromothiophene **1** underwent a selective zinc-mediated reductive debromination, with the resulting 3,4-dibromothiophene **2** utilized as the substrate for a Kumada coupling with the corresponding alkyl bromide to form the 3, 4-dihexyl- or dioctyl- thiophenes **3a** and **3b**, respectively. These then underwent an iridium-catalyzed C-H borylation to yield the bis-borylated thiophene cores **4a** and **4b** in high yields. Following this, the pentathiophene dialdehydes were obtained via Suzuki coupling. Purification was greatly facilitated by precipitation of the crude material in isopropanol which removed all unreacted starting materials, and high yields of **6a** and **6b** were obtained.



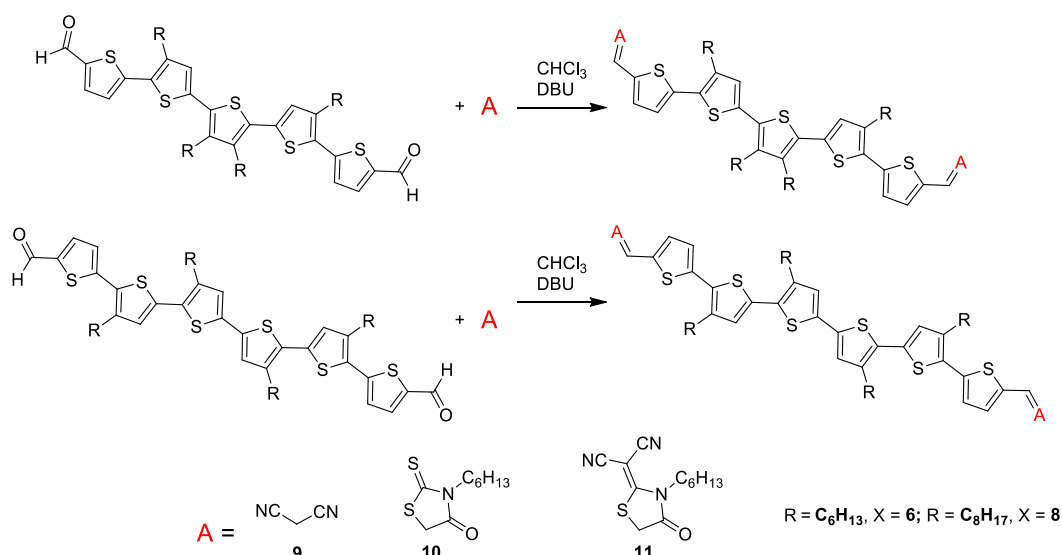
Scheme 4-1: Pentathiophene dialdehyde synthetic pathway

For the alkylated hexathiophene dialdehydes, instead of a central core here the correspondingly-alkylated iodinated terthiophenes **7a** and **7b** were dimerized through a Yamamoto-type nickel-mediated homocoupling modified from a procedure in the literature (Scheme 4-2).^[198] Again, precipitation in isopropanol was utilized prior to purification via column chromatography, and yields of 75-80% were obtained for **8a** and **8b**.



Scheme 4-2: Hexathiophene dialdehyde synthetic pathway

With the required penta- and hexa- thiophene dialdehydes in hand, it was a simple matter to use the Knoevenagel condensation conditions previously discussed in Chapters 2 and 3 to couple the three acceptor moieties -**MN** (**9**), **HR** (**10**); and **CHR** (**11**) to the four dialdehyde cores, yielding the 12 target oligothiophene-acceptor series (Scheme 4-3). These reactions all yielded products in high yields of 60-80%, with reaction times varying based on the solubilities of the target products. Purification to the high standard required for OPV device fabrication was accomplished via a combination of silica column chromatography, size-exclusion chromatography and precipitation in isopropanol.



Scheme 4-3: Knoevenagel condensations leading to target oligothiophene analogues

4.4 Physical, spectroscopic and electrochemical properties of oligothiophenes

4.4.1 Thermal properties

The thermal behaviour of the oligothiophene series has been studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All twelve materials show good thermal stability with >5% weight loss occurring above 350°C (Figure 4-12 and Table 3) under a nitrogen atmosphere. The phase transition behaviours of the oligothiophenes were analyzed by DSC (see Figure 4-13 and Table 4 for melting point data). Consistent melting-point (T_m) trends are evident for all materials as a function of the 1) electron-poor acceptor moiety, ordered from lowest to highest as **HR**<**MN**<**CHR**, 2) the number of conjugated units in the backbone, with **5T**<**6T**, and 3) the length of the alkyl sidechains, with octyl-functionalized materials possessing a lower T_m than hexyl functionalized materials. As discussed previously, melting points are affected by the force of attraction between molecules, and as such the higher T_m possessed by the **CHR**-and

MN-functionalized materials are in good agreement with the reports from the literature which suggest a high degree of hydrogen bonding between molecules with dicyanomethylene moieties.^[196a, 196b] This bonding occurs between the malononitrile nitrogens and the vinyl protons adjacent to the oligothiophene backbone, as seen in the single-crystal structure of **MN5T**⁸ (Figure 4-6). With this in mind, it is also likely that the octyl sidechains also serve to disrupt the intermolecular packing to some degree, resulting in a lowered T_m , with this behaviour similar to that of the **BT_xR** analogues in Chapter 2.

From the DSC thermograms, it can be seen that most of the oligothiophenes possess a single melting and crystallization peak save for the hexyl-functionalized pentathiophenes, which feature more complex phase behaviours with multiple peaks on both the heating and cooling cycles. POM results however reveal no obvious morphological changes, indicating that these are likely to be subtle reorganizations of the molecular backbone or sidechains, as suggested by the low enthalpic changes of these transitions. The oligothiophenes also lack the NLC transitions common to the BTR-type materials. Curiously, unlike the other materials discussed in this thesis, a number of the oligothiophene DSC traces also exhibit small exothermic transitions upon heating, with these hypothesized to be thermally-assisted reorganizations leading to cold crystallizations of the materials. These transitions also do not exhibit visible changes under POM.

4.4.2 Absorption spectrum and electronic energy levels

UV-vis absorption spectra of the oligothiophene materials were measured in dilute chloroform solution (Figure 4-3) and as thin films cast from chloroform (Figure 4-4) with the complete data presented in Table 1. When dissolved in chloroform all twelve analogues exhibited similar absorption maxima (λ_{max}) within a narrow range of 520-540 nm, although slightly redshifted maxima could be observed as a function of the different electron-poor endgroups, with λ_{max} increasing from **HR**<**MN**<**CHR** due to increased charge-transfer character. A small redshift of ~5-10 nm can be observed as a function of increasing conjugation length, with this relatively small shift rationalized in the literature to be due to the effective conjugation length having been reached at five aryl units for similar end-capped oligothiophene substrates.^[191c] As the fundamental chromophore remains unchanged, as expected no significant difference is observed between the hexyl and octyl analogues. What is curious however is that the addition of two methylene units per sidechain results in roughly doubled ϵ_{max} values for all analogues, with this phenomenon currently unable to be explained. There is a noticeable change in the absorption spectra upon shifting from solution to the solid-state films, with all molecules manifesting redshifts of ~60-80 nm (resulting in a decreased energy gap of ~0.2-0.3 eV) along with the evolution of a vibronic shoulder. This new absorption band is attributed to an enhanced electronic transition stemming from increased π - π stacking (resulting in H-aggregate formation) and crystallinity in the thin-film. The wavelength maxima for both peaks are presented in Table 1. Not all the analogues experience these increased interactions to the same degree; **CHR5T**⁶, **CHR5T**⁸, **HR 6T**⁸ and **CHR6T**⁶ all possess relatively diminished shoulder absorption peaks. Optical energy gaps (E_g^{opt}) were calculated from the absorption onsets

of the solid-state spectra (Table 1). The oligothiophenes were found to possess similar energy gaps regardless of the end-group acceptor, save for the **MN**-functionalized analogues which feature slightly larger E_g^{opt} values of around ~ 0.05 eV. Additionally, there is a small but consistent decrease of ~ 0.05 - 0.10 eV between the pentathiophene and hexathiophene analogues. The difference in sidechain lengths between the analogues appear to have had a limited impact upon the optical energy gap, with no functional difference observed.

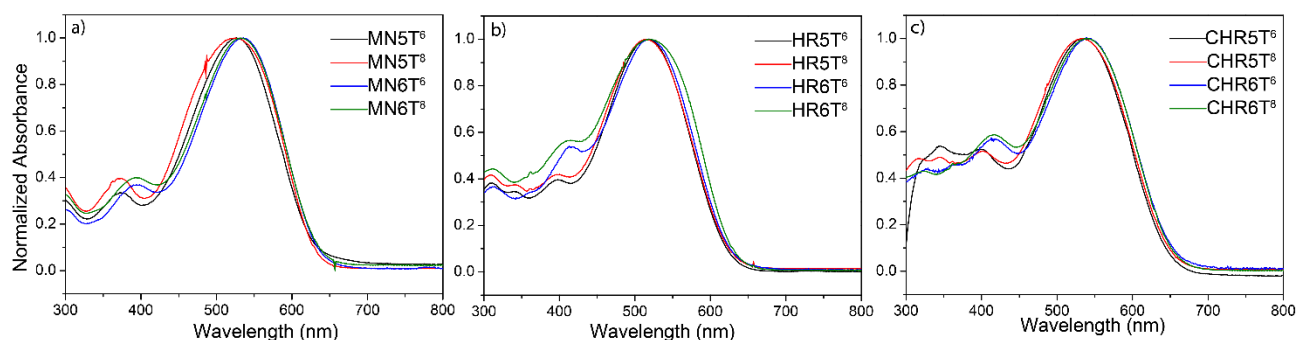


Figure 4-3: Normalized UV-vis absorption spectra of our oligothiophene materials with a) MN-, b) HR- and c) CHR-end-group acceptors, in chloroform solutions.

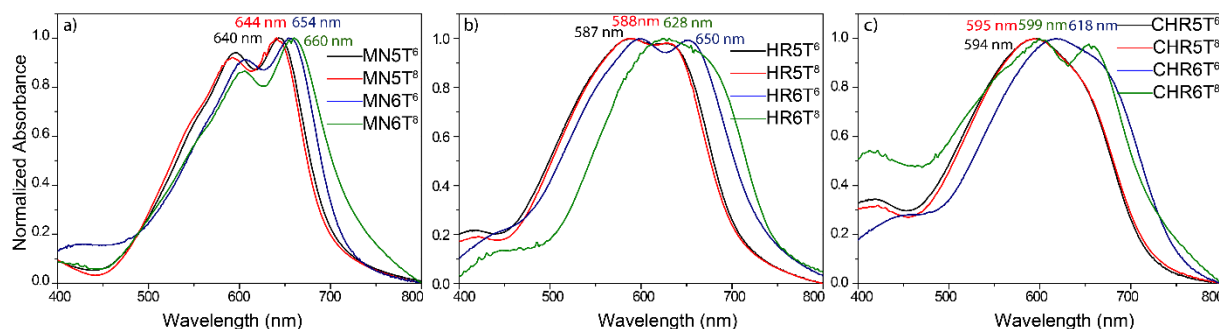


Figure 4-4: Normalized as-cast (from CHCl_3) solid-state UV-Vis absorption spectra for the a) MN-, b) HR-, and c) CHR-functionalized materials. The highest absorption peak maxima are labelled.

Cyclic voltammetry was used to further investigate the energy levels of the oligothiophene materials (Figure 4-14 with the data again summarized in Table 1). Here the compounds were referenced against ferrocene, and from oxidation and reduction onset potentials the ionization potentials and electron affinities, respectively, can be estimated. From this the electrochemical energy gap E_g^{CV} can be calculated. All 12 oligothiophenes were found to display two reversible oxidation processes and one irreversible reduction process within the accessible solvent window. All materials display a range of IP energy levels between -5.42 and -5.65 eV and a comparatively larger range of EA energy levels between -3.43 and -3.90 eV. As a function of the conjugation length, as expected the hexathiophene analogues confer correspondingly increased IP levels relative to their pentathiophene counterparts of about 0.1 eV. As the matching EA levels remain constant with increasing conjugation this results in noticeably smaller energy gaps, a trend which is in good agreement with the optical energy gaps.

Also as expected are changing EA levels as a function of the end-group acceptors within the same conjugation series, with this manifesting as decreasing values from **HR**>**MN**>**CHR**, with a 0.2 eV average difference between the **HR** and **MN** analogues and a 0.1 eV difference between the **MN** and **CHR** analogues. This shift is consistent with the higher electron withdrawing nature of the **MN** and **CHR** groups with respect to n-hexyl rhodanine. While the electrochemical energy gaps themselves remain relatively similar between analogues of different sidechain lengths, this conceals the uniform decrease in both the IP and EA energy levels of around ~0.1-0.2 eV with an increase in sidechain length, with this potentially a factor of altered intermolecular packing on backbone planarity.

Table 2. Absorption and electronic energy levels of the oligothiophene analogues

Material	UV-Vis					Cyclic Voltammetry			
	Solution λ_{max} (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	Film λ_{max} (nm)	Film λ_{ons} (nm)	Film E _g ^{opt} (eV)	Film IP (eV)	Film (eV)	EA	Film E _g ^{CV} (eV)
MN5T ⁶	525	3.2 × 10 ⁴	596, 640	705	1.76	-5.54	-3.67		1.87
MN5T ⁸	523	7.3 × 10 ⁴	592, 640	703	1.76	-5.64	-3.81		1.83
MN6T ⁶	534	2.4 × 10 ⁴	607, 654	715	1.73	-5.42	-3.63		1.79
MN6T ⁸	532	7.1 × 10 ⁴	605, 660	733	1.69	-5.60	-3.89		1.71
HR5T ⁶	518	4.9 × 10 ⁴	587, 628	718	1.73	-5.57	-3.43		2.14
HR5T ⁸	515	8.3 × 10 ⁴	587, 628	708	1.75	-5.59	-3.50		2.09
HR6T ⁶	524	5.0 × 10 ⁴	598, 650	741	1.67	-5.53	-3.46		2.07
HR6T ⁸	522	8.2 × 10 ⁴	628	750	1.65	-5.58	-3.59		1.99
CHR5T ⁶	533	5.7 × 10 ⁴	594	719	1.72	-5.54	-3.76		1.78
CHR5T ⁸	531	9.8 × 10 ⁴	594	719	1.72	-5.72	-3.94		1.78
CHR6T ⁶	539	5.4 × 10 ⁴	618	751	1.65	-5.42	-3.71		1.71
CHR6T ⁸	539	1.6 × 10 ⁵	599, 659	733	1.69	-5.53	-3.92		1.61

4.5 Photovoltaic properties and performance

Solution-processed BHJ devices were fabricated utilizing the 12 oligothiophene compounds and PC₇₁ BM as the p-type and n-type semiconductors respectively in order to assess the oligothiophenes' OPV performances. These devices were fabricated using a conventional device architecture of ITO/PEDOT:PSS (30 nm)/active layer (~240 nm)/Ca (30 nm)/Al (100 nm) similar to that found in Figure 2-9a. The high work function PEDOT:PSS interlayer and the low work function Ca interlayer are present as hole and electron transport layers, respectively. Devices were spin-coated from a chloroform solution with the data for the as-cast devices, as well as those annealed under a variety of conditions presented in Table 2. The optimized conditions and performance parameters for those devices which gave the best PCEs are highlighted in red, and given as an average of 10 devices. The corresponding J-V curves for the optimized films under AM 1.5 irradiation are reported in Figure 4-5. The active layers of all devices were produced without the use of any additives, and as such this presents a potential route to further improvement.

The device efficiencies of the oligothiophene materials, much like their optoelectronic properties, are seen to vary consistently as a function of the conjugation length and the end-group acceptor. Across the board,

the as-cast blend films of all oligothiophene materials are seen to possess poor device efficiencies of 0.3-0.8% (**MN**), 1.0-1.6% (**HR**) and 1.4-2.6% (**CHR**), with these devices generally limited by poor short-circuit currents and fill factors. Interestingly, the **HR**- and **CHR**-functionalized materials at this point display significantly improved FFs of around 1.5-fold on the hexathiophene and pentathiophene substrates, respectively, relative to their counterparts with alternate conjugation lengths as seen in Table 3. That this relationship is apparent, prior to any form of annealing, potentially suggests that the pairing of these end-groups acceptors to specific oligothiophene conjugation lengths results in the formation of optimal morphologies even in the as-cast films.

To improve the performances of the as-cast films, solvent vapor annealing treatments were applied. Unexpectedly however, the PCEs of all **MN**- and **CHR**-functionalized materials either remain relatively unchanged or even decreased upon SVA, which was primarily due to significantly lower J_{SC} s. While lower open-circuit voltages are also observed post-SVA, as discussed in Chapter 2 these are not unexpected and are due to the increasing intermolecular interactions between the donor and acceptor red shifting the absorption profile of the active-layer blend, and subsequently reducing the optical bandgap.^[140a] This drop in performance upon SVA has been observed in other **CHR**-functionalized oligothiophene-based materials with outwards-facing sidechains (but not those with inwards-facing sidechains),^[195] and suggests that the increased intermolecular interactions induced by the less sterically-hindering sidechains influences the SVA-enabled molecular diffusion into non-optimal morphologies. Curiously this same behaviour is not observed for the **HR**-functionalized materials where all four analogues display improved performances, particularly in the case of **HR6T**⁶ and **HR6T**⁸ where PCEs markedly improve from 1.5% and 1.6% to 6.6% and 7.0%, respectively. This further suggests that the strong hydrogen bonding between dicyanomethylene moieties found in the **MN** and **CHR** acceptors is a combinatorial factor with the outwards-facing sidechains, with these resulting in non-optimal morphologies upon SVA. As previously discussed, the **HR** acceptor appears to respond favourably to the hexathiophene substrate, as while both the **5T** and **6T** materials evolve relatively similar FFs of 60-70%, the **HR-5T** analogues (which possess PCEs of 4.2-4.5% are limited by their lower J_{SC} s.

Conversely, the **HR**-functionalized materials all evolve much poorer performances upon thermal annealing where their PCEs drop to $\leq 1\%$ while the **MN**- and **CHR**-functionalized materials are all seen to noticeably benefit. In the case of the **MN**-functionalized materials, a three- to five-fold improvement is observed, however overall performances remain low with PCEs of $< 3\%$. In the case of the **CHR**-functionalized materials, it was found that a combination of both SVA and TA on the as-cast film served to greatly improve PCEs of the **CHR5T**^x oligothiophenes (relative to either process in isolation), increasing from 2.4-2.6% to an impressive 8.2% with outstanding V_{OC} s of 1.02-1.04 V, J_{SC} s of 11.7-12.7 mA cm⁻² and FFs of 63-70%. For the **CHR6T**^x analogues however TA by itself was found to be the optimal processing condition, although this saw a much smaller PCE improvement from 1.4-1.6% to 3.7-3.9%. As with the **HR**-functionalized materials there is an

apparent dependence of performance on the oligothiophene conjugation length, with the **MN**- and **CHR** end-groups showing improved PCEs when paired with the pentathiophene substrate.

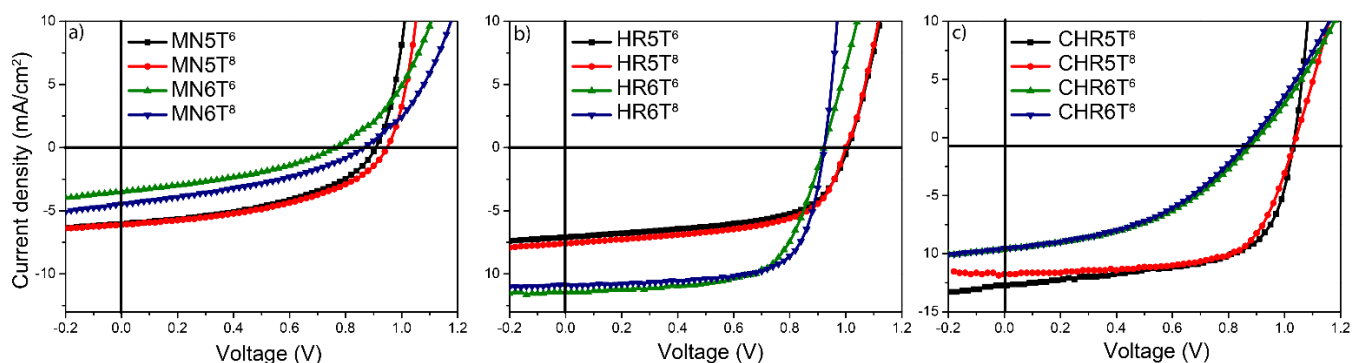


Figure 4-5: Current-voltage characteristics of the optimized oligothiophene:PC71BM photovoltaic devices for the a) MN-functionalized materials, b) HR-functionalized materials and c) CHR-functionalized material

Curiously, though the PCEs for analogues of different sidechain lengths appear superficially similar and differ by no more than around 0.1-0.2% in most cases, here too can a trend be observed, with the octyl-functionalized materials generally possessing slightly higher PCEs due to slightly higher J_{sc} s and FFs across all processing conditions. While this increased performance is both apparent even in the as-cast films and is too small to be able to make conclusive claims, nevertheless these findings do not preclude the initial hypothesis regarding the relationship between sidechain length and molecular diffusion during the annealing process.

Table 3: Photovoltaic performances of the oligothiophene:PC71BM cells with different processing conditions. The optimized conditions are presented in red.

Active Layer (1:1 Donor: PC71BM)	Processing conditions	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
MN5T ⁶	As-cast	0.90	2.3	30	0.6
MN5T ⁸		0.92	2.8	31	0.8
MN6T ⁶		0.84	0.8	24	0.2
MN6T ⁸		0.86	1.2	27	0.3
MN5T ⁶	SVA (THF) ^a	0.84	1.8	38	0.6
MN5T ⁸		0.82	1.4	44	0.5
MN6T ⁶		0.78	1.7	32	0.4
MN6T ⁸		0.84	2.1	36	0.6
MN5T ⁶	TA (120°C) ^b	0.90±0.01	6.1±0.2	46±2	2.5±0.2
MN5T ⁸		0.94 ± 0.02	6.1 ± 0.2	46±2	2.6±0.2
MN6T ⁶		0.76±0.02	3.5 ± 0.3	37±3	1.0±0.3
MN6T ⁸		0.88± 0.02	4.5 ± 0.3	40±2	1.6±0.3
HR5T ⁶	As-cast	1.00	3.3	29	1.0
HR5T ⁸		0.98	3.9	31	1.2
HR6T ⁶		0.92	3.4	49	1.5
HR6T ⁸		0.92	3.8	46	1.6
HR5T ⁶	SVA (THF) ^a	0.98±0.01	7.1±0.2	60±2	4.2±0.2
HR5T ⁸		0.96 ± 0.02	7.6 ± 0.2	62±	4.5±0.2
HR6T ⁶		0.92±0.01	11.4 ± 0.3	63±2	6.9±0.2
HR6T ⁸		0.92 ± 0.02	10.9 ± 0.3	69±2	7.0±0.2

HR5T ⁶		0.60	3.3	47	0.9
HR5T ⁸		0.58	3.0	44	0.8
HR6T ⁶	TA (120°C) ^b	0.82	2.3	52	1.0
HR6T ⁸		0.82	1.1	59	0.5
CHR5T ⁶		1.00	5.0	48	2.4
CHR5T ⁸		0.98	6.5	46	2.6
CHR6T ⁶	As-cast	0.92	4.9	36	1.6
CHR6T ⁸		0.90	4.7	33	1.4
CHR5T ⁶		0.96	5.6	42	2.3
CHR5T ⁸		0.92	4.8	48	2.1
CHR6T ⁶	SVA (THF) ^a	0.90	3.2	29	1.0
CHR6T ⁸		0.88	3.9	31	1.1
CHR5T ⁶	SVA/TA ^c	1.04 ± 0.01	11.7 ± 0.3	67±2	8.2 ±0.2
CHR5T ⁸	SVA/TA ^c	1.02±0.01	12.7±0.2	63±2	8.2 ± 0.3
CHR6T ⁶	TA (120°C) ^b	0.90±0.02	9.6±0.0	45±2	3.9±0.2
CHR6T ⁸	TA (120°C) ^b	0.86± 0.02	9.6 ± 0.3	45±2	3.7±0.2

^aSVA THF (20 sec), ^bTA 120 °C (10 min), ^cSVA THF (60 sec) / TA 120 °C (10 min)

4.6 Nanoscale structure and bulk morphology

To gain an insight into the film morphologies of the oligothiophene analogues as a function of their conjugation length, sidechain length and end-group acceptor, AFM and GIWAXS studies were performed. Like the work in previous chapters, here Miller indices are assigned to specific d-spacings, i.e. alkyl lamellar spacings (*h*00), π - π spacings (*0k*0) or along the long axis of the backbone (*00l*). As previously discussed molecular orientation is also important, as intermolecular charge delocalization occurs primarily through π - π interactions and thus a vertically π -stacked ‘face-on’ active layer facilitates charge transport to the electrodes more so than an ‘edge-on’ orientation.^[48, 173a] Spin-coated thin films of each analogue were prepared under different sets of processing conditions i) neat, ii) in a 1:1 blend with PC₇₁BM, and iii) in a 1:1 blend of PC₇₁BM annealed using identical conditions to those that gave the best PCE, as reported in Table 2. For the **MN**- and **CHR**-functionalized materials SVA-annealed films are also obtained to understand their low performances when processed from these conditions. GIWAXS scattering patterns for the **MN5T^x** (Figure 4-6), **MN6T^x** (Figure 4-7), **HR5T^x** (Figure 4-8), **HR6T^x** (Figure 4-9), **CHR5T^x** (Figure 4-10) and **CHR6T^x** (Figure 4-11) materials are presented here. Again, scattering peaks along the q_{xy} horizontal and q_z vertical axes are indicative of reflections in-plane (I-P) and out-of-plane (OOP) to the film substrate, respectively, with linecuts of peak intensity as a function of their q -spacing along the axes found in Figures 4-15 to 4-20. Approximations of the coherent crystallite size using the Scherrer equation are measured from the 100 reflections of greatest intensity.^[178] D-spacings and CCLs from the scattering patterns can be found in Tables 5-10. Following the presentation of results, correlations between the device performances and the morphological behaviours observed by AFM/GIWAXS studies are drawn, however it is worth bearing in mind that device performance depends on many morphological parameters that control the various light-harvesting processes (i.e. exciton

diffusion and quenching to charge generation and extraction), with the studies conducted here insufficient to examine all of these parameters. As such, interpretations made are correlative and not intended to be causative.

4.6.1 AFM studies

The surface topography of various representative oligothiophene:PC₇₁BM films are examined through AFM studies (Figure 4-22). These films are annealed through conditions that grant the best performance. For **MN5T⁶**, large, plate-like domains with diameters in excess of 100 nm are observed, with this morphology likely due to its poor solubility in chloroform resulting in the rapid formation of aggregates during the spin-coating process. **HR5T⁶**, **HR6T⁶** and **CHR5T⁶** all feature much smaller, interpenetrating fibrils, with domain sizes (and the degree of intermixing) decreasing in that order.

4.6.2 GIWAXS studies – MN-functionalized oligothiophenes

GIWAXS patterns of the neat, as-cast films for **MN5T⁶** (Figure 4-6a) show two peaks in the $q = 0.3\text{--}0.5 \text{ \AA}^{-1}$ region corresponding to d-spacings of 1.80 nm and 1.36 nm, which are suggestive of two different *h*00 lamellar stacking polymorphs, both with distinct 1st to 3rd-order reflections. This large difference in d-spacing could potentially be attributed to varying degrees of sidechain interdigitation, with similar polymorphic behaviour observed from P3HT in the literature.^[199] The as-cast film of **MN5T⁸** (Figure 4-6e) on the other hand does not exhibit polymorphic behaviour, but possesses 1st to 4th-order *h*00 reflections which suggest good long-range order with a d-spacing of 1.62 Å. This is slightly increased relative to the **MN5T⁶** polymorph of greatest population as expected from the longer alkyl chains. After the addition of the acceptor in the as-cast blend films, d-spacings and the degree of crystalline structure decrease for both analogues (with this likely due to fine intermixing of the donor material with PC₇₁BM) and only one set of lamellar reflections is observed for **MN5T⁶**. SVA treatment of the blend (Figures 4-6c and g) appears to have no significant impact upon the film morphology with only a slight increase in the CCLs. Upon thermal annealing however, the evolution of sharper Bragg peaks can be observed for both analogues indicative of a high degree of crystallinity, although interestingly for **MN5T⁶** the annealing process also results in both peak broadening - with a correspondingly lower CCL- as well as a reduction in isotropy for the 100 reflection, which is particularly noticeable in the linecut. (Figure 4-15). Both analogues are seen to possess a clear edge-on orientation across all films, with the *h*00 and 010 π -stacking reflections confined to the vertical and horizontal axes, respectively. A single-crystal structure for **MN5T⁸** (Figure 5i) was obtained, from which lamellar packing distances of 1.59 nm were calculated from the simulated powder diffraction pattern (Figure 4-23) that are in good agreement from the GIWAXS-derived data. Notably, from the single-crystal structure **MN5T⁸** is seen to ‘flip’ along the long axis of the conjugated backbone on alternate molecules, so as to achieve a head-to-tail packing motif that allows hydrogen bonding between the dicyanomethylene moieties. This motif is likely present within the **CHR** moiety as well and contributes to previously mentioned strong intermolecular attraction.

The GIWAXS scattering patterns for the neat, as-cast films of **MN6T⁶** and **MN6T⁸** (Figure 6a, e) also exhibit lamellar packing polymorphs. **MN6T⁶** possesses two polymorphs corresponding to d-spacings of 1.35 nm and 1.21 nm, the second of which can be identified with 1st to 3rd-order reflections. **MN6T⁸** is observed with three polymorphs with d-spacings of 1.95, 1.54 and 1.47 nm, the latter two of which also possess 1st to 3rd-order reflections. These are more easily seen in the corresponding linecut as overlapping peaks (Figure S10.2e). It is interesting that the polymorphs of lowest intensity for both analogues are largely confined to the vertical axis, while those of higher intensities are more isotropic. For both materials, multiple smeared reflections can also be observed throughout the $q = 0.8\text{--}1.05\text{ \AA}^{-1}$ region, and strong peaks we attribute to 010 reflections can be seen in both horizontal axes corresponding to a π -stacking distance of 0.37 nm. As with their pentathiophene counterparts, after the addition of PC₇₁BM in the as-cast blend the degree of crystalline structure for both **MN6T^x** materials are seen to lessen slightly, and the populations of all low-intensity polymorphs in the as-cast neat films are seen to decrease further. SVA treatment is not seen to significantly affect the film morphology, however upon thermal annealing, for **MN6T⁶** the peak intensity of the polymorph with a lower q value of $0.46\text{ \AA}^{-1}$ is seen to increase, suggesting that it is thermodynamically favoured under TA conditions. For **MN6T⁸**, peak-fitting suggests that only one polymorph remains after thermal annealing, however curiously in both cases the thermodynamically-favoured polymorph also develops increased isotropy with a more pronounced reflection in the horizontal axis.

Using the data obtained from these morphological studies the photovoltaic performances observed can be partially rationalized. That the apparent morphologies of the as-cast blends for both **MN5T^x** or **MN6T^x** analogues do not substantially change upon SVA treatment is in agreement with the device data. In the thermally treated films, however, the relatively large increase in PCE is matched by a significant change in the crystalline structure of our films – that is, the formation of the sharper Bragg peaks for the **MN5T^x** analogues and a change in polymorph population and increasing isotropy for the **MN6T^x** analogues. This increased crystallinity can be correlated with the improved J_{SCs} and PCEs, with this potentially occurring through the formation of a network of pure semiconductor domains facilitating charge transport to the electrodes. Overall however, PCEs for the **MN**-functionalized materials remain low, and it is possible that the molecular orientation and polymorphic behaviours observed are also responsible. In the case of the former, all **MN**-functionalized analogues exhibit a clear edge-on molecular orientation with respect to the device substrate, which as previously mentioned is not optimal for efficient charge transport. For the latter, the presence of lamellar packing polymorphs in the **MN6T^x** films could potentially result in offsets between adjacent π -stacked layers, with this going on to reduce charge transfer integrals and thus also hindering charge transport. A similar phenomenon has been observed for **MN**-functionalized quarterthiophenes in the literature, with a correspondingly detrimental effect on OPV performance.^[200]

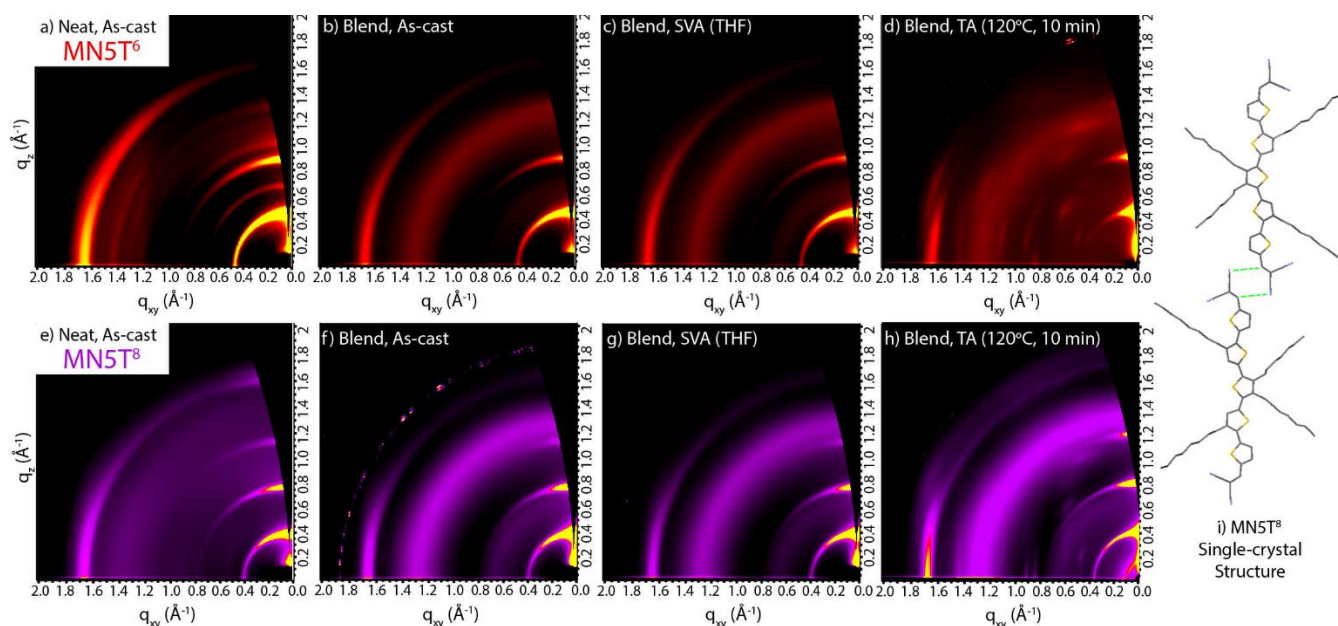


Figure 4-6: GIWAXS diffraction patterns for MN5T⁶ and MN5T⁸ films that are: a/e) neat, as-cast; and 1:1 blends with PC₇₁BM that are: b/f) as-cast; c/g) SVA (THF, 20 seconds); d/h) TA (120°C, 10 minutes), and i) the solid-state geometry of MN5T⁸ as determined by its single-crystal structure. Hydrogen bonding between the dicyanomethylene moieties is marked in green.

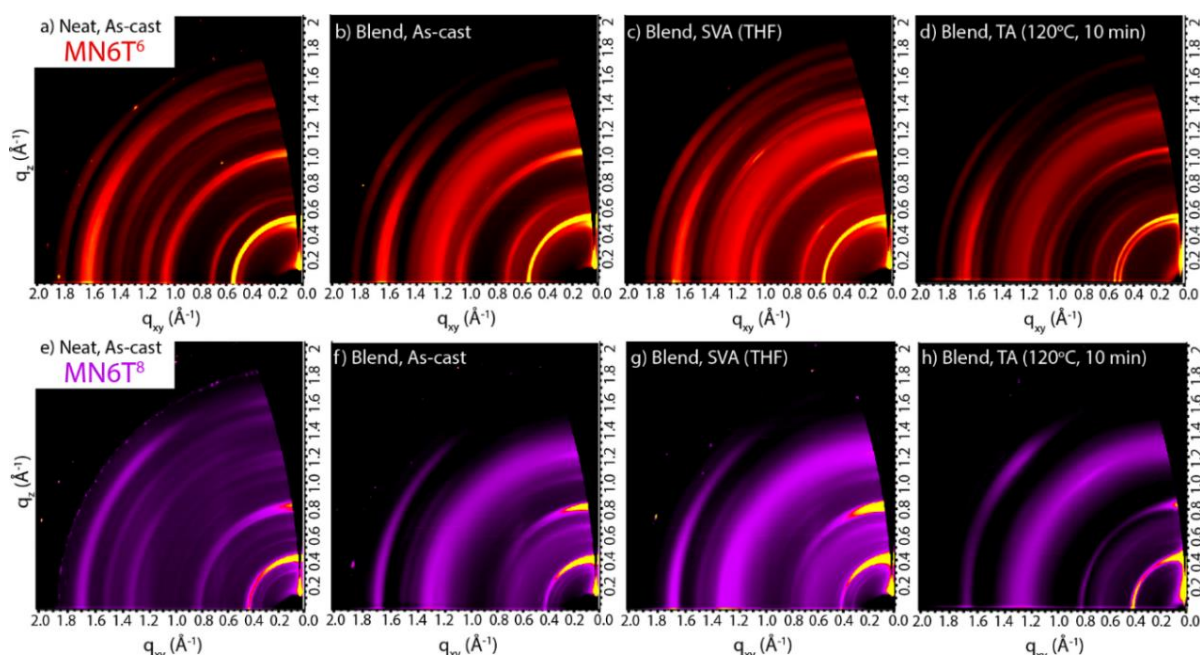


Figure 4-7: GIWAXS diffraction patterns for MN6T⁶ and MN6T⁸ films that are: a/e) neat, as-cast; and 1:1 blends with PC₇₁BM that are: b/f) as-cast; c/g) SVA (THF, 20 seconds) and d/h) TA (120°C, 10 minutes)

4.6.3 GIWAXS studies – HR-functionalized oligothiophenes

The HR5T⁶ and HR5T⁸ neat, as-cast scattering patterns (Figures 4-8a, d) show sharp 100 reflections, with d-spacings of 1.66 and 1.91 nm respectively. Although these rings are typically indicative of poorly-oriented lamellar layers, 010 π -stacking reflections with d-spacings of 0.38 nm are also observed and are located primarily in the vertical axis. Interestingly, examination of the Bragg peaks seen in the as-cast HR5T⁸ film suggests that there are two distinct crystallite orientations. These peaks have been able to be indexed according

to two different unit cells, (see Figure 4-8d), from which 1st to 2nd-order *h*00 reflections in both the vertical and horizontal axes can be identified. This, in conjunction with the indexed 102 and 103 reflections, suggests that of the two populations of crystallites, those that possess I-P lamellar packing have a higher degree of crystalline structure and undergo strong OOP π -stacking (i.e. those with a ‘face-on’ orientation), relative to those that possess OOP lamellar packing. This face-on π -stacking is however lost after the addition of the fullerene acceptor, with the crystalline structure of both oligothiophenes significantly disrupted as seen in the as-cast blend films (Figures 4-8b, e) and here only broad, diffuse halos corresponding to the 100 and amorphous fullerene reflections are identifiable. SVA treatment, however, has a marked effect on the thin-film morphology, with the evolution of multiple smeared Bragg peaks for both analogues. As seen in Figures 4-8c and f, both scattering patterns have been indexed according to single unit cells, the details of which can be found in Table 7. Simulated unit cells can be compared to the experimental results in Figure 4-21. Interestingly, two reflections in the horizontal axis are assigned to 2nd and 3rd-order 00/ reflections, with the corresponding 1st-order reflection obscured by the beam stop. These possess d-spacings of 39.5 nm for both analogues, indicating that each unit cell is comprised of two head-to-tail stacked molecules aligned in the plane of the substrate. This, in conjunction with the 1st to 4th order *h*00 reflections in the vertical axis and the weak 010 reflections in the horizontal axis, suggest that the addition of the acceptor prompts a shift from a face-on to edge-on orientation for the **HR5T^x** crystallites. Here, both the **HR5T⁶** and **HR5T⁸** analogues possess relatively large π -stacking distances of 0.39 and 0.38 nm, respectively. The large change in film morphology upon SVA relative to the **MN**-functionalized analogues is possibly due to the presence of an additional alkyl chain on the rhodanine moiety, thus increasing molecular mobility and allowing the oligothiophene to diffuse into more thermodynamically-favoured domains.

The as-cast **HR6T⁶** film (Figure 4-9a) possesses multiple reflections in the vertical axis that suggest the existence of two lamellar polymorphs with d-spacings of 1.63 and 1.25 nm. 1st to 2nd-order *h*00 reflections are identified for each polymorph, with at least one of these producing a π -stacking reflection in the horizontal axis. The polymorph of greatest population exhibits a 100 d-spacing in good agreement with the spacing obtained for the closely-related **HR5T⁶** analogue (1.63 vs 1.66 nm). On the other hand, the lengthened alkyl chains of **HR6T⁸** have resulted in a significantly different morphology for the neat, as-cast film (Figure 4-9d), with a multitude of smeared reflections that defy easy identification. Curiously, while every other material in this study consistently exhibits a 100 d-spacing increase of 1-2 Å upon lengthening of the sidechains from hexyl to octyl, the spacing from **HR6T⁶** to **HR6T⁸** actually decreases from 1.63 nm to 1.31 nm. Of note is a reflection with a low *q* value of 0.24 Å⁻¹ corresponding to a d-spacing of 2.56 nm, which corresponds well to repetition of the conjugated backbone as determined from molecular modelling and agrees with the 00/ d-spacing of the similar **CHR6T⁸** analogue. That this is in the vertical axis implies a ‘end-on’ orientation (where the long axis of the conjugated backbone is normal to the plane of the substrate) that is rare for oligothiophenes but not without precedent.^[201] However, a 100 reflection is also identified which

implies a population of crystallites with OOP lamellar stacking that is incompatible with an end-on orientation (as such an orientation would necessitate I-P lamellar stacking). Along with what we tentatively identify as a 010 π -stacking reflection in the vertical axis at $q = 1.69 \text{ \AA}^{-1}$ (corresponding to a π -stacking distance of 0.37 nm), this then suggests that **HR6T⁸** possesses a distribution of crystallite orientations spanning end-on to edge-on to face-on, but which still maintains a degree of crystallinity above that of a completely disordered film. In Figure 4-9b, while after the addition of the acceptor the film morphology of **HR6T⁶** resembles an amorphous powder, **HR6T⁸** on the other hand (Figure 4-9e) retains a degree of crystallinity similar to that of the neat film, with the reflections assigned to the 100, 010 and 001 reflections still visible. With SVA treatment, the 100 and 010 reflections of **HR6T⁶** narrow relative to the as-cast blend, but the calculated CCL of 8.2 nm remains low and the π -stacking reflection is weak. It can be observed that both the 100 and 010 reflections of greatest intensity are located in the vertical axis, which is curious as for oligothiophene-derivative structures, it is expected that the direction of lamellar stacking be normal to that of π -stacking. Unlike the **HR5T^x** materials, here there are no additional reflections to suggest a face-on orientation. This is reminiscent of the 'rolling log' orientation observed for the BTR-type material, and it is theorized that this is present for **HR6T⁶** too. Surprisingly, SVA treatment does not appear to alter the morphology of **HR6T⁸** to a significant extent, with the calculated CCLs and d-spacing of the 100 reflection remaining relatively constant. The relative lack of morphological change upon SVA compared to the pentathiophene analogues can perhaps be attributed to the greater aromatic interaction induced by an additional aryl unit, a phenomenon also observed for the **CHR6T^x** materials.

Several factors are observed that allow correlations to be drawn between device performance and the morphology of the **HR**-functionalized materials. First, the differences in J_{SC} between the **HR6T^x** and **HR5T^x** analogues can also be explained by the latter's strong edge-on π -stacking orientation and the large π - π distance of ~ 0.39 nm, while the former is believed to possess a non-trivial population of face-on oriented crystallites that are beneficial for charge harvesting. Second, though the AFM surface only allow resolution of the film surfaces, it is possible that the stronger domain intermixing exhibited by AFM images of the **HR6T^x** materials, relative to the **HR5T^x** materials, are representative of similar levels of intermixing within the film bulk as well. This would then also contribute to the higher J_{SC} s observed due to more efficient exciton separation. However as previously mentioned, these studies can be insufficient to explain the observed performances. To wit, two phenomena observed from the **HR6T^x** GIWAXS results -namely, the significant improvement of the J_{SC} s upon SVA despite relatively similar scattering patterns, and the relatively similar PCEs between **HR6T⁶** and **HR6T⁸** despite obvious difference in crystallinity- make it clear that other morphological factors outside the scope of this study (for example, domain size and purity or donor/acceptor interface structure) are dominant here in determining performance.

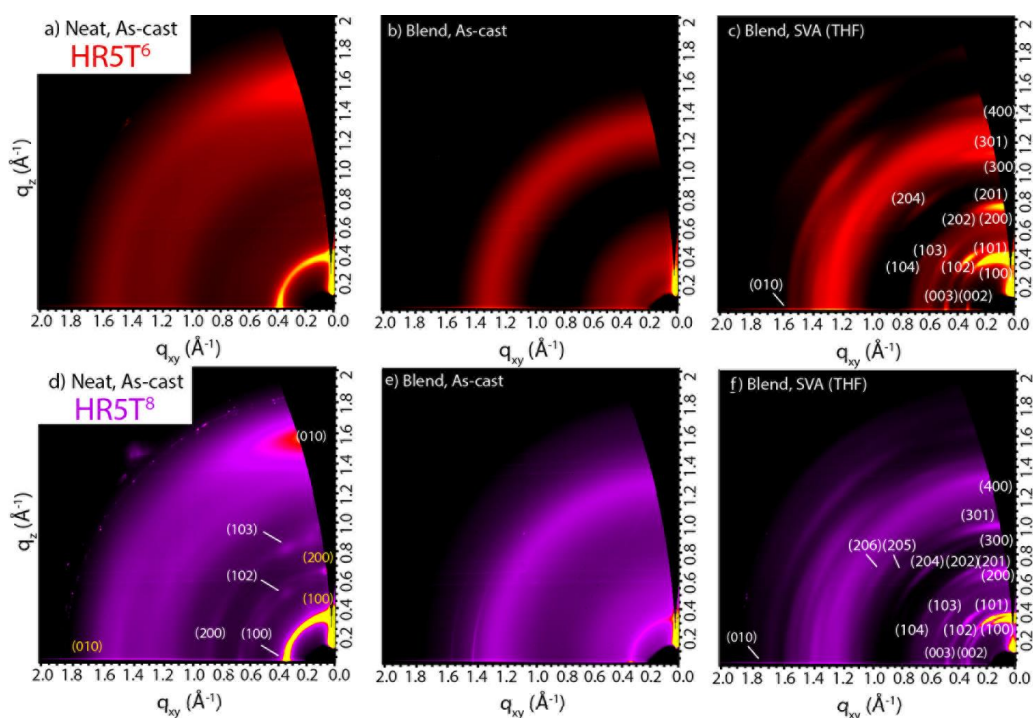


Figure 4-8: GIWAXS diffraction patterns for HR5T⁶ and HR5T⁸ films that are: a/e) neat, as-cast; and 1:1 blends with PC₇₁BM that are: b/f) as-cast; and c/g) SVA (THF, 20 seconds). Labelled indices of different colours belong to different unit cells.

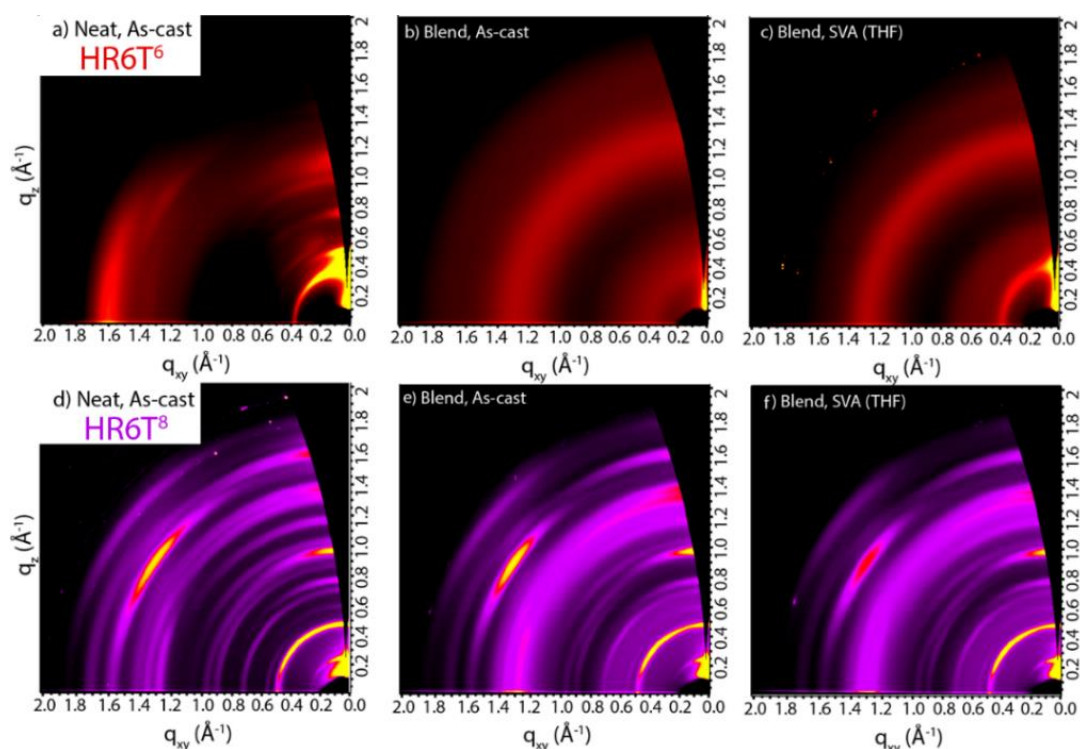


Figure 4-9: GIWAXS diffraction patterns for HR6T⁶ and HR6T⁸ films that are: a/e) neat, as-cast; and 1:1 blends with PC₇₁BM that are: b/f) as-cast; and c/g) SVA (THF, 20 seconds).

4.6.4 GIWAXS studies – CHR-functionalized oligothiophenes

The scattering patterns for both neat **CHR5T^x** films (Figures 4-10a, e) show relatively diffuse scattering with broad 100 reflections present in both axes, although **CHR5T⁶** shows enhanced I-P 100 and OOP 010 scattering

indicative of a face-on orientation. While **CHR5T**⁸ also possesses an OOP π -stacking reflection it also features an I-P peak assigned to a 001 reflection (with a d-spacing of 2.62 nm) and isotropic reflections in the $q = 0.45$ - $0.60 \text{ \AA}^{-1}$ region. For both materials, addition of PC₇₁BM disrupts both lamellar and π -stacking as evidenced by the diminished reflections in the as-cast blend films (Figures 4-10b, f). Upon SVA, increased crystallite structure is observed, with the development of 1st and 2nd order I-P 00/ reflections (with a d-spacing of 2.42 nm) and an obvious OOP π -stacking reflection for **CHR5T**⁶ (Figure 4-10c). This increased crystallinity is mirrored in **CHR5T**⁸ (Figure 4-10g), with the development of long-range order, a 001 reflection in the q_{xy} axis (corresponding to a d-spacing of 2.42 nm), and a 101 reflection overlapping an OOP 100 reflection. Curiously, the two SVA-treated analogues exhibit different π stacking behaviour, as **CHR5T**⁶ appears to possess a face-on orientation (as per the strong I-P 100 and strong OOP 010 reflections) whereas **CHR5T**⁸ has long-range OOP lamellar order but poor π - π stacking. Though the thermally-annealed films result in the evolution of even more crystalline structure – as evidenced by the multitude of smeared Bragg peaks for **CHR5T**⁸ that facilitate estimation of the unit cell, described in Table 9- crystallite orientations remain relatively similar to those present in the SVA-treated films. Curiously, despite the degree of crystallinity atypical for alkyl-substituted organic semiconductors that observed in **CHR5T**⁸, the 010 reflection is still not visible. Also of note is that the d-spacings for 00/ reflections have increased from 2.43 nm in the SVA-treated films to 3.94 nm here, indicating that like the **HR5T**^x analogues, the unit cell contain two molecules aligned head-to-tail.

The neat, as-cast films of both **CHR6T**^x analogues (Figures 4-11a, e) exhibit similar scattering patterns with a high degree of crystalline structure and multiple higher-order reflections, although in both cases the Bragg peaks are noticeably smeared indicating some degree of isotropy. Notably, in both films high-order 00/ reflections are identified (from 1st to 3rd- and 5th-order reflections for **CHR6T**⁶ and **CHR6T**⁸ corresponding to d-spacings of 26.1 and 26.6 nm, respectively) indicating strong alignment along the head-to-tail packing direction, akin to the **CHR5T**^x materials. In addition to this, **CHR6T**⁸ is seen to possess polymorphic behaviour, with two distinct peaks assigned to 100 reflections of 1.54 and 1.37 nm. In terms of molecular orientation, π -stacking peaks at $q = 1.64 \text{ \AA}^{-1}$ can be identified in the q_{xy} axis, which, along with the $h00$ reflections confined to the vertical axis, suggest edge-on crystallites. In the as-cast blend films the decrease in crystallinity is slight, as is the change in the scattering patterns upon SVA, and suggests that strong intermolecular attraction between the donor materials -induced by a combination of the hexathiophene backbone and the dicyanomethylene moiety- result in a stable film morphology. Upon thermal annealing, while **CHR6T**⁶ has noticeably narrowed peaks indicative of increasing crystallinity – with an increased 100 CCL from 25.4 to 35.0 nm relative to the as-cast blend- it is **CHR6T**⁸ that exhibits a startling morphological change from the as-cast blend and SVA films, with the development of multiple reflections in the vertical axis. Analysis of these peaks suggests the formation of three different lamellar polymorphs with higher-order reflections, with d-spacings ranging from 2.13 to 1.37 nm. The 100 peaks of highest and lowest intensity correspond to d-spacings of 1.54 nm and 1.37 nm respectively, which match the d-spacings of the two extant polymorphs present within all

other **CHR6T⁸** films. As the population of the polymorph with the larger d-spacing increases dramatically after thermal annealing, this is identified as the thermodynamically-favoured polymorph under the TA conditions. In addition, weak π -stacking peaks at $q = 1.64 \text{ \AA}^{-1}$ in the horizontal axis can be observed, indicating an edge-on orientation.

Much like the **HR6T^x** materials, few correlations can be drawn between the GIWAXS structures observed and device performance. Though out of all the oligothiophene analogues the annealed **CHR5T⁶** film is seen to possess the strongest OOP π -stacking reflection (indicative of face-on behaviour), and thus accounting for its high PCE, conversely while the **CHR5T⁸** analogue exhibits a similar PCE it also possesses a very different π -stacking behaviour. In addition to this, there is evidently a stark difference in film morphology between the **CHR6T^x** materials, which nonetheless also exhibit similar PCEs.

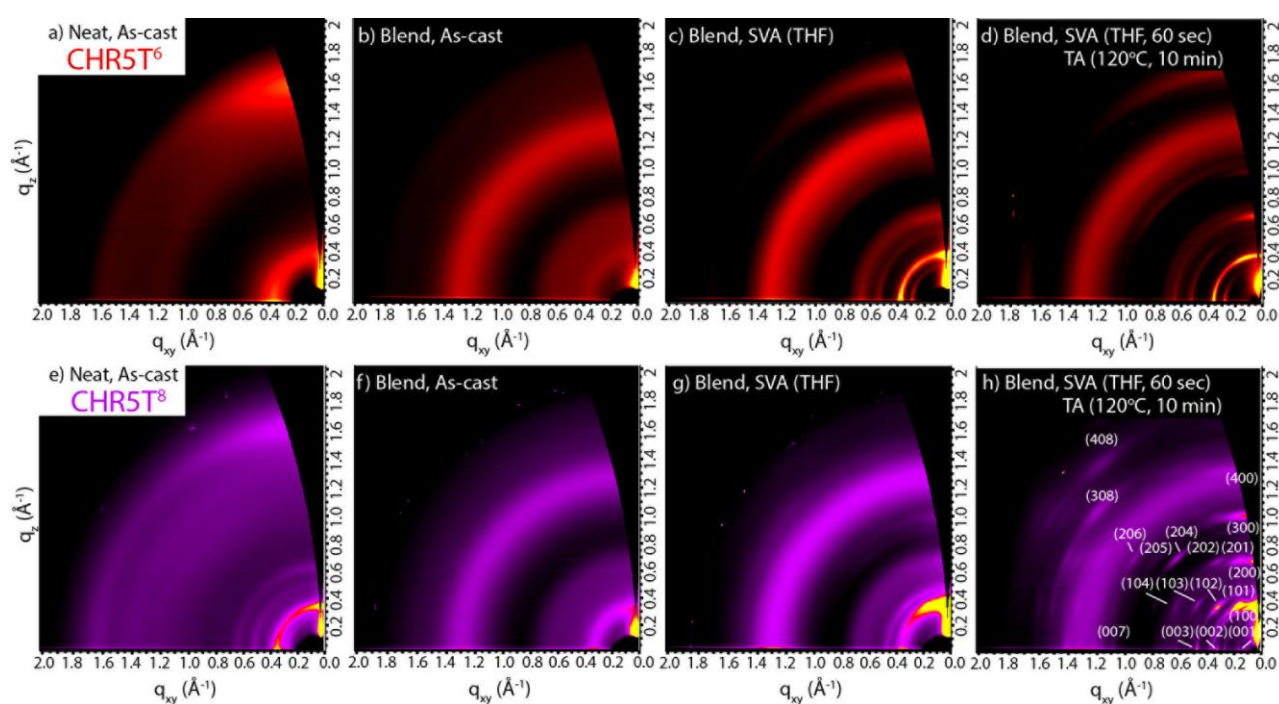


Figure 4-10 GIWAXS diffraction patterns for **CHR5T⁶** and **CHR5T⁸** films that are: a/e) neat, as-cast; and 1:1 blends with PC₇₁BM that are: b/f) as-cast; c/g) SVA (THF, 20 seconds) and d/h) SVA (THF, 60 seconds) and TA (120°C, 10 minutes).

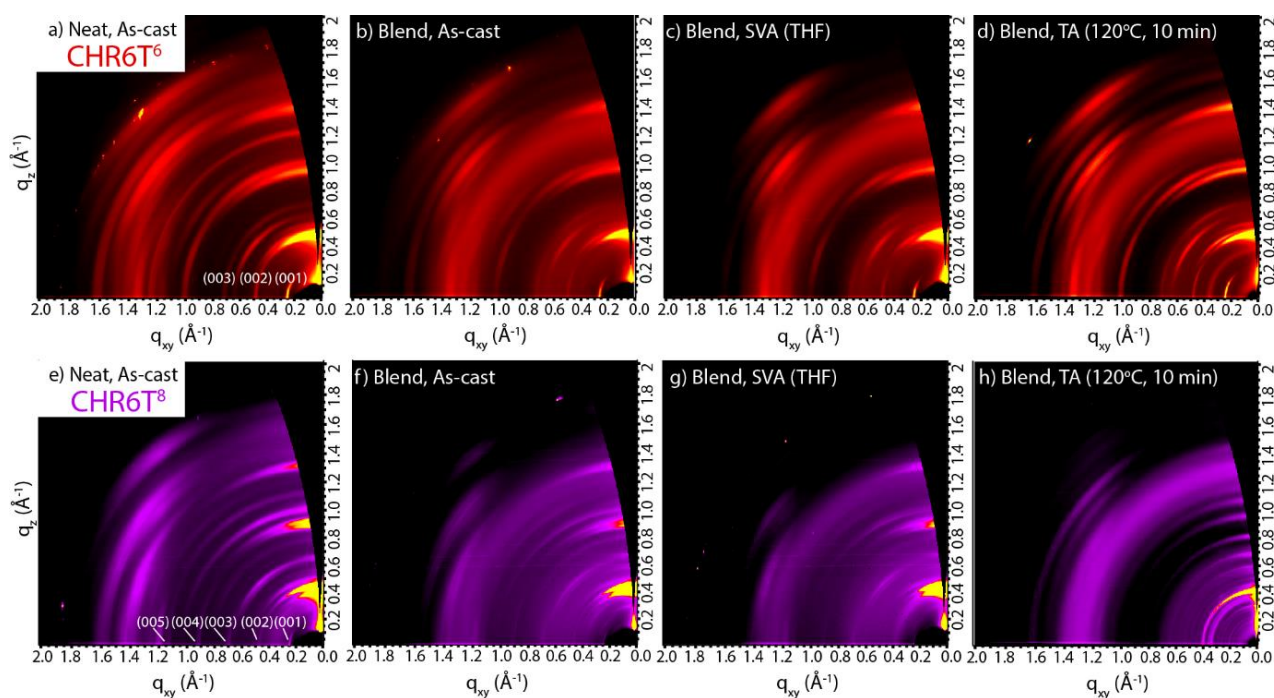


Figure 4-11: GIWAXS diffraction patterns for CHR6T⁶ and CHR6T⁸ films that are: a/e) neat, as-cast; and 1:1 blends with PC₇₁BM that are: b/f) as-cast; c/g) SVA (THF, 20 seconds) and d/h) SVA (THF, 60 seconds) and TA (120°C, 10 minutes).

4.6.5 Summary of the morphological studies

To summarize the findings from the GIWAXS studies, highly crystalline morphologies are generally observed throughout the thin-films of the oligothiophene analogues, particularly amongst those that have been undergone solvent-vapor or thermal annealing (save for **HR6T⁶** as a notable exception). Polymorphic behavior from analogues across the **MN**, **HR** and **CHR** series are also observed, which typically manifest as different lamellar packing configurations. As theorized earlier these polymorphs may hinder charge transport, and tellingly the annealed films of the higher-performing materials (i.e. the SVA-treated **HR6T^x** and TA-treated **CHR5T^x** analogues) do not exhibit polymorphism. The cause of this polymorphism, however, is still unknown. Nevertheless, in terms of establishing structure-property correlations, the following key observations can be made.

First, the outwards-facing alkyl sidechains, which have previously been established to be less sterically hindering than inwards-facing sidechains, appear to actually *indirectly* hamper π - π stacking. While it is found that the neat, as-cast films do exhibit relatively strong π -stacking reflections, the addition of the PC₇₁BM acceptor is seen to disrupts this packing in the **HR**- and **CHR**-functionalized analogues. The π -stacking reflection is either diminished in intensity or absent completely, even after an annealing process. It is hypothesized that outwards-facing sidechains here hinder molecular diffusion to the point where the degree of π -stacking originally present in the neat films is unable to be regained through the annealing processes. It is worth mentioning that it is unlikely that these sidechains *directly* sterically prohibit π -stacking, as the π - π distances do not significantly differ between the neat and the blend films.

Second, as a general rule lengthening of the alkyl sidechains from six to eight methylene units results in increased crystalline structure within the films, which correlates with slightly higher J_{sc} s and PCEs. This is potentially due to the higher degree of sidechain interdigitation induced by the increased Van der Waals forces (as seen from the BT_xR analogues),^[122b, 148] however as per the initial hypothesis, it is also possible that these longer sidechains do indeed confer larger diffusion distances during the annealing process, thereby allowing pure domains of greater crystallinity to form through enhanced phase separation. Unfortunately, this theory remains conjectural without in-situ measurements performed during annealing. This potential increased diffusion is also observed to only result in minor increases in PCE, however the possibility that longer sidechains could facilitate even higher diffusion rates cannot be ruled out.

Lastly, a notable increase in crystalline structure is observed for many of the materials based on the centrosymmetric hexathiophene substrate. While the relationship between molecular packing and the structural symmetry of the oligothiophene analogues is unable to be explored further due to a lack of single-crystal structures, it is worthwhile to note that the previous work by Chen et al. also found that the centrosymmetric oligothiophenes in their study possessed much larger fibrillar domains than the axisymmetric oligothiophenes.^[118] Furthermore, this increased crystallinity is seemingly exacerbated for molecules that feature the dicyanomethylene moiety, with a cumulative effect on molecular stability also observed. In this study this crystallinity also manifests as higher phase transition temperatures, and may be linked to the relative ineffectiveness of the solvent-vapor annealing process, resulting in the similar morphologies of the as-cast and SVA-treated films. Furthermore, this strong intermolecular attraction may also be responsible for the widespread presence of higher-order 00/ reflections (corresponding to packing along the conjugated backbone in the plane of the substrate), most notably from neat films of the **CHR6T^x** analogues. This strong molecular alignment in the plane of the substrate exhibited by these materials may be of interest to those working in the organic transistor fields due to the device architectures involved.

4.7 Chapter conclusion

At the onset of the work in this chapter it was theorized that the regioregular, outwards-facing sidechain orientation that proved to be effective on the BTR-based materials would also result in a similar increase in π -stacking and performance for a series of oligothiophene-based materials, with the majority of similar materials in the literature only featuring inwards-facing sidechains. This sidechain engineering was performed on a series of 12 oligothiophene analogues of different conjugation lengths, sidechain lengths and end-group acceptors. Unfortunately, the results from this study indicate that analogues with this outwards-facing orientation instead produce devices with lowered PCEs. As suggested by the literature, this is likely due to reduced effectiveness of the device annealing process on molecular reorganization compared to molecules with inwards-facing sidechains. Analogues designed with longer sidechains to confer increased molecular diffusion do exhibit slightly higher PCEs than their shorter-chain counterparts, however this

improvement is small and it is unclear whether this is correlative or causative. Nonetheless, several key structure-morphology relationships were found, with longer sidechains, the dicyanovinylene moiety and the hexathiophene substrate found to confer increased degrees of crystallinity. An end-group dependence on the optimal oligothiophene conjugation length was also found, with **HR**- and **CHR**- acceptor moieties exhibiting the highest PCEs of ~7.0% and ~8.2% when coupled to hexathiophene and pentathiophene substrates, respectively. This work grants a valuable insight into oligothiophene-based materials for OPV applications and the complex crystallization behaviour in thin-films, and it is anticipated that these results will contribute to design guidelines for molecular materials.

4.8 Experimental and supporting information

4.8.1 Materials and methods

Unless noted, all materials were reagent grade and used as received without further purification. Anhydrous solvents were prepared by drying HPLC grade solvents using freshly activated molecular sieves. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using an Agilent 8453 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were carried out on either a Varian 400 MHz spectrometer, an Agilent 500 MHz spectrometer, or a Varian 600 MHz spectrometer. All NMR data was referenced to the chloroform signal, unless stated otherwise, and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad). MALDI-TOF mass spectrometry was performed on a Bruker microflex instrument, using chloroform as solvent and DCTB or terthiophene as the assisted matrix. ESI mass spectrometry was performed on a Thermo Scientific Q Exactive Plus Orbitrap LC-MS/MS instrument, using 50% acetonitrile/0.1% formic acid as the solvent. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE-440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC at a ramp rate of $10\text{ }^\circ\text{C min}^{-1}$ unless otherwise noted. Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mVs^{-1} . CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/Ag^+ pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate in acetonitrile. The solutions were deoxygenated by sparging with nitrogen prior to each scan and blanketed with nitrogen during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the materials were drop-casted on the electrode from dichloromethane solution to form a film. A ferrocene/ferrocenium redox couple was used as the internal standard.

4.8.1.1 Device fabrication and characterization

Organic photovoltaic devices were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. The devices were fabricated with a conventional device geometry of glass/ITO/PEDOT:PSS/active layer/Ca/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone and isopropyl alcohol for 15 minutes each and subsequently treated in UV–Ozone for 15 minutes. A thin layer (30 nm) of PEDOT:PSS (Clevios P VP Al 4083, filtered at 0.45 μm) was spin-coated onto the ITO surface. After being baked at 150 $^{\circ}\text{C}$ for 10 minutes, the substrates were transferred into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated from a blended chloroform solution (20 mg/mL) with weight ratio of oligothiophene and PC₇₁BM at 1:1 and the active layer thicknesses of all films were measured as 210–260 nm. Then, the substrates were placed in a glass Petri dish containing 1 mL THF for solvent vapour annealing (SVA) or thermally annealed, as specified in the text. After treatment, the films were transferred to a metal evaporation chamber and a bilayer cathode consisted of Ca (30 nm) capped with Al (100 nm) was deposited through a shadow mask (active area was 0.1 cm²) at approximately 1×10^{-6} Torr. Film thickness was determined by a Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m² AM 1.5G illumination conditions.

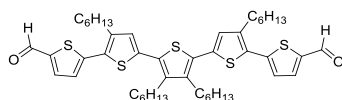
4.8.1.2 Thin-film fabrication and GIWAXS characterization

Samples were prepared for GIWAXS by spin-coating solutions of the oligothiophenes onto PEDOT:PSS coated Si substrates using the same deposition condition and annealing conditions as for the photovoltaic devices. The Si wafers had been sonicated in acetone and isopropanol for 30 minutes each followed by 15 minutes of UV/Ozone treatment. GIWAXS experiments were performed at the Australian Synchrotron on the SAXS/WAXS beamline under ambient conditions.^[144] A Pilatus 200K detector was used for 2D diffraction pattern collection. The energy of the incident beam was 11 keV at a range of incident angles from $\theta = 0.02 - 0.20^{\circ}$. The sample-to-detector range was 29.6 cm for the thermally-annealed films and 23.9 cm for all other films. Data from GIWAXS experiments was analysed using a customized version of NIKA 2D based in IgorPro.^[152] Single-crystal data was gathered from the MX1 beamline at the Australian synchrotron.^[141] Atomic force microscopy images were acquired using an Asylum Research Cypher scanning probe microscope operated in tapping mode.

4.8.2 Synthesis

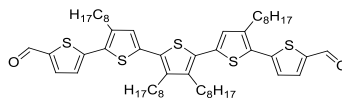
The end-group acceptor **9** was purchased from Sigma-Aldrich, the synthesis of **10** has been described in previous chapters and the synthesis of **11** has been previously described in the literature.^[39a, 202] The synthesis of the other known intermediates are found in references in the chapter.

4.8.2.1 3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (**6a**)



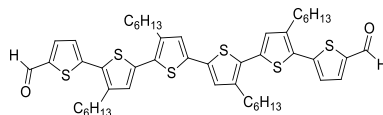
4a (0.24 g, 0.48 mmol), **5a** (0.40 g, 0.99 mmol) and P(o-tolyl)₃ (0.03 g, 0.1 mmol) were dissolved in THF (4 mL), and K₃PO₄ (1 mL, 2M aqueous solution), and the solution was bubbled for 30 minutes. Pd₂(dba)₃ (0.02 g, 0.02 mmol) was then added and the reaction stirred at 60 °C overnight. The organic layer was precipitated in isopropanol and then purified via column chromatography in hexanes/dichloromethane (1:1) to give **6a** as an orange solid (282 mg, 0.36 mmol, 75%). ¹H NMR (CDCl₃, 600 MHz) δ 9.89 (s, 2H); 7.72 (d, *J* = 4.0 Hz, 2H); 7.23 (d, *J* = 4.0 Hz, 2H); 7.02 (s, 2H); 2.82 (t, *J* = 7.8 Hz, 4H); 2.72 (t, *J* = 8.4 Hz, 4H); 1.69 (q, *J* = 7.6 Hz, 4H); 1.61 – 1.51 (m, 4H), 1.48 – 1.39 (m, 8H), 1.37 – 1.29 (m, 16H), 0.92 – 0.87 (m, 12H). ¹³C NMR (CDCl₃, 151 MHz) δ 182.53, 146.10, 142.47, 142.17, 141.04, 136.83, 136.15, 129.70, 129.40, 129.09, 125.82, 31.63, 31.47, 30.57, 30.20, 29.76, 29.57, 29.21, 28.27, 22.61, 22.57, 14.06, 14.05. IR (neat): ν = 2953, 2924, 2853, 1665, 1436, 1225, 1057 cm⁻¹. MS (MALDI⁺) calculated for C₄₆H₆₀O₂S₅ [M⁺] = 804.32, found = 804.26. Elemental analysis calculated for C₄₆H₆₀O₂S₅ (%): C, 68.61; H, 7.51; S, 19.91. Found, C, 68.82; H, 7.70; S, 19.72.

4.8.2.2 3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (**6b**)



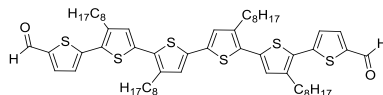
4b (0.78 g, 1.39 mmol), **4b** (1.5 g, 3.46 mmol) and P(o-tolyl)₃ 106 mg, 0.35 mmol) were dissolved in THF (12 mL), and K₃PO₄ (3 mL, 2M aqueous solution), and the solution was bubbled for 30 minutes. Pd₂(dba)₃ (90 mg, 0.09 mmol, 2.5%) was then added and the reaction stirred at 60 °C overnight. The organic layer was precipitated in isopropanol and then purified via column chromatography in 2:1 DCM/petroleum spirits, then 1:10 ethyl acetate:petroleum spirits to give **6b** as an orange solid (1.08 g, 1.19 mmol, 85%). ¹H NMR (CDCl₃, 600 MHz) δ 9.89 (s, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.01 (d, *J* = 5.9 Hz, 4H), 2.82 (t, *J* = 7.8 Hz, 4H), 2.77 (t, *J* = 7.9 Hz, 4H), 1.70 (m, 8H), 1.68 (m, 8H), 1.30 (m, 30H), 0.88 (m, 12H). ¹³C NMR (CDCl₃, 151 MHz) δ 182.52, 146.09, 142.54, 142.15, 141.16, 136.82, 136.06, 135.12, 129.32, 129.14, 128.92, 126.83, 125.82, 31.88, 31.86, 30.39, 30.24, 29.76, 29.59, 29.55, 29.42, 29.41, 29.25, 29.24, 22.67, 14.11. IR (neat): ν = 2953, 2924, 2853, 1665, 1436, 1225, 1057 cm⁻¹. MS (MALDI⁺) calculated for C₅₄H₇₆O₂S₅ = 916.44, found = 916.363. Elemental analysis calculated for C₅₄H₇₆O₂S₅ (%): C, 70.69; H, 8.35; O, 3.49; S, 17.47. Found, C: 70.86; H: 8.15

4.8.2.3 3',3'',4''',4''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5'''''-sexithiophene]-5,5'''''-dicarbaldehyde (**8a**)



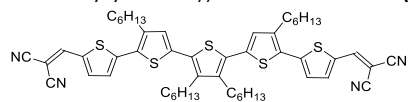
A solution of Ni(COD)₂ (0.35 g, 1.26 mmol), 2,2-bipyridine (0.19 g, 1.26 mmol) and COD (0.14 g, 1.26 mmol) in anhydrous DMF/toluene (5 mL, 1:1 mixture) were stirred at 80°C for 30 minutes. **7a** (0.72 g, 1.26 mmol) in anhydrous toluene (5 mL) was added in 1 portion and stirred for 4 hours. 30 mL of H₂O was added, and the organic layer was extracted in DCM (3 x 30 mL). The crude material was precipitated in isopropanol, then purified via column chromatography in DCM:hexanes (2:1) to get **8a** (0.46 g, 0.52 mmol, 86 %) as a red solid. ¹H NMR (CDCl₃, 400 MHz) δ 9.84 (s, 2H); 7.67 (d, *J* = 4.0 Hz, 2H); 7.20 (d, *J* = 5.0 Hz, 2H); 6.97 (d, *J* = 3.8 Hz, 2H); 2.77 (t, *J* = 7.8 Hz, 4H); 2.77 (t, *J* = 8.0 Hz, 4H); 1.64 (qq, *J* = 7.2 Hz, 8H); 1.45-1.25 (m, 25H); 0.85 (t, *J* = 7.0 Hz, 12H). ¹³C NMR (CDCl₃, 100 MHz) δ 182.54, 146.09, 142.55, 142.16, 141.17, 136.84, 136.06, 135.13, 129.33, 129.13, 128.94, 126.84, 125.84, 31.64, 30.37, 30.21, 29.76, 29.59, 29.22, 22.59, 22.58, 14.08, 14.06. IR (neat): ν = 2953, 2924, 2853, 1665, 1436, 1225, 1057 cm⁻¹. HRMS (ESI-LTQ-FTICP) calculated for C₅₀H₆₂O₂S₆ = 886.3069, found = 886.3101 m/z. Elemental analysis calculated For C₅₀H₆₂O₂S₆ (%): C, 67.67; H, 7.04. Found C, 67.66; H, 7.07.

4.8.2.4 3',3'',4''',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5'''''-sexithiophene]-5,5'''''-dicarbaldehyde (**8b**)



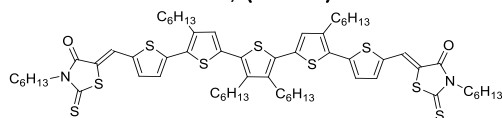
A solution of Ni(COD)₂ (0.20 g, 0.72 mmol), 2,2-bipyridine (0.11 g, 0.72 mmol) and COD (78 mg, 0.72 mmol) in anhydrous DMF/toluene (2 mL, 1:1 mixture) were stirred at 80 C for 30 minutes. **7b** (0.3 g, 0.48 mmol) in anhydrous toluene (2 mL) was added in 1 portion and stirred for 4 hours. 30 mL of H₂O was added, and the organic layer was extracted in DCM (3 x 30 mL). The crude material was precipitated in isopropanol, then purified via column chromatography (2:1 DCM:hexanes) to yield the product **8b** as a red solid (0.18 g, 0.18 mmol, 75%). ¹H NMR (CDCl₃, 400 MHz) δ 9.89 (s, 2H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.01 (d, *J* = 5.9 Hz, 4H), 2.82 (t, *J* = 7.8 Hz, 4H), 2.77 (t, *J* = 7.8 Hz, 4H), 1.68 (m, 8H), 1.42 (m, 8H), 1.29 (m, 32H), 0.88 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz) δ 182.52, 146.09, 142.54, 142.15, 141.16, 136.82, 136.06, 135.12, 129.32, 129.14, 128.92, 126.83, 125.82, 31.88, 31.86, 30.39, 30.24, 29.76, 29.59, 29.55, 29.42, 29.41, 29.25, 29.24, 22.67, 14.11. IR (neat): ν = 2952, 2852, 1665, 1436, 1228, 1059 cm⁻¹. MS (MALDI⁺) calculated for C₅₈H₇₈O₂S₆ = 998.43, found = 998.49 m/z. Elemental analysis calculated For C₅₈H₇₈O₂S₆ (%): C, 69.69; H, 7.86; O, 3.20; S, 19.25. Found C, 69.70; H, 7.68.

4.8.2.5 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinoxethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile (**MN5T⁶**)



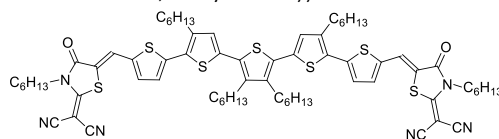
6a (0.1 g, 0.12 mmol) and **9** (0.08 g, 1.24 mmol), were dissolved in chloroform (10 mL), DBU (2 drops) were added and the reaction stirred at room temperature for 3 hours. The reaction was stopped, and the crude material precipitated in isopropanol before being purified by column chromatography in toluene followed by size exclusion chromatography in toluene to get **MN5T⁶** (80 mg, 0.08 mmol, 74%) as a green solid. ¹H NMR (CDCl₃, 600 MHz) δ 7.75 (d, J = 0.4 Hz, 2H), 7.71 (d, J = 4.2 Hz, 2H), 7.26 (d, J = 4.2 Hz, 2H), 7.04 (s, 2H), 2.86 – 2.82 (t, J = 8.4 Hz, 4H), 2.76 – 2.71 (m, 4H), 1.70 (qq, J = 7.5 Hz, 4H), 1.61 – 1.54 (m, 4H), 1.45 (m, 8H), 1.39 – 1.29 (m, 16H), 0.94 – 0.86 (m, 12H). ¹³C NMR (CDCl₃, 151 MHz) δ 149.76, 148.25, 143.91, 141.58, 139.01, 137.38, 133.93, 129.87, 129.42, 128.96, 126.04, 114.35, 113.51, 75.86, 31.61, 31.45, 30.48, 30.14, 30.10, 29.55, 29.19, 28.32, 22.60, 22.55, 14.06, 14.05. IR (neat): ν = 2956, 2926, 2858, 2215, 1717, 1582, 1528, 1420, 1387, 1359, 1127, 1065. HRMS (ESI-LTQ-FTICP) [M^+] calculated for C₅₂H₆₀N₄S₅ = 900.34, found = 900.3447 m/z. Elemental analysis calculated for C₅₂H₆₀N₄S₅ (%): C, 69.29; H, 6.71; N, 6.22; S, 17.78. Found, C, 69.49; H, 6.76; N, 6.13; S, 17.66.

4.8.2.6 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinoxethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR5T⁶**)



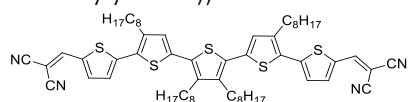
6a (0.08 g, 0.10 mmol) and **10** (0.22 g, 1.00 mmol) were dissolved in chloroform (10 mL), DBU (2 drops) was added and the reaction stirred overnight. The crude material precipitated in isopropanol before being purified by column chromatography in a hexane/dichloromethane mixture (2:1), followed by size exclusion chromatography (SX1 beads) in toluene to get **HR5T⁶** as a green solid (75 mg, 0.07 mmol, 67%). ¹H NMR (CDCl₃, 400 MHz) δ 7.85 (s, 2H); 7.36 (d, J = 4.0 Hz, 2H); 7.22 (d, J = 4.0 Hz, 2H); 7.02 (s, 2H); 4.11 (t, J = 7.6 Hz, 4H); 2.83 (t, J = 8.0 Hz, 4H); 2.74 (t, J = 8.2 Hz, 4H); 1.71 (pentet; J = 6.8 Hz, 8H); 1.65-1.55 (m, 4H); 1.52-1.42 (m, 8H); 1.42-1.26 (m, 28H); 0.99-0.80 (m, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 192.16, 167.51, 144.32, 141.89, 140.98, 137.08, 135.84, 134.67, 129.77, 129.57, 129.08, 126.54, 124.99, 120.25, 44.88, 31.69, 31.48, 31.33, 30.55, 30.29, 29.83, 29.59, 29.28, 28.30, 26.93, 26.44, 22.64, 22.49, 14.11, 12.99. IR (neat): ν = 2928, 2855, 2217, 1568, 1412, 1354, 1267, 1068 cm⁻¹. HRMS (ESI-LTQ-FTICP) [M^+] calculated for C₆₄H₈₆N₂O₂S₉ = 1202.47, found = 1202.4161 m/z. Elemental analysis calculated for C₆₄H₈₆N₂O₂S₉ (%): C, 63.85; H, 7.20; N, 2.33; S, 23.97. found C, 63.68; H, 7.20; N, 2.11; S, 24.11.

4.8.2.7 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR5T⁶**)



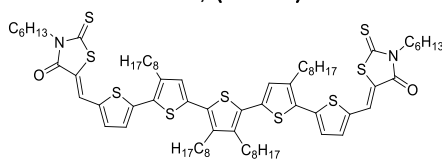
6a (0.1 g, 0.12 mmol) and **11** (0.31 g, 1.24 mmol) were dissolved in chloroform (10 mL), DBU (2 drops) were added and the reaction stirred at room temperature for three hours. The reaction was stopped, solvent removed and the crude material precipitated in isopropanol before being purified by column chromatography in toluene and size exclusion chromatography (SX1 beads) in toluene to get **CHR5T⁶** (100 mg, 0.08 mmol, 64%) as a green solid. ¹H NMR (CDCl₃, 600 MHz) δ 8.00 (s, 2H), 7.41 (d, *J* = 4.1 Hz, 2H), 7.22 (d, *J* = 4.0 Hz, 2H), 7.01 (s, 2H), 4.18 (t, *J* = 7.8 Hz, 4H), 2.80 (t, *J* = 8.2 Hz, 4H), 2.72 (t, *J* = 8.2 Hz, 4H), 1.78 – 1.67 (m, 8H), 1.58 (m, 4H), 1.52 – 1.29 (m, 36H), 0.96 – 0.86 (m, 18H). ¹³C NMR (CDCl₃, 151 MHz) δ 165.92, 165.28, 145.27, 142.61, 141.19, 136.42, 135.68, 135.62, 129.81, 129.09, 129.00, 128.34, 126.65, 113.33, 113.11, 112.27, 55.83, 45.31, 31.63, 31.45, 31.22, 30.42, 30.19, 30.00, 29.57, 29.24, 28.73, 28.36, 25.60, 22.62, 22.55, 22.41, 14.10, 13.92. IR (neat): ν = 2954, 2927, 2856, 2216, 1568, 1415, 1353, 1267, 1066, 792. HRMS (ESI-LTQ-FTICP) [*M*⁺] calculated for C₇₀H₈₆N₆O₂S₇ = 1266.45, found = 1266.4853 *m/z*. Elemental analysis calculated For C₇₀H₈₆N₆O₂S₇ (%): C, 66.31; H, 6.84; N, 6.63; S, 17.70. Found, C, 66.53; H, 6.84; N, 6.66; S, 17.51.

4.8.2.8 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile (**MN5T⁸**)



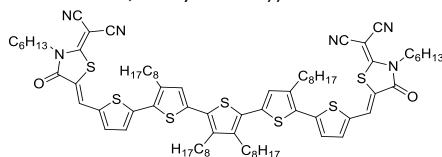
6b (0.15g, 0.15 mmol) and **9** (99 mg, 1.5 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at room temperature in the dark for 1.5 hours. The reaction was stopped, solvent removed and the crude material precipitated in isopropanol before being purified by column chromatography in 2:1 DCM:hexanes and and size exclusion chromatography (SX1 beads) in toluene, then precipitated in methanol to yield **MN5T⁸** as a dark purple solid (0.1 g, 0.14 mmol, 94%). ¹H NMR (CDCl₃, 600 MHz) δ 7.76 (s, 2H), 7.72 (d, *J* = 4.2 Hz, 2H), 7.28 (d, *J* = 4.2 Hz, 2H), 7.05 (s, 2H), 2.87 – 2.82 (t, *J* = 8.4 Hz, 4H), 2.76 – 2.71 (m, 4H), 1.64-1.56 (pentet, *J* = 7.5 Hz, 4H), 1.50 – 1.42 (m, 8H), 1.38 – 1.22 (m, 32H), 0.94 – 0.86 (m, 12H). ¹³C NMR (CDCl₃, 151 MHz) δ 149.77, 148.27, 143.92, 141.59, 138.97, 137.38, 133.94, 129.87, 129.46, 128.96, 126.08, 114.36, 113.51, 77.31, 76.99, 76.68, 75.90, 31.87, 31.84, 30.53, 30.14, 29.88, 29.52, 29.41, 29.26, 29.21, 28.31, 22.68, 22.66, 14.11. IR (neat): ν = 2952, 2925, 2854, 2218, 1567, 1416, 1067 cm⁻¹. MS (MALDI⁺) calculated for C₆₀H₇₆N₄S₅ = 1012.47, found = 1012.354 *m/z*. Elemental analysis calculated for C₆₀H₇₆N₄S₅: C, 71.10; H, 7.56; N, 5.53; S, 15.82. Found: C, 70.99; H, 7.67; N, 5.34; S, 15.72

4.8.2.9 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR5T⁸**)



6b (0.15 g, 0.16 mmol) and **10** (0.35 g, 1.60 mmol) were dissolved in chloroform (5 mL). DBU (1 drop) was added and the reaction stirred for 5 hours in the dark. The reaction was stopped, solvent removed and the crude material precipitated in isopropanol before being purified by column chromatography in a petroleum spirits/DCM mixture (1:2), followed by a size exclusion column (SX1 beads) in toluene to yield **HR5T⁸** as a green solid (110 mg, 0.84 mmol, 56%). ¹H NMR (CDCl₃, 600 MHz) δ 7.85 (s, 2H), 7.37 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.02 (s, 2H), 4.13 (t, J = 7.6 Hz, 4H), 2.83 (t, J = 8.0 Hz, 4H), 2.74 (t, J = 8.2 Hz, 4H), 1.75-1.65 (p, J = 6.8 Hz, 8H), 1.65 – 1.58 (m, 4H), 1.48 – 1.42 (m, 8H), 1.40 – 1.25 (m, 44H), 0.99 – 0.80 (m, 18H). ¹³C NMR (CDCl₃, 151 MHz) δ 192.15, 167.52, 144.31, 141.89, 140.98, 137.09, 135.84, 134.64, 129.77, 129.58, 129.09, 126.56, 124.99, 120.25, 44.87, 31.89, 31.33, 30.57, 30.32, 29.91, 29.81, 29.61, 29.48, 29.29, 29.26, 28.29, 26.94, 26.44, 22.69, 22.49, 14.12, 13.99. IR (neat): ν = 2954, 2924, 2855, 1698, 1578, 1424, 1329 cm⁻¹. MS (MALDI⁺) calculated for C₇₂H₁₀₂N₂O₂S₉ = 1314.54, found = 1314.322 m/z. Elemental analysis calculated for C₇₂H₁₀₂N₂O₂S₉: C, 65.70; H, 7.81; N, 2.13; O, 2.43; S, 21.93. Found: C, 65.85; H, 7.99; N, 2.04; S, 21.78

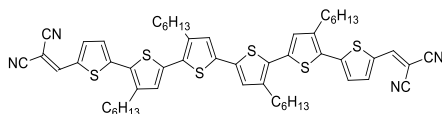
4.8.2.10 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR5T⁸**)



6b (0.15 g, 0.16 mmol) and **11** (0.4 g, 1.60 mmol) were dissolved in chloroform (5 mL). DBU (1 drop) was added and the reaction stirred for 3 hours in the dark. The crude material was precipitated in isopropanol before being purified by column chromatography in toluene, followed by a size exclusion column (SX1 beads) in toluene to yield **CHR5T⁸** as a green solid (0.15 g, 0.11 mmol, 68%). ¹H NMR (CDCl₃, 600 MHz) δ 8.03 (s, 2H), 7.44 (d, J = 4.0 Hz, 2H), 7.26 (d, J = 4.0 Hz, 2H), 7.03 (d, J = 4.0 Hz, 2H), 4.23 (t, J = 7.6 Hz, 4H), 2.83 (t, J = 8.0 Hz, 4H), 2.75 (t, J = 8.2 Hz, 4H), 1.74 (m, 4H), 1.69 (m, 4H), 1.59 (m, 4H), 1.44 (m, 16H), 1.35-1.20 (m, 38H), 0.88 (m, 18H). ¹³C NMR (CDCl₃, 151 MHz) δ 166.25, 165.61, 145.58, 142.86, 141.46, 136.73, 136.00, 135.91, 130.06, 129.39, 128.73, 127.06, 122.63, 113.61, 113.38, 112.54, 56.12, 45.60, 32.13, 31.49, 30.79, 30.50, 30.15, 29.78, 29.67, 29.52, 29.45, 29.01, 28.55, 25.86, 22.93, 22.66, 14.36. IR (neat): ν = 2955, 2925, 2855, 2217, 1697, 1581, 1541, 1421, 1387, 1357, 1131, 764, 750 cm⁻¹. MS (MALDI⁺) calculated for C₇₈H₁₀₂N₆O₂S₇ =

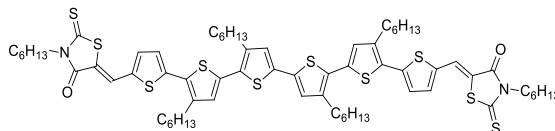
1378.61, found = 1378.41 m/z. Elemental analysis calculated for $C_{78}H_{102}N_6O_2S_7$: C, 67.88; H, 7.45; N, 6.09; O, 2.32; S, 16.26. Found: C, 67.54; H, 7.47; N, 5.96; S, 16.32

4.8.2.11 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (**MN6T⁶**)



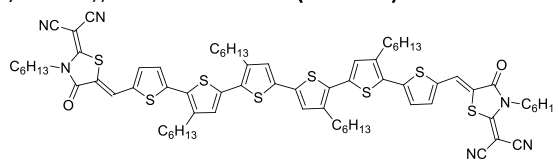
8a (0.1 g, 0.11 mmol) and **9** (0.07 g, 1.13 mmol) were dissolved in chloroform (10 mL), DBU (2 drops) were added and the reaction stirred overnight. The crude material was precipitated in isopropanol before being purified by column chromatography in chloroform, followed by a size exclusion column (SX1 beads) in toluene to yield **MN6T⁶** as a green solid (80 mg, 0.08 mmol, 73 %). 1H NMR ($CDCl_3$, 600 MHz) δ 7.25 (d, J = 3.5 Hz, 2H), 7.20 (s, 2H), 6.99 (m, 4H), 6.96 (s, 2H), 2.68 (m, 8H), 1.65-1.50 (m, 8H), 1.38 – 1.25 (m, 8H), 1.22-1.10 (m, 17H), 0.75 (m, 12H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.69, 148.54, 147.64, 143.74, 141.65, 138.48, 138.35, 137.34, 135.54, 133.72, 125.81, 125.56, 114.02, 113.34, 75.89, 31.56, 31.54, 30.24, 30.09, 30.04, 29.74, 29.32, 29.18, 22.52, 22.50, 13.89, 13.74. IR (neat): ν = 2926, 2854, 1688, 1579, 1420, 1332 cm^{-1} . HRMS (ESI-LTQ-FTICP) [M^+] calculated for $C_{56}H_{62}N_4S_6$ = 982.33, found = 982.3603 m/z. Elemental analysis calculated for $C_{56}H_{62}N_4S_6$ (%): C, 68.39; H, 6.35; N, 5.70; S, 19.56. Found, C, 68.27; H, 6.32; N, 5.50

4.8.2.12 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR6T⁶**)



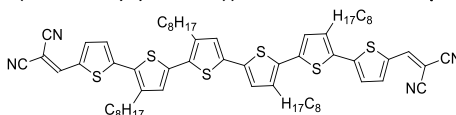
8a (0.2 g, 0.23 mmol) and **10** (0.49 g, 2.25 mmol) were dissolved in chloroform (20 mL), DBU (2 drops) were added and the reaction stirred overnight. The crude material was precipitated in isopropanol before being passed through a silica plug in chloroform, then purified multiple times by a size exclusion chromatography (SX1) in toluene to get a green solid which was recrystallized from 1,4-dioxane to get **HR6T⁶** as a green solid (200 mg, 1.58 mmol, 70 %). 1H NMR ($CDCl_3$, 600 MHz) δ 7.84 (s, 2H); 7.37 (d, J = 4.1 Hz, 2H); 7.22 (d, J = 4.0 Hz, 2H); 7.01 (d, J = 6.9 Hz, 4H); 4.11 (t, J = 7.8 Hz, 4H); 2.82 (t, J = 8.1 Hz, 4H); 2.77 (t, J = 8.1 Hz, 4H); 1.75-1.66 (m, 12H); 1.50-1.40 (m, 8H); 1.40-1.30 (m, 30H); 0.95-0.85 (m, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.18, 167.51, 144.33, 141.96, 141.08, 137.08, 135.76, 135.08, 134.68, 129.52, 129.25, 128.93, 126.83, 126.54, 124.99, 120.24, 44.88, 31.70, 31.67, 31.34, 30.35, 30.30, 29.84, 29.70, 29.65, 29.31, 29.26, 26.95, 26.45, 22.66, 22.62, 22.51, 14.13, 14.00. IR (neat): ν = 2955, 2926, 2855, 1696, 1578, 1412, 1329, 1182, 1140 cm^{-1} . HRMS (ESI-LTQ-FTICP) [M^+] calculated for $C_{68}H_{88}N_2O_2S_{10}$ = 1984.41, found = 1284.4031 m/z. Elemental analysis calculated for $C_{68}H_{88}N_2O_2S_{10}$ (%): C, 63.50; H, 6.90; N, 2.18; O, 2.49; S, 24.93. Found, 63.88; H, 6.94; N, 2.06; S, 24.75.

4.8.2.13 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR6T⁶**)



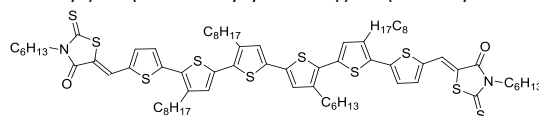
8a (0.22 g, 0.25 mmol) and **11** (0.62 g, 0.47 mmol) were dissolved in chloroform (20 mL). DBU (4 drops) was added and the reaction stirred at room temperature for 3 hours. The crude material was precipitated in isopropanol then purified with silica gel chromatography in toluene to get **CHR6T⁶** (240 mg, 0.36 mmol, 80%) as a green solid. ¹H NMR (CDCl₃, 600 MHz) δ 8.02 (s, 2H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.01 (d, *J* = 3.0 Hz, 4H), 4.22 (t, *J* = 7.8 Hz, 4H), 2.83 (t, *J* = 7.8 Hz, 4H), 2.76 (t, *J* = 4.0 Hz, 2H), 1.78 – 1.66 (m, 12H), 1.48 – 1.39 (m, 12H), 1.38 δ 165.96, 165.26, 145.26, 142.64, 141.35, 136.48, 135.86, 135.42, 135.33, 129.22, 129.04, 128.99, 128.29, 126.88, 126.83, 113.58, 113.02, 112.18, 56.02, 45.37, 31.59, 31.57, 31.18, 30.26, 30.20, 29.89, 29.64, 29.15, 28.71, 25.59, 22.52, 22.48, 22.33, 13.96, 13.94, 13.78. IR (neat): ν = 2955, 2927, 2856, 2217, 1695, 1576, 1541, 1412, 1386, 1356, 1168, 1133, 1065, 842 cm⁻¹. HRMS (ESI-LTQ-FTICP) [M+H⁺] calculated for C₇₄H₈₈N₆O₂S₈ = 1341.48, found = 1349.4693 m/z. Elemental analysis calculated for C₇₄H₈₈N₆O₂S₈ (%): C, 65.83; H, 6.57; N, 6.22; O, 2.37; S, 19.00. Found, C, 65.80; H, 6.75; N, 6.31.

4.8.2.14 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile (**MN6T⁸**)



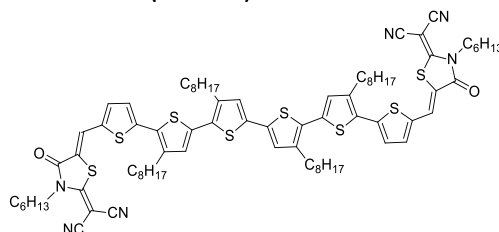
8b (90 mg, 0.9 mmol) and **9** (59 mg, 9 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at room temperature in the dark for 1.5 hours. The solvent was removed and the crude solid purified via precipitation in isopropanol and silica column chromatography in chloroform, then size exclusion column in toluene to get **MN6T⁸** as a green solid (90 mg, 0.08 mmol, 84%). ¹H NMR (600 MHz, CDCl₃) δ 7.78 (s, 2H), 7.74 (d, 2H, *J* = 4.2 Hz), 7.30 (d, *J* = 4.2 Hz, 2H), 7.05 (s, 4H), 2.88 (t, *J* = 7.8 Hz, 4H), 2.81 (t, *J* = 7.8 Hz, 4H), 1.74 (m, 8H), 1.46 (m, 8H), 1.38 – 1.29 (m, 32H), 0.88, (m, 12H). ¹³C-NMR (126 MHz, CDCl₃) δ 149.75, 148.33, 143.98, 141.69, 139.00, 137.41, 135.42, 133.89, 129.24, 129.05, 128.79, 127.06, 126.03, 114.37, 113.52, 75.81, 31.86, 31.83, 30.30, 30.14, 30.11, 29.65, 29.52, 29.40, 29.23, 29.20, 22.66, 14.10. IR (neat): ν = 2952, 2925, 2852, 1698, 1587, 1422, 1260, 1275, 764 cm⁻¹. MS (MALDI⁺) calculated for C₆₄H₇₈N₄S₆ = 1094.46, found = 1094.759 m/z. Elemental analysis calculated for C₆₄H₇₈N₄S₆ (%): C, 68.93; H, 7.48; N, 4.76; S, 18.83. Found: C, 68.61; H, 7.03; N, 4.47; S, 18.65

4.8.2.15 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR6T⁸**)



8b (0.16g, 0.16 mmol) and **10** (347 mg, 1.6 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at room temperature in the dark for 1.5 hours. The solvent was removed and the crude precipitated in isopropanol then purified via silica gel column chromatography in chloroform and size-exclusion chromatography in toluene, then precipitated in methanol to yield **HR6T⁸** as a dark purple solid (170 mg, 0.12 mmol, 76%). ¹H NMR (600 MHz, CDCl₃) δ 7.85 (s, 2H), 7.37 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.01 (d, J = 7.1 Hz, 4H), 4.13 (dd, J = 8.8, 6.5 Hz, 4H), 2.80 (t, J = 7.8 Hz, 4H), 2.78 (t, J = 7.8 Hz, 4H), 1.70 (m, 12H), 1.42 (m, 8H), 1.36 – 1.29 (m, 44H), 0.88 (m, 18H). ¹³C NMR (101MHz, CDCl₃) δ 149.77, 148.34, 143.99, 141.69, 139.03, 137.41, 135.41, 133.88, 129.24, 129.06, 128.79, 127.06, 126.03, 114.39, 113.53, 75.78, 31.87, 31.84, 30.31, 30.14, 29.66, 29.53, 29.41, 29.24, 29.21, 22.66, 14.11. IR (neat): ν = 2952, 2925, 2852, 1698, 1587, 1422, 1275, 1260, 764 cm⁻¹. MS (MALDI⁺) calculated for C₇₆H₁₀₄O₂N₂S₁₀ = 1094.46, found = 1396.504 m/z. Elemental analysis calculated for C₇₆H₁₀₄O₂N₂S₁₀ (%): C, 65.28; H, 7.50; N, 2.00; O, 2.29; S, 22.93. Found: C, 65.32; H, 7.71; N, 1.98; S, 23.05.

4.8.2.16 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene)) dimalononitrile (**CHR6T⁸**)

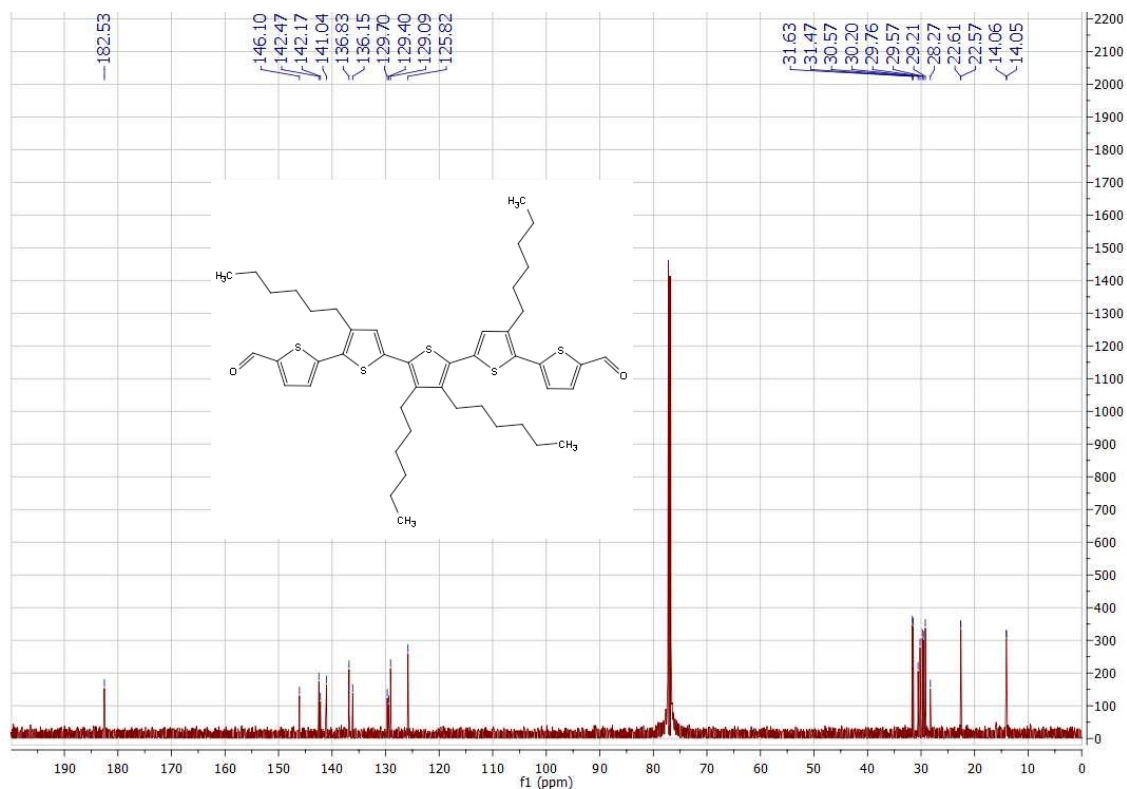
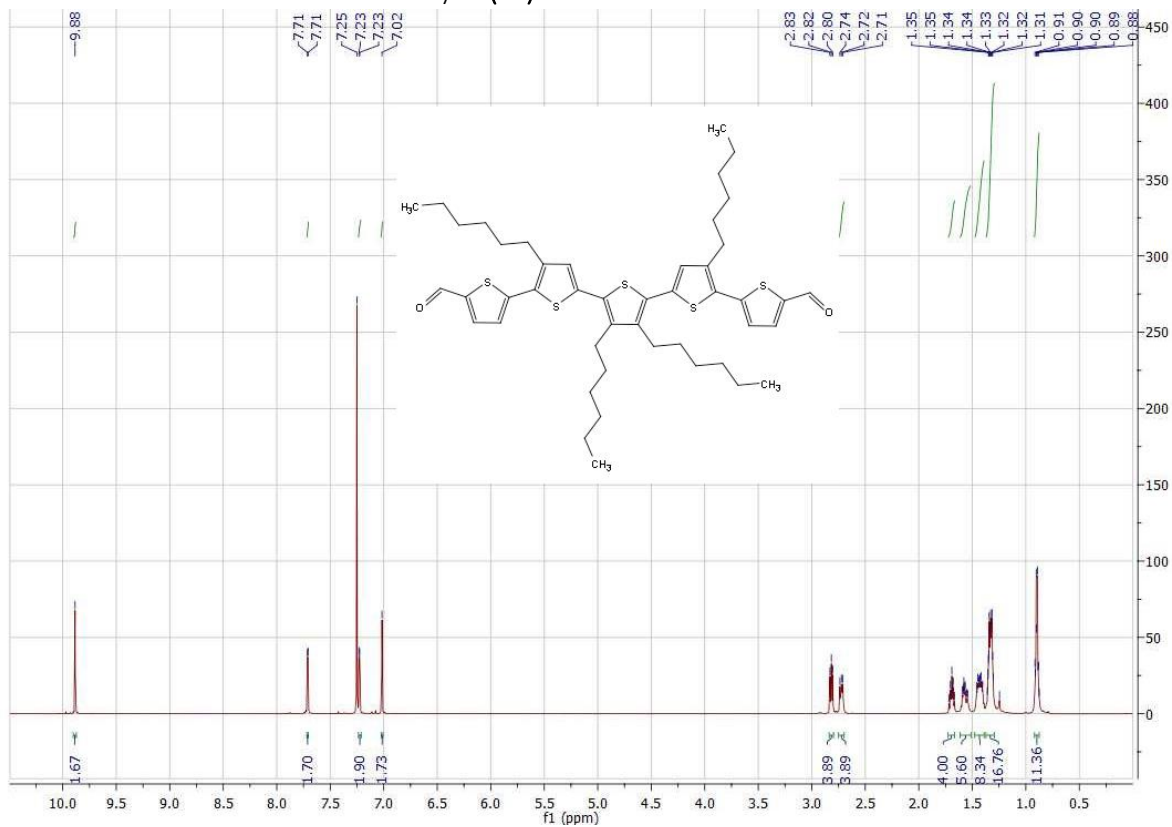


8b (0.16g, 0.16 mmol) and **11** (0.40 g, 1.6 mmol) were dissolved in chloroform (5 mL). 1 drop of DBU was added and the reaction left to stir at 60°C in the dark for 2 hours. The solvent was removed and the crude solid purified via silica column chromatography in chloroform and size-exclusion chromatography in toluene, then precipitated in methanol to yield **CHR6T⁸** as a dark purple solid (131 mg, 0.09 mmol, 56%). ¹H NMR (600 MHz, CDCl₃) δ 8.04 s, 2H), 7.45 (d, J = 4.0 Hz, 2H), 7.26 (d, J = 4.0 Hz, 2H), 7.03 (m, 4H), 4.24 (t, J = 7.9 Hz, 4H), 2.85 – 2.76 (m, 8H), 1.75 (m, 12H), 1.36-1.25 (m, 54 H) 0.88 (m, 18H). ¹³C NMR (151MHz, CDCl₃) δ 165.98, 165.36, 145.34, 142.65, 141.30, 136.41, 135.71, 135.66, 135.21, 129.15, 128.98, 128.95, 128.46, 126.89, 126.78, 113.32, 113.13, 112.28, 55.84, 45.33, 31.86, 31.84, 31.22, 30.32, 30.30, 30.27, 30.23, 29.89, 29.68, 29.62, 29.52, 29.48, 29.44, 29.40, 29.36, 29.24, 29.22, 29.18, 29.16, 28.74, 25.60, 22.66, 22.64, 22.40, 14.10, 13.91. IR (neat): ν = 2954, 2923, 2853, 2217, 1693, 1575, 1540, 1421, 1386, 1355, 1336, 1132, 1062, 764, 750 cm⁻¹. MS (MALDI⁺) calculated for C₈₂H₁₀₄N₆O₂S₆ = 1460.60, found = 1460.996 m/z. Elemental analysis

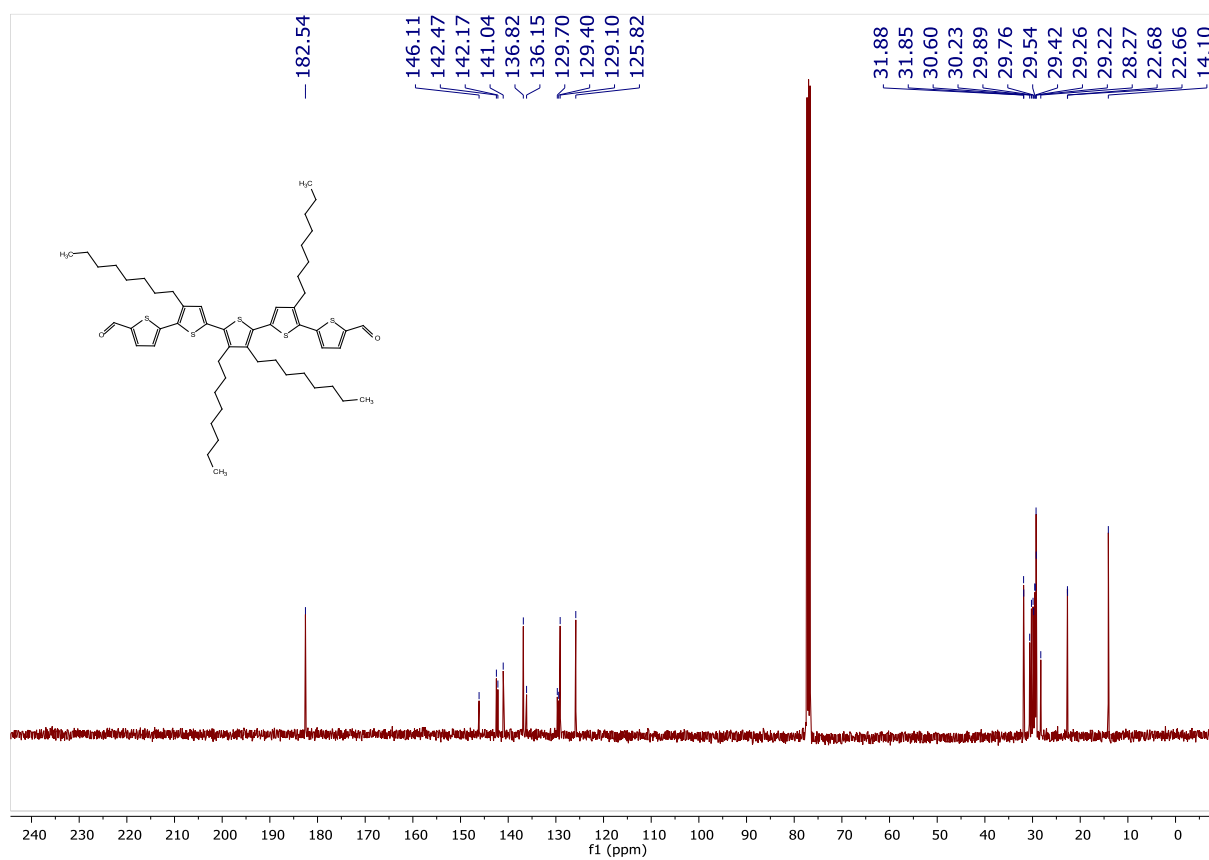
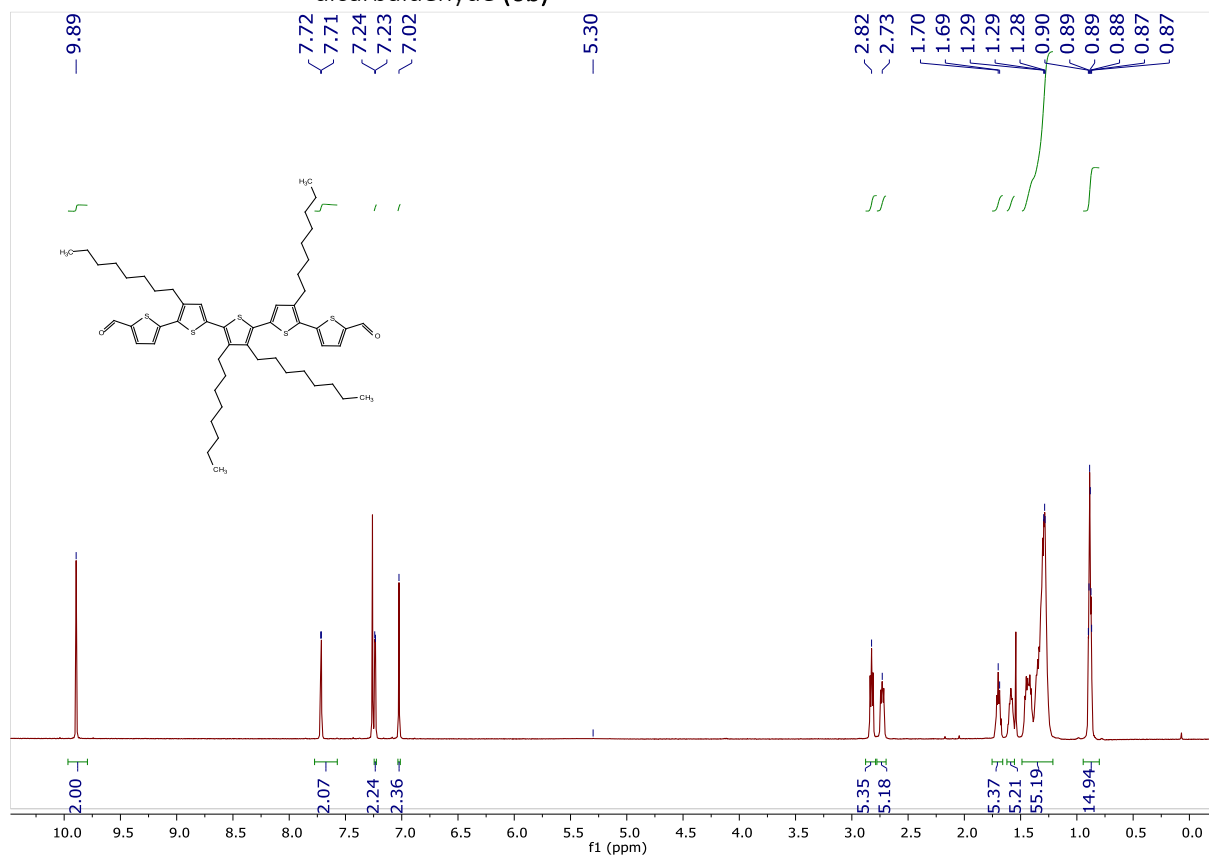
calculated for $C_{82}H_{104}N_6O_2S_6$ (%): C, 66.23; H, 7.27; N, 4.75; O, 3.21; S, 18.54. Found: C, 66.01; H, 7.47; N, 4.95; S, 18.31.

4.8.3 1H and ^{13}C spectra of unpublished compounds

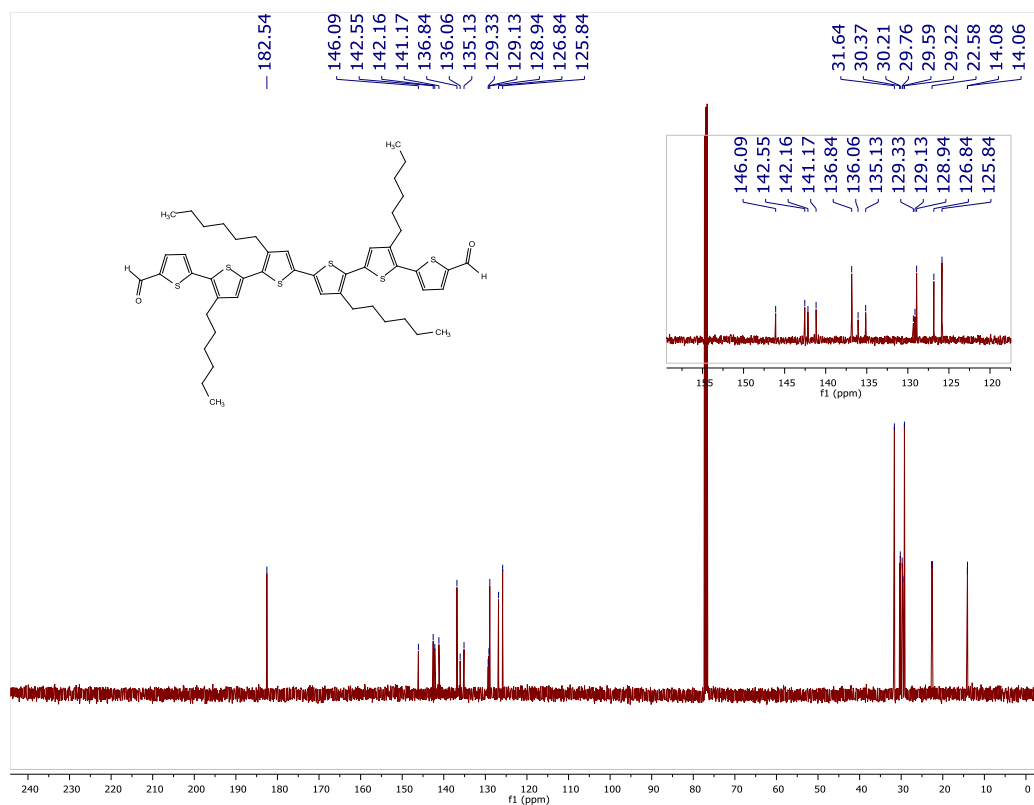
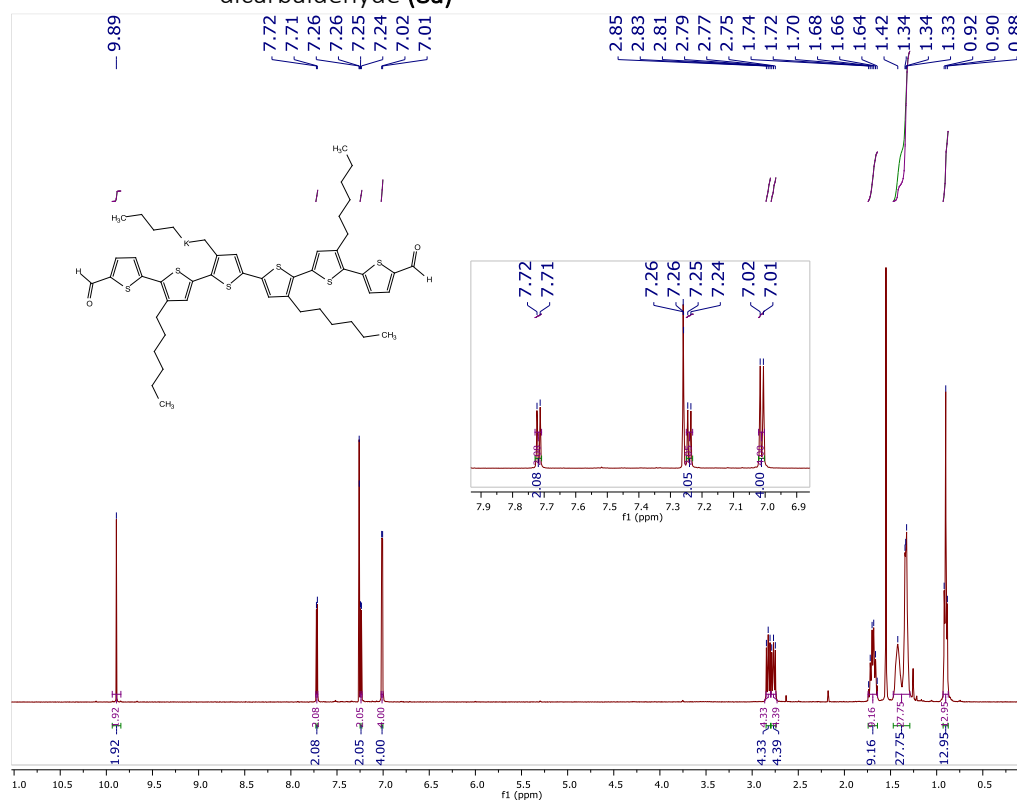
4.8.3.1 3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (**6a**)



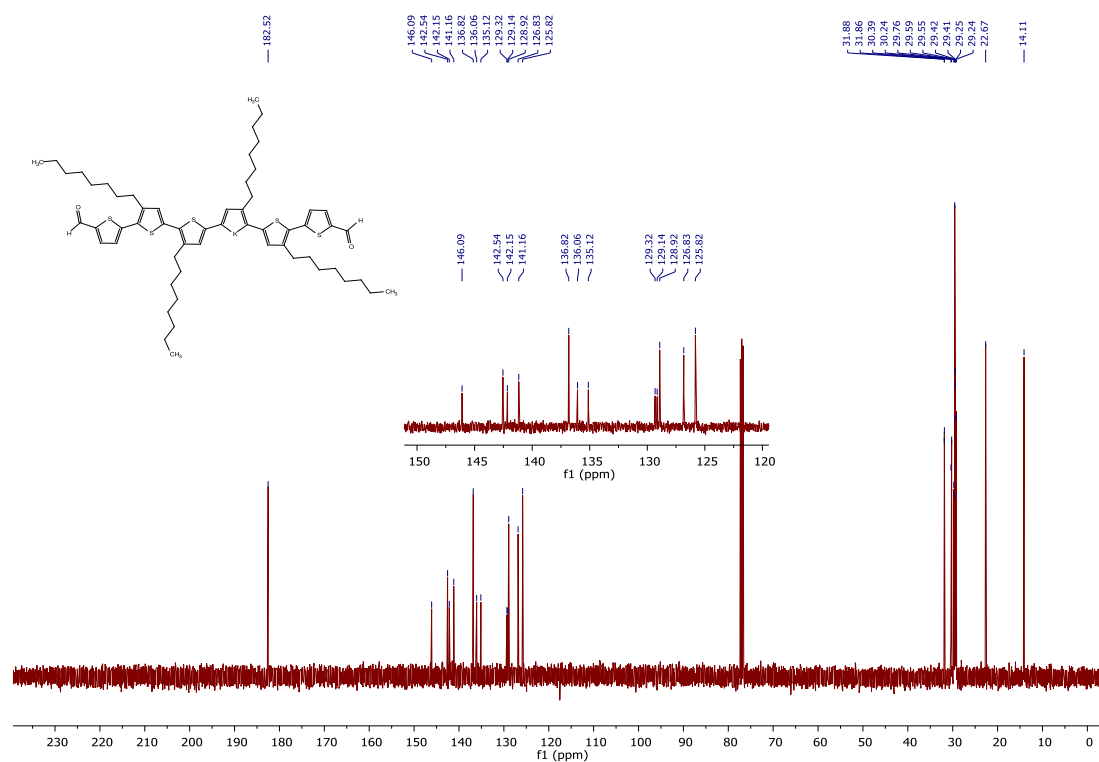
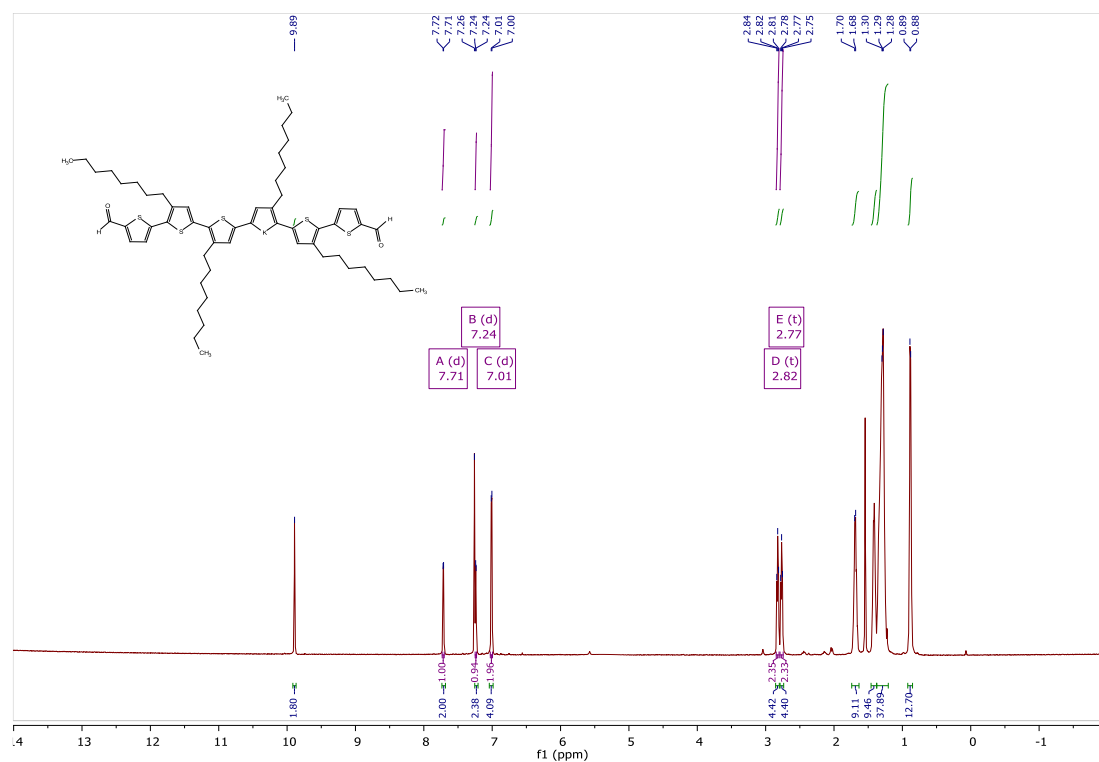
4.8.3.2 3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (**6b**)



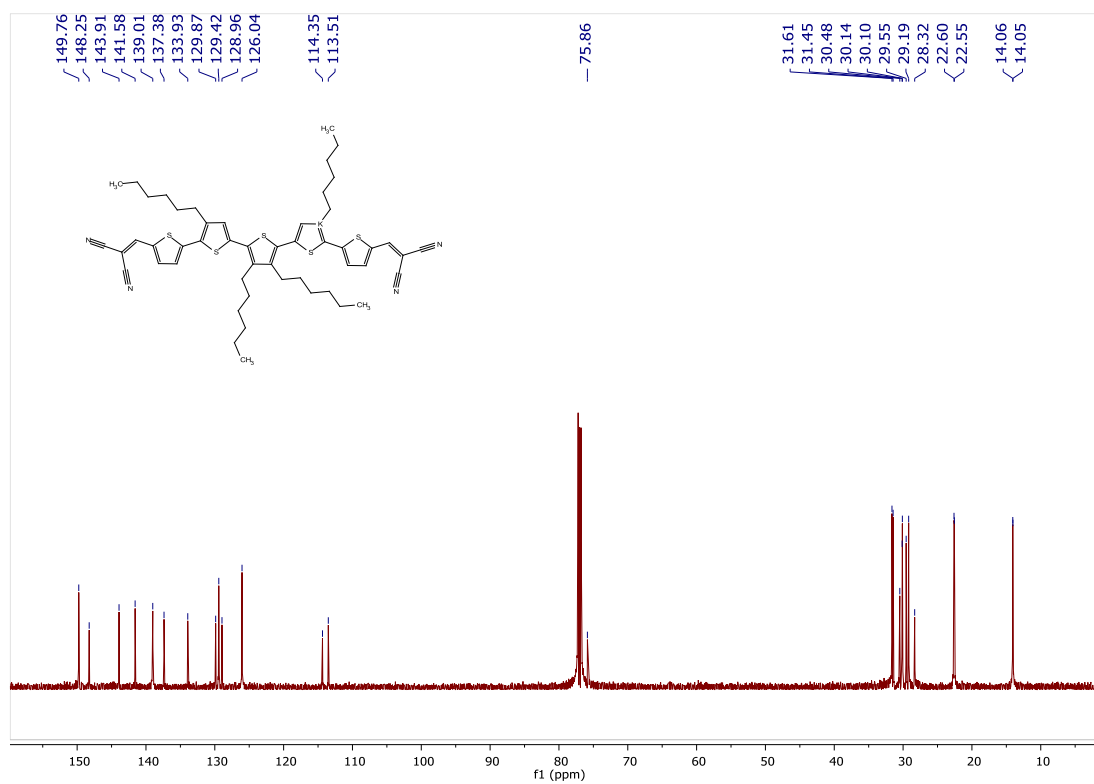
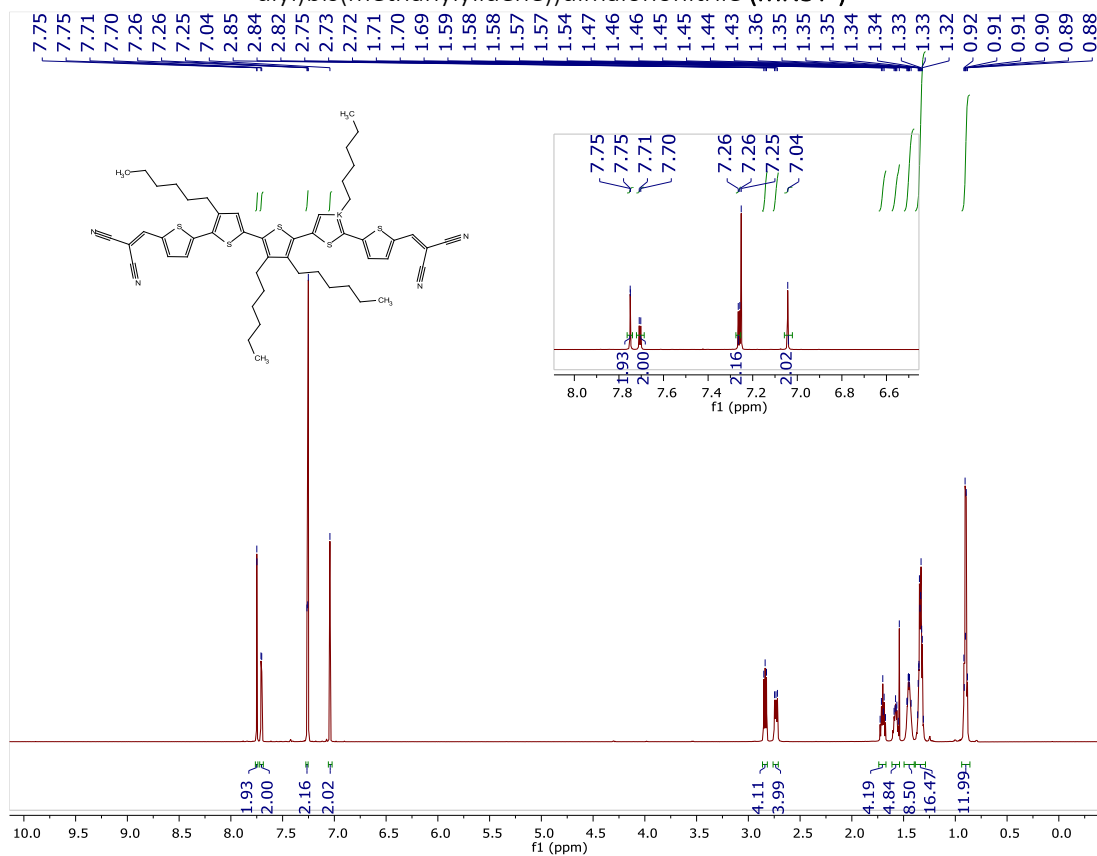
4.8.3.3 3',3'',4'',4''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''':5''',2''''-sexithiophene]-5,5''''-dicarbaldehyde (**8a**)



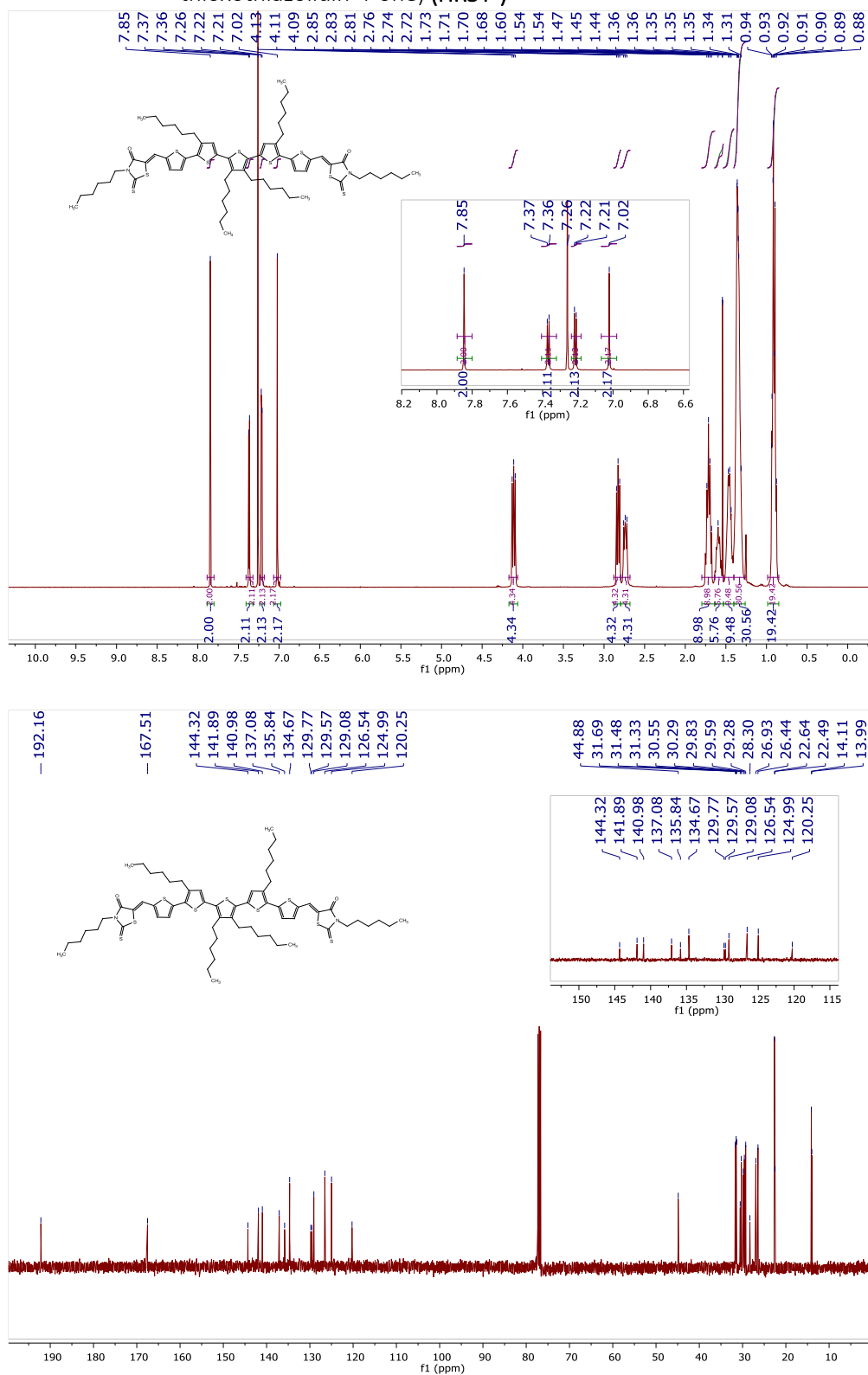
4.8.3.4 3',3'',4''',4''''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5'''''-sexithiophene]-5,5'''''-dicarbaldehyde (**8b**)



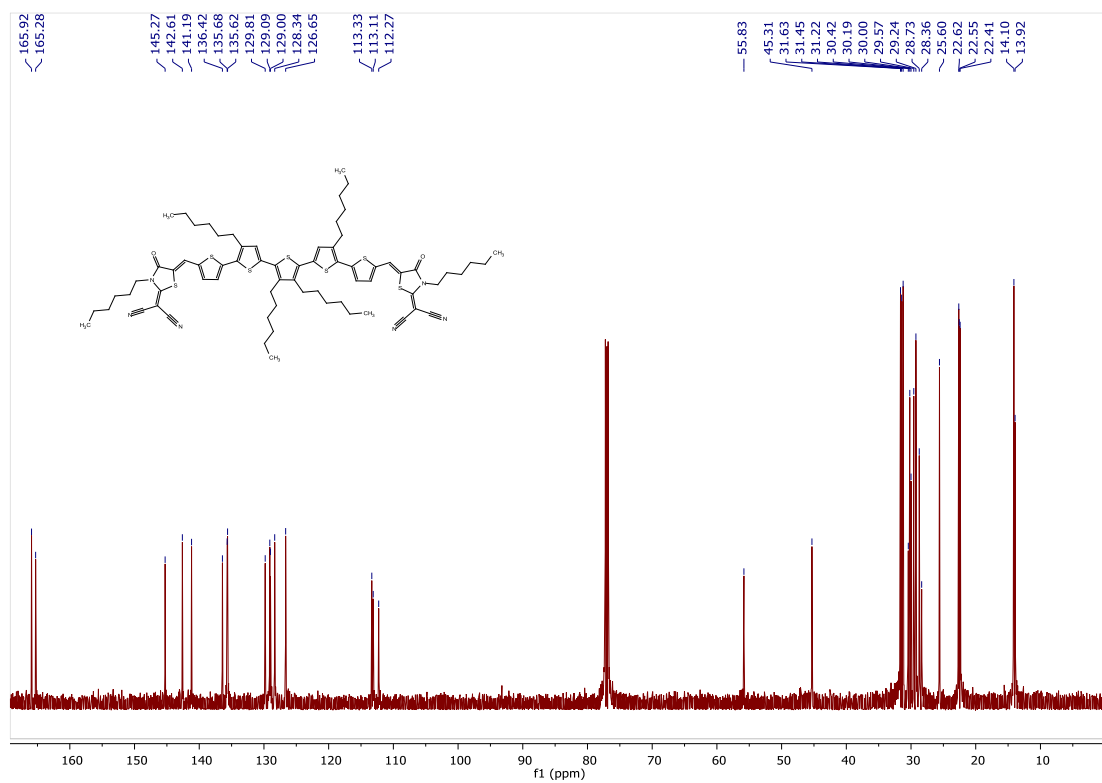
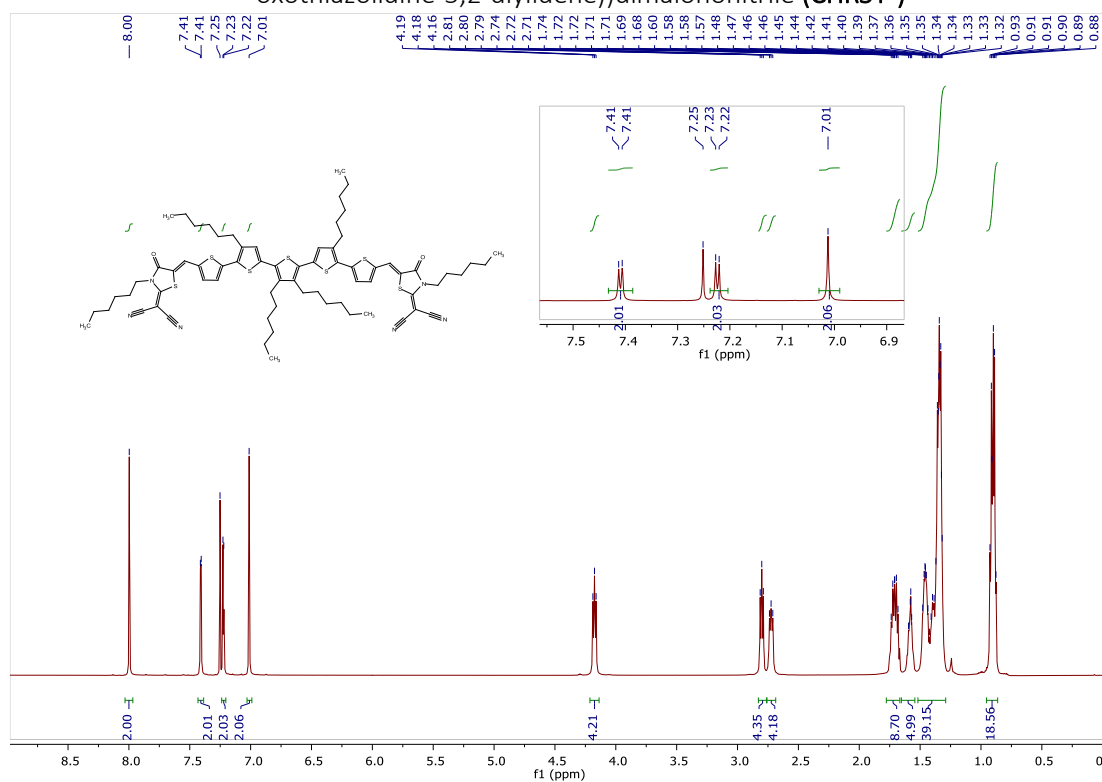
4.8.3.5 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (**MN5T⁶**)



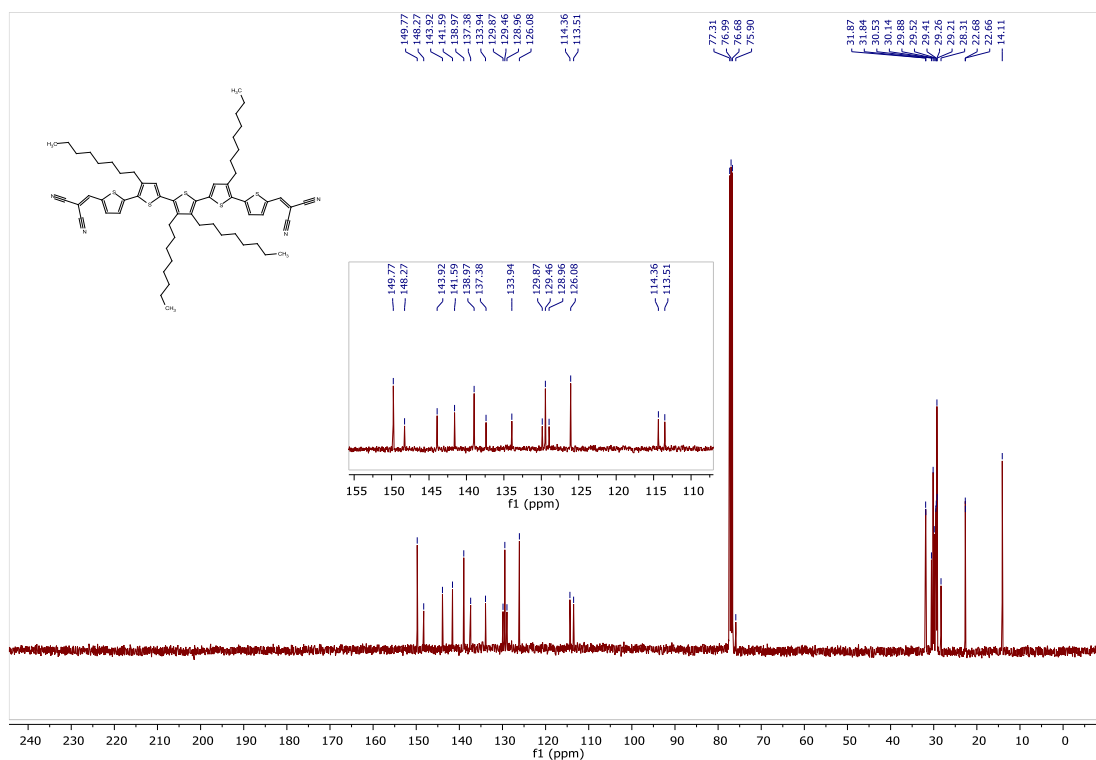
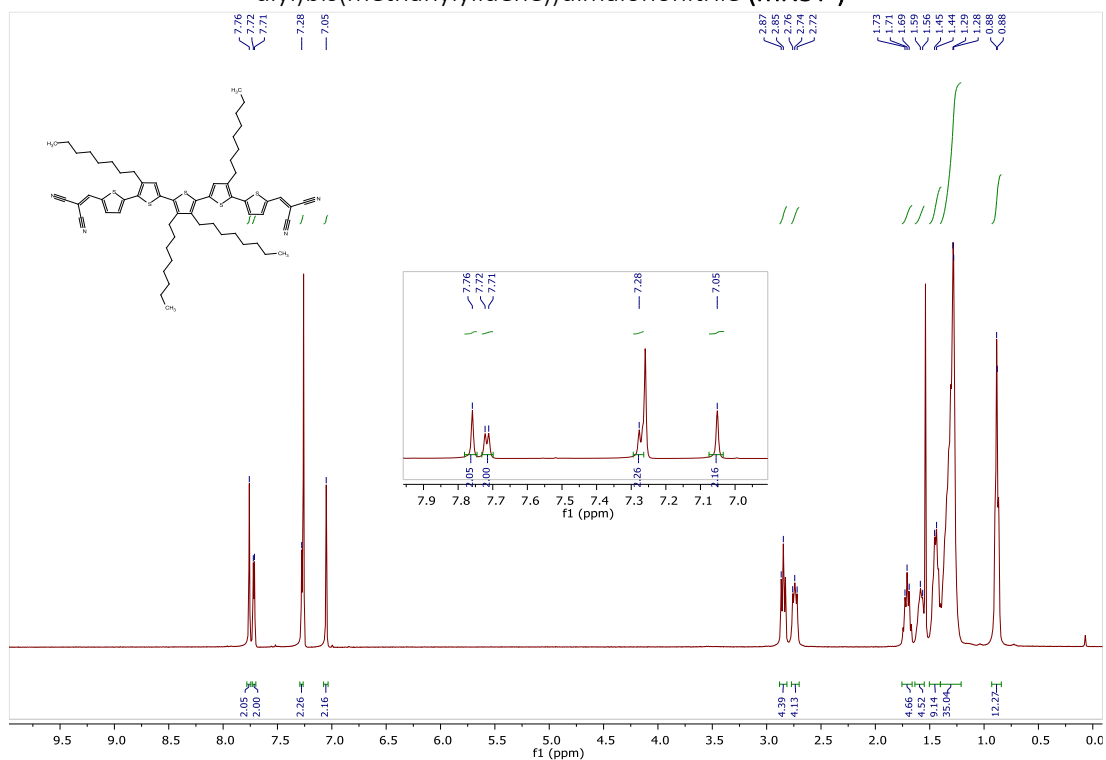
4.8.3.6 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (HR5T⁶)



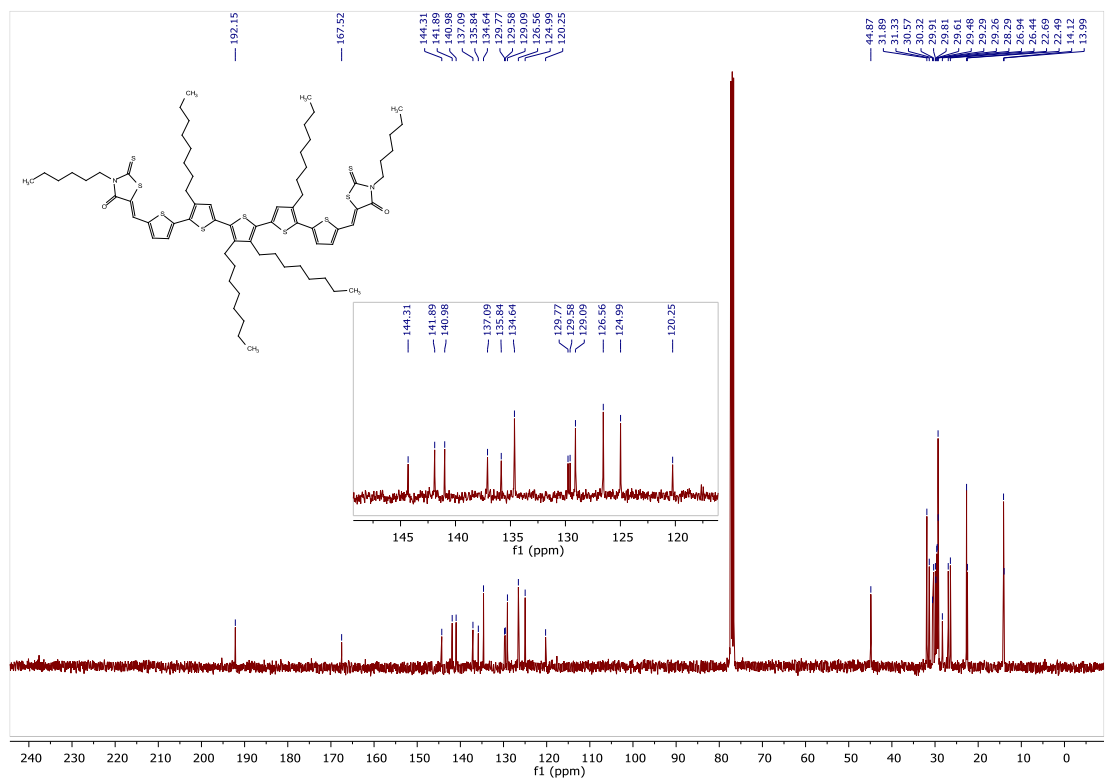
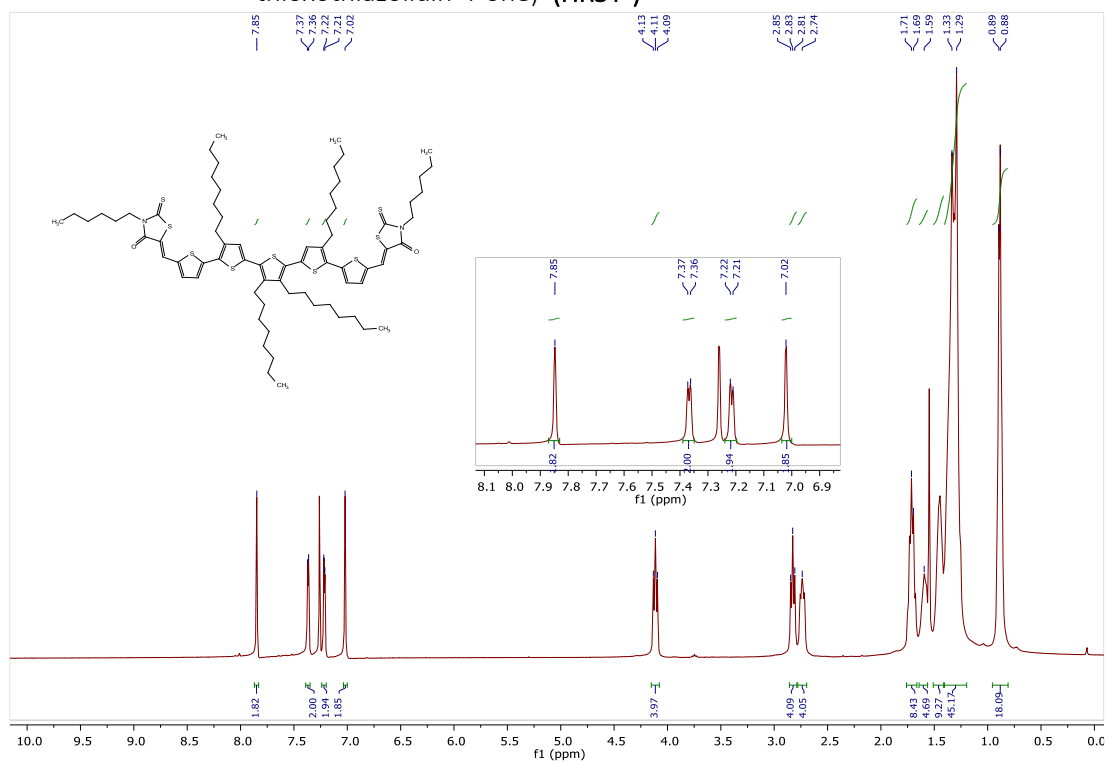
4.8.3.7 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2'''-quinquethiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (CHR5T⁶)



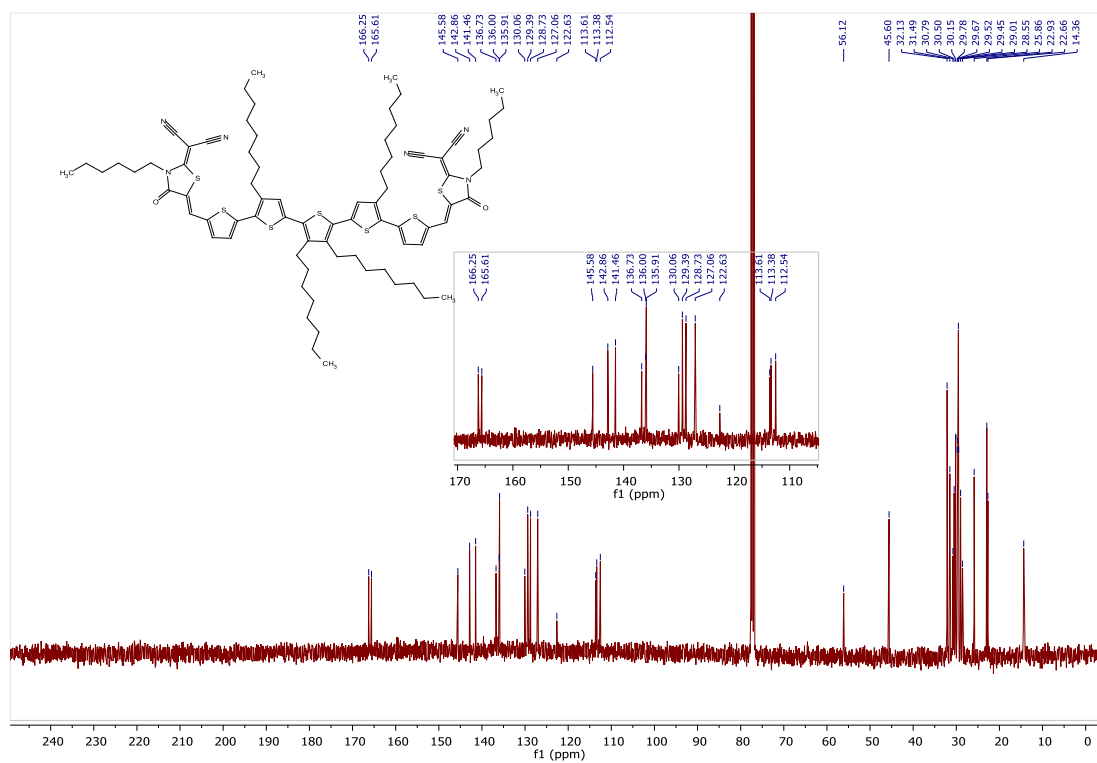
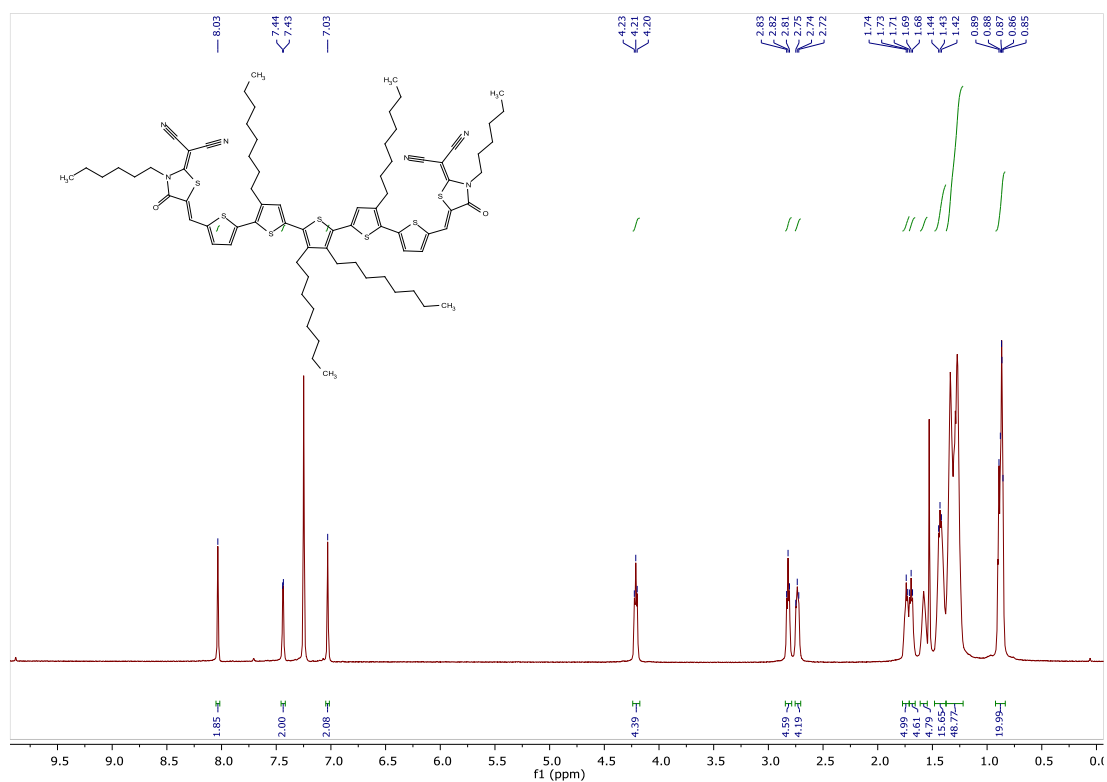
4.8.3.8 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''-quinquethiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (**MN5T⁸**)



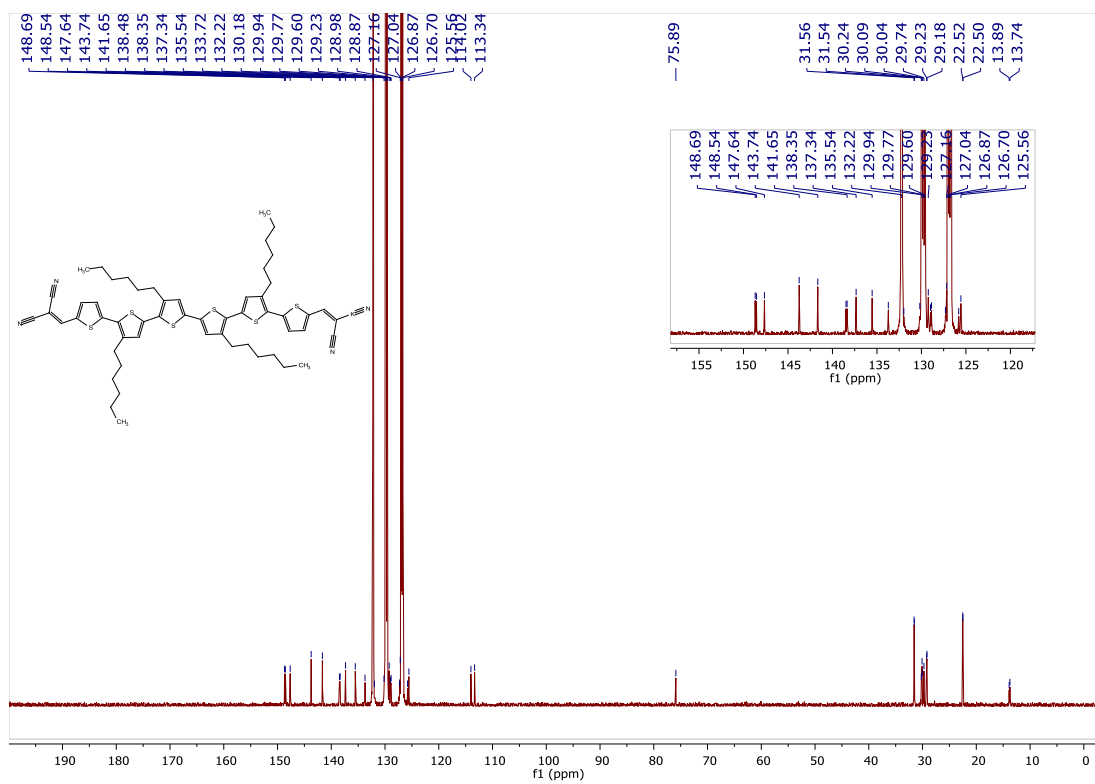
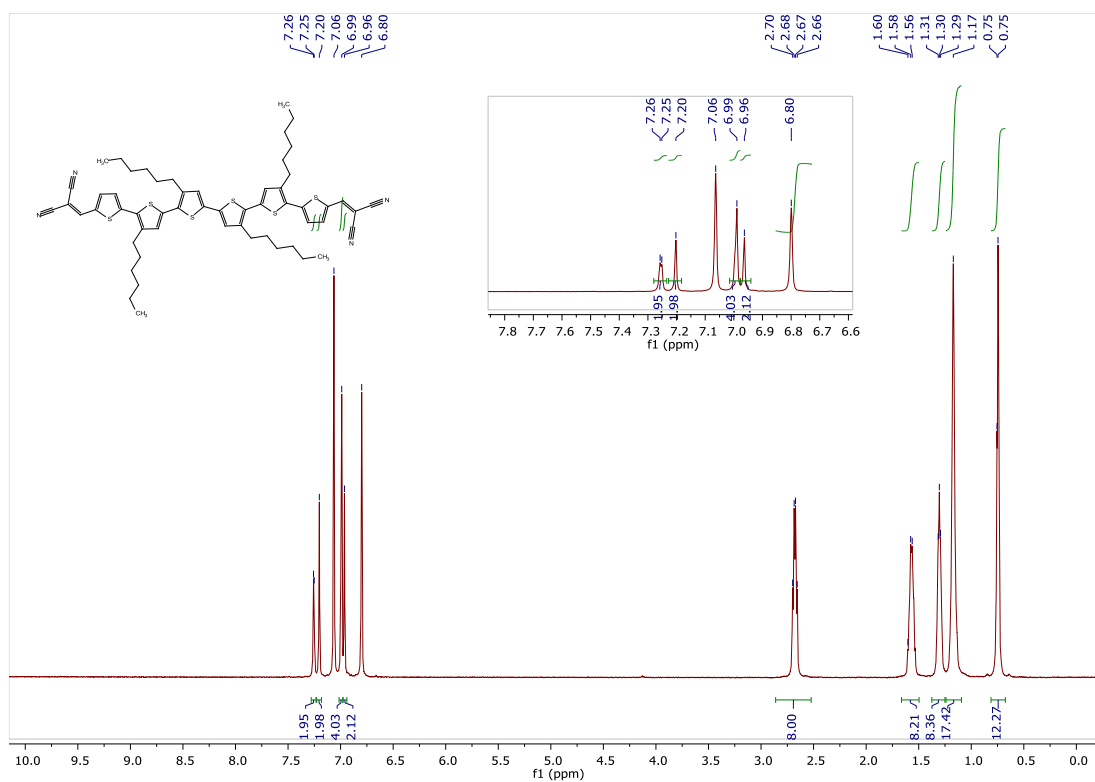
4.8.3.9 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2'''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (HR5T⁸)



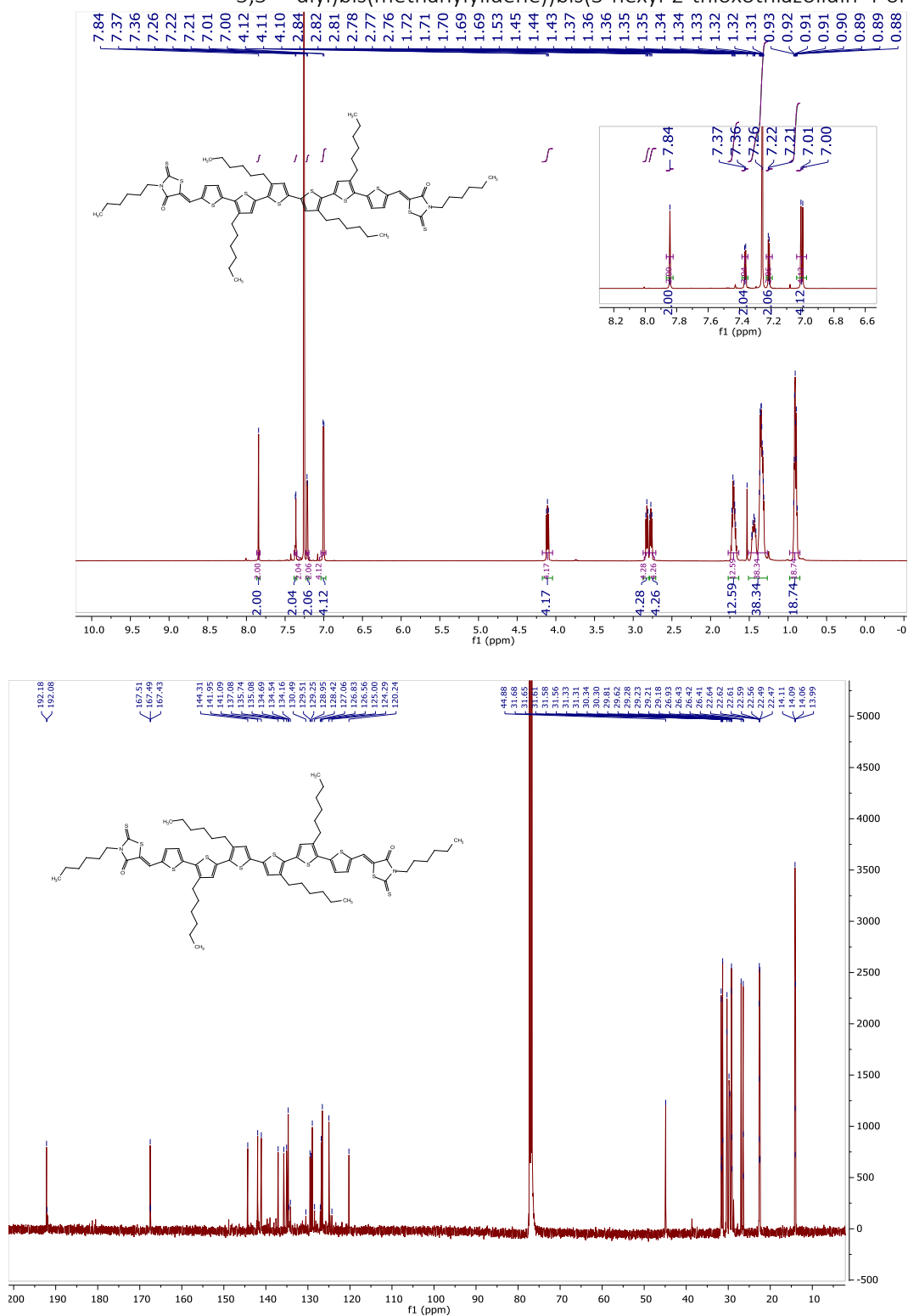
4.8.3.10 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''-quinquethiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (CHR5T[®])



4.8.3.11 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2'''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (**MN6T⁶**)

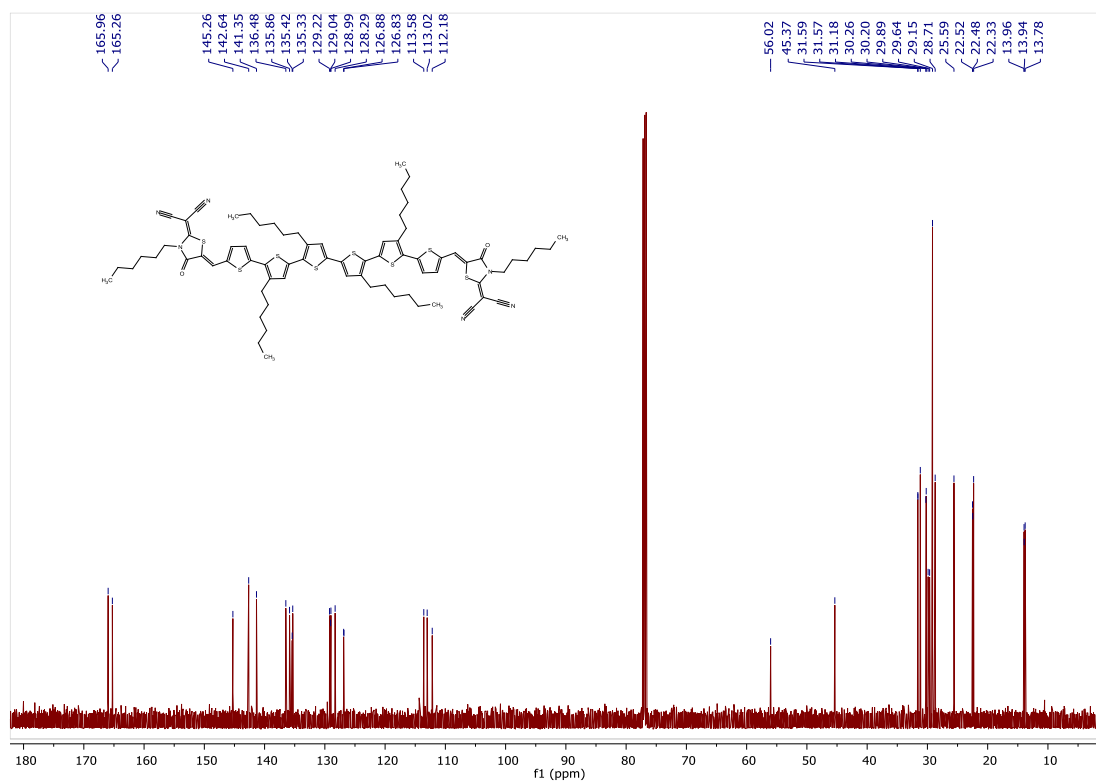
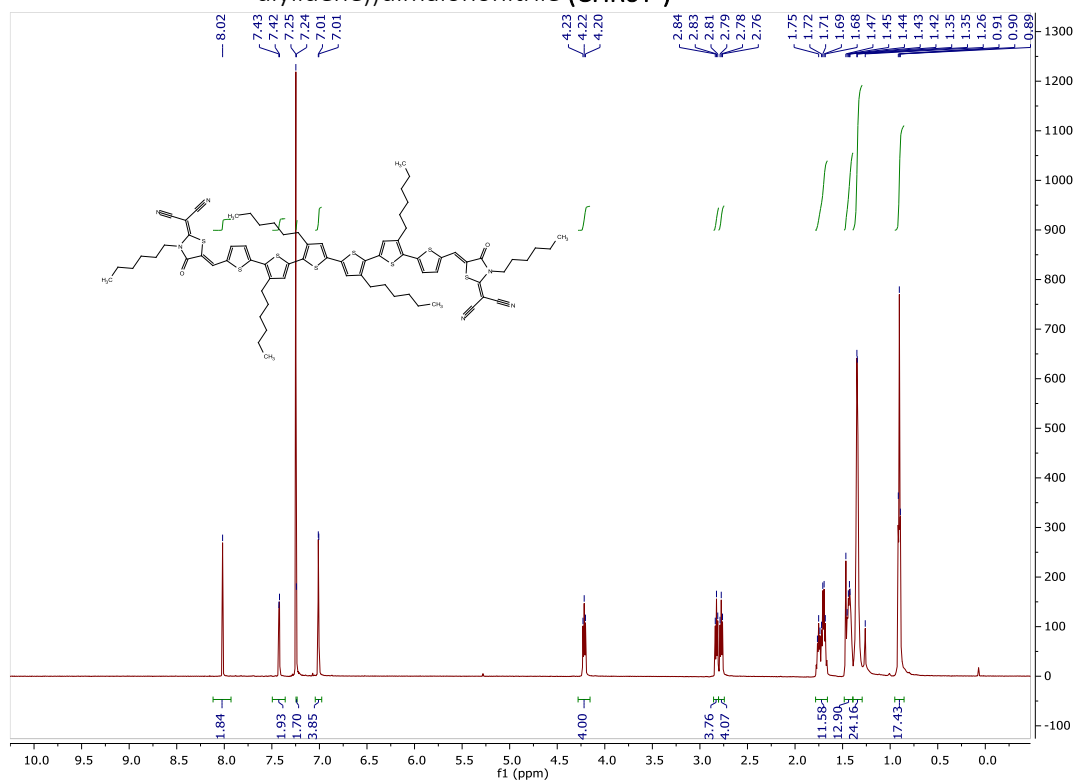


4.8.3.12 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2'''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (HR6T⁶)

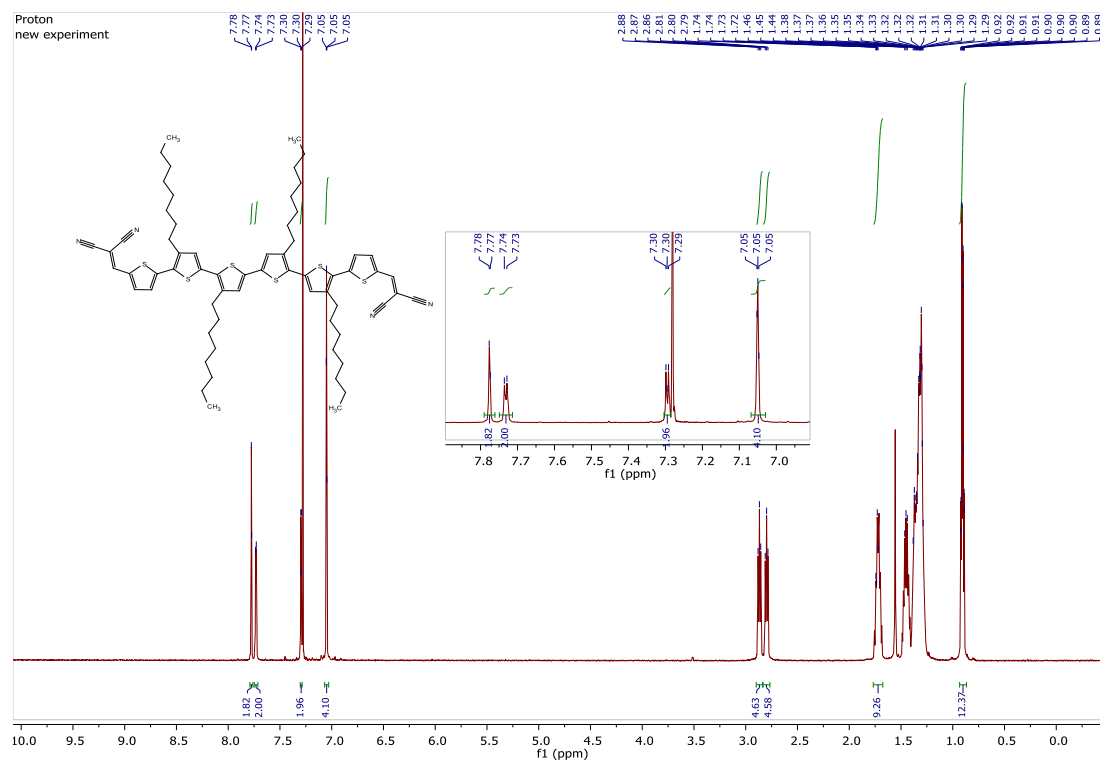
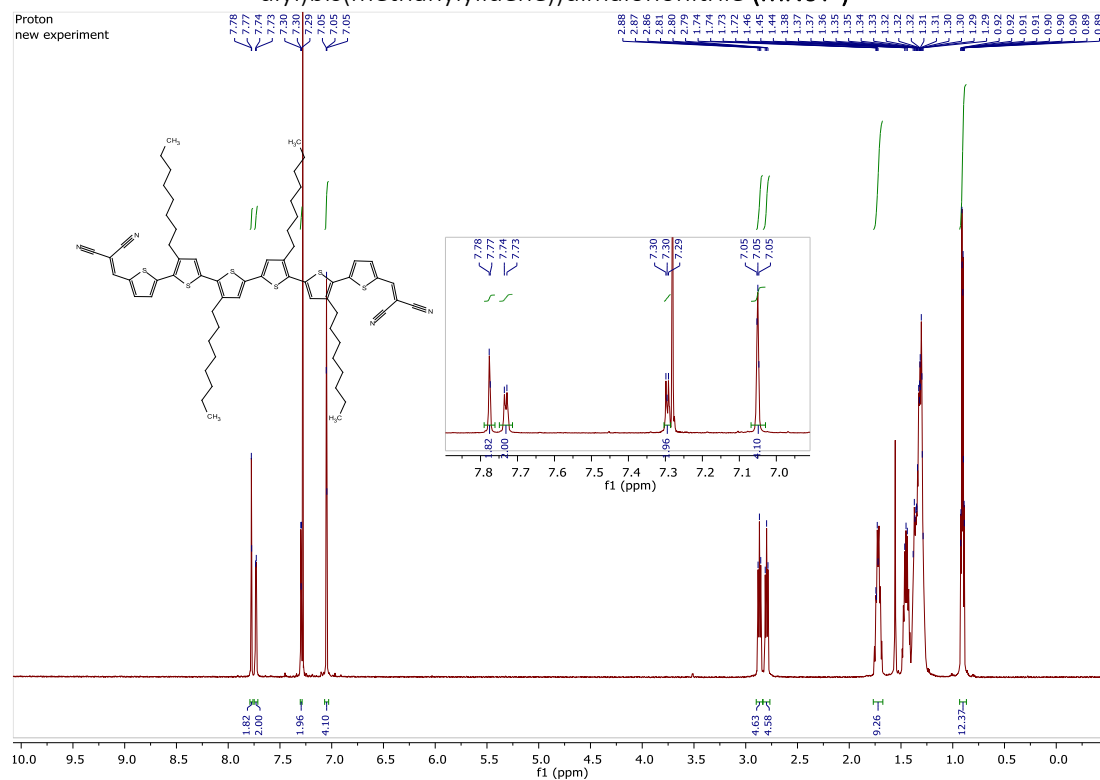


Figure

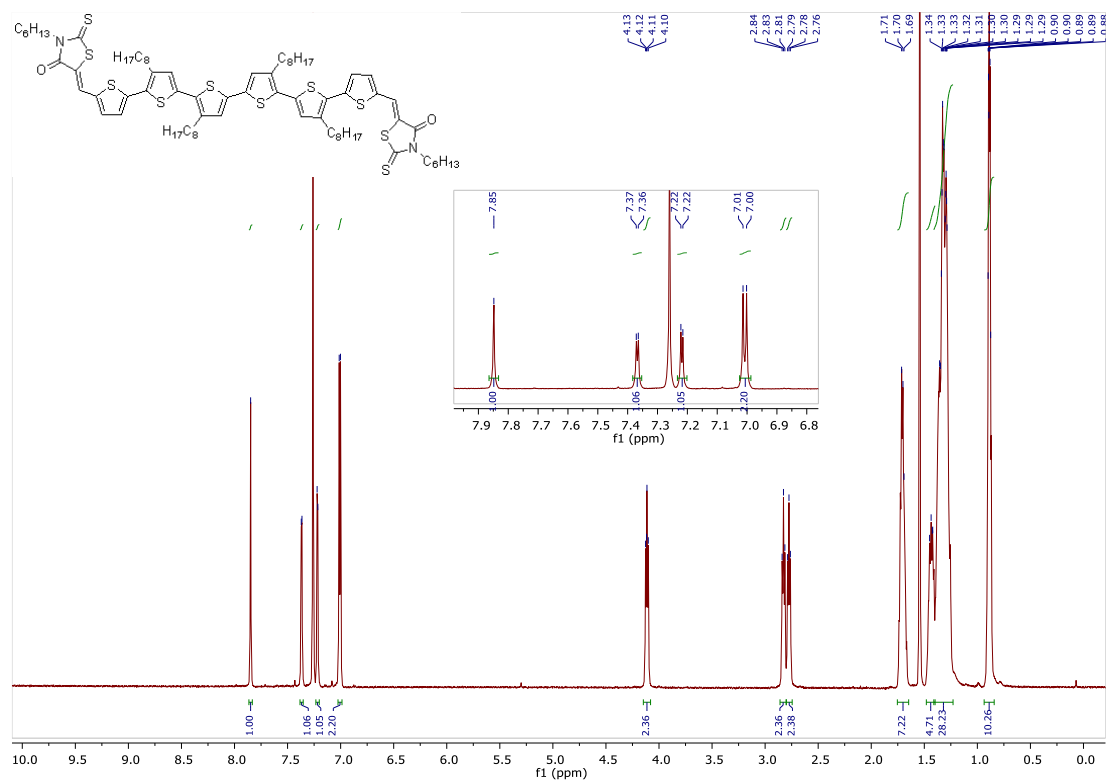
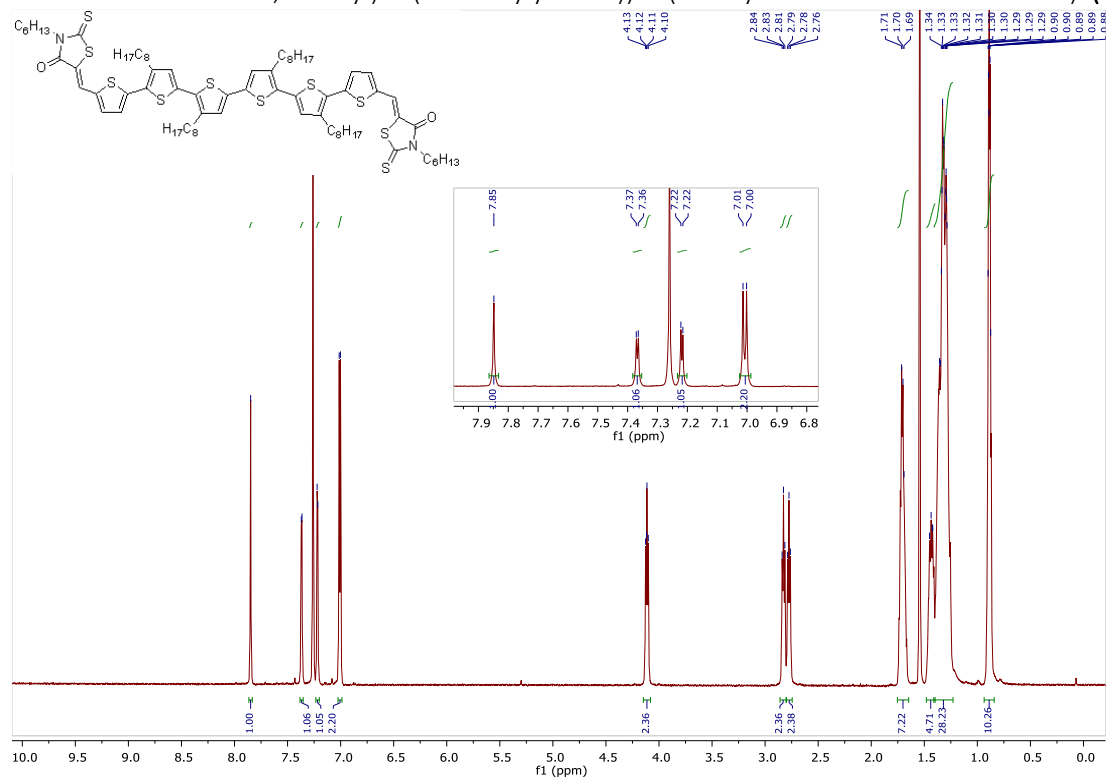
4.8.3.13 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2''':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR6T⁶**)



4.8.3.14 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2'''':5''',2'''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (**MN6T⁸**)

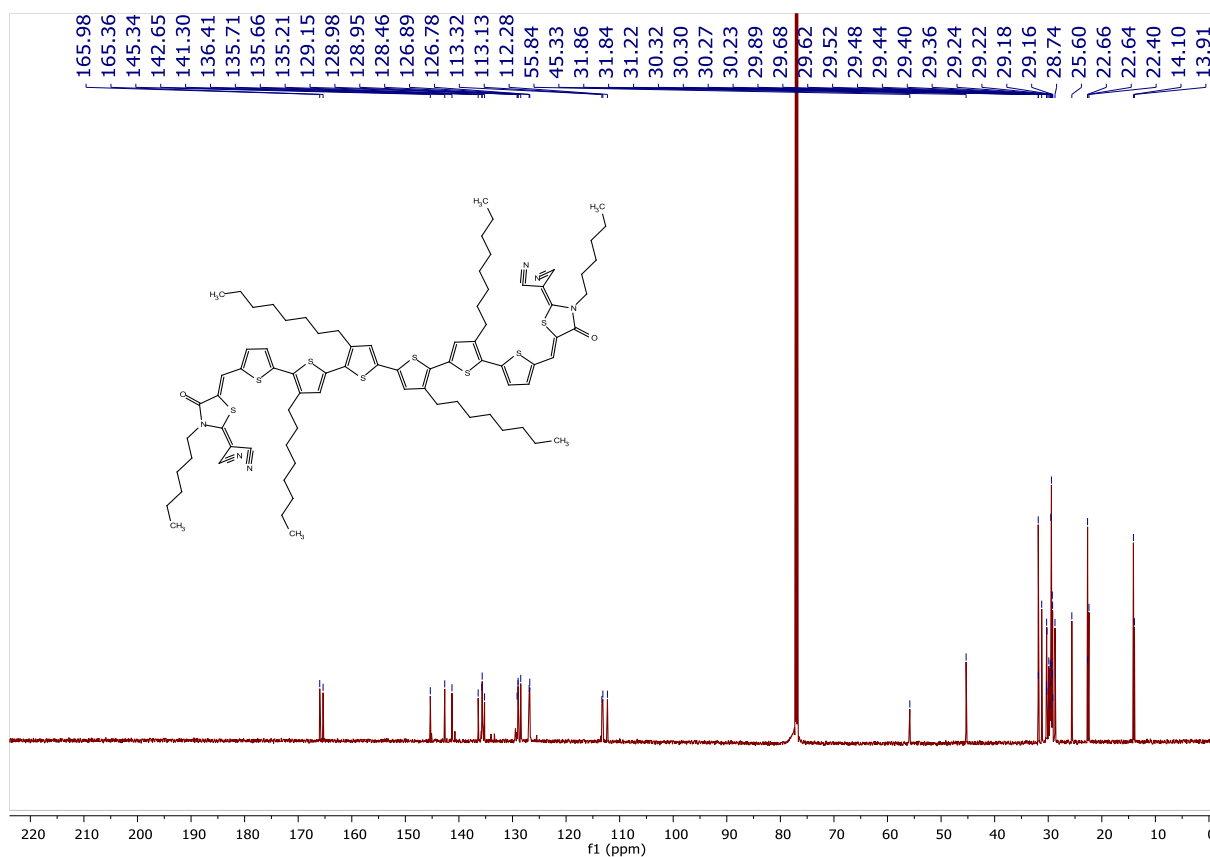
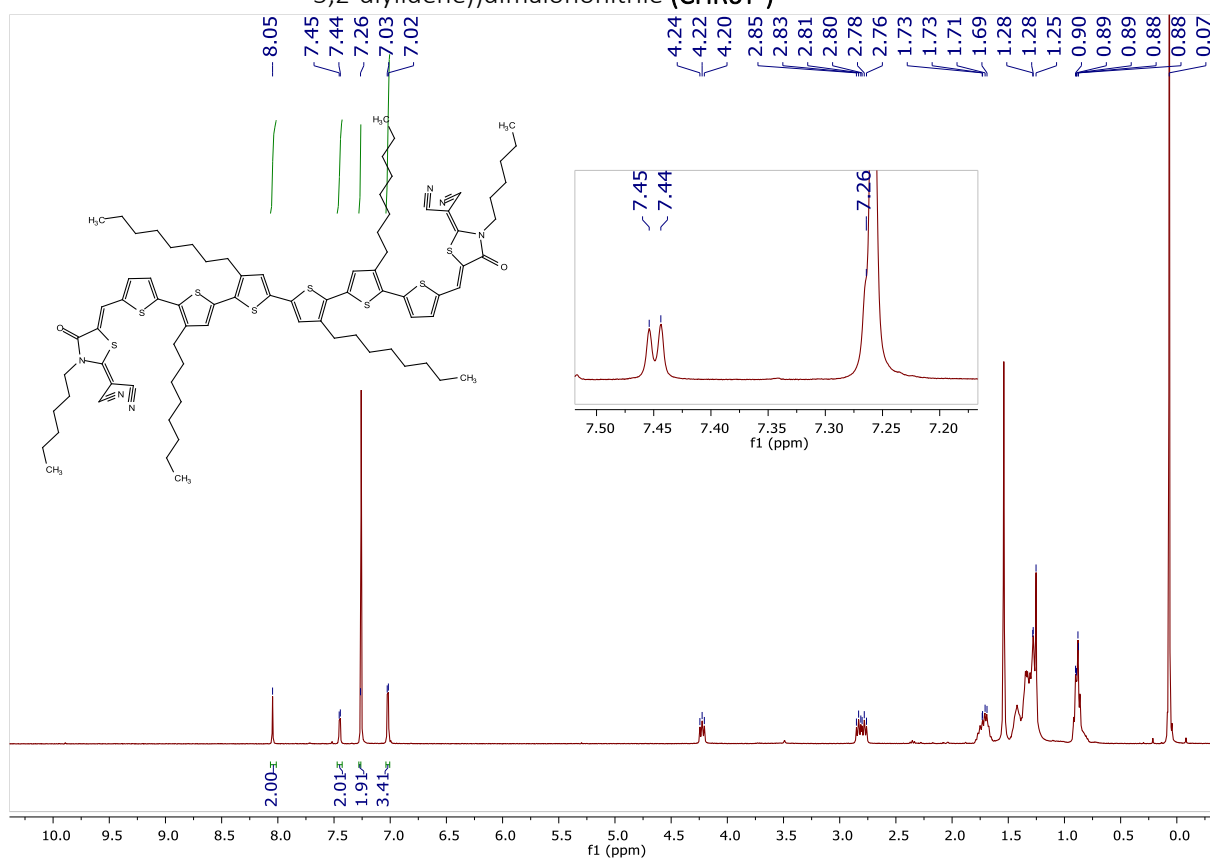


4.8.3.15 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2'''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (HR6T⁸)



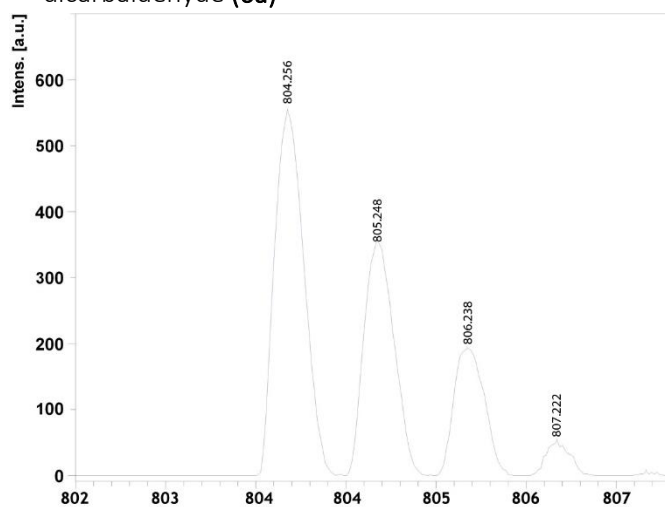
4.8.3.16 S3.16

2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (CHR6T[®])

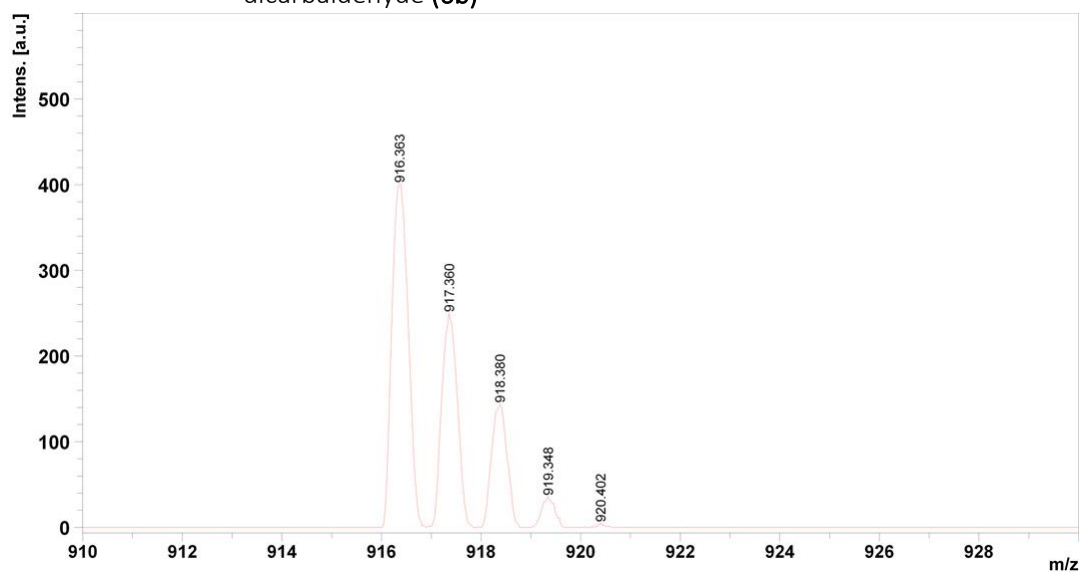


4.8.4 MALDI mass spectra for unpublished compounds

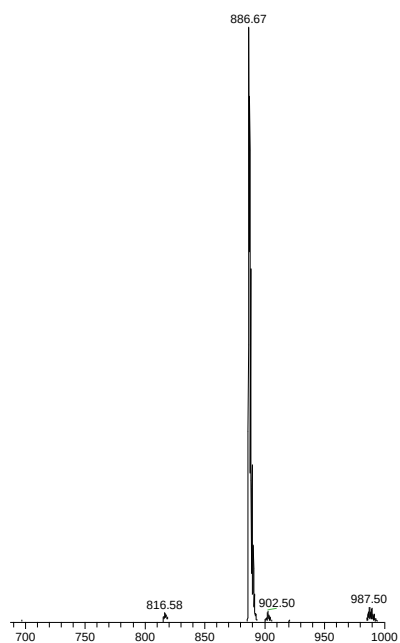
4.8.4.1 3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5,5''''-dicarbaldehyde (**6a**)



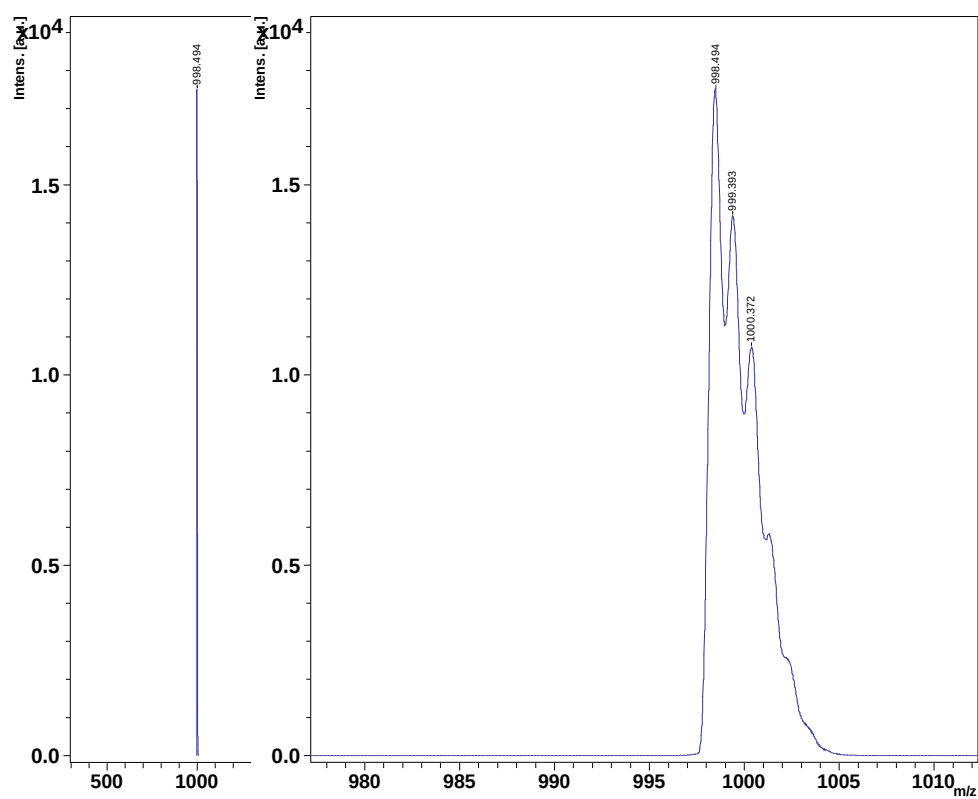
4.8.4.2 3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5,5''''-dicarbaldehyde (**6b**)



4.8.4.3 3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''':5''',2''''-sexithiophene]-5,5''''-dicarbaldehyde (**8a**)

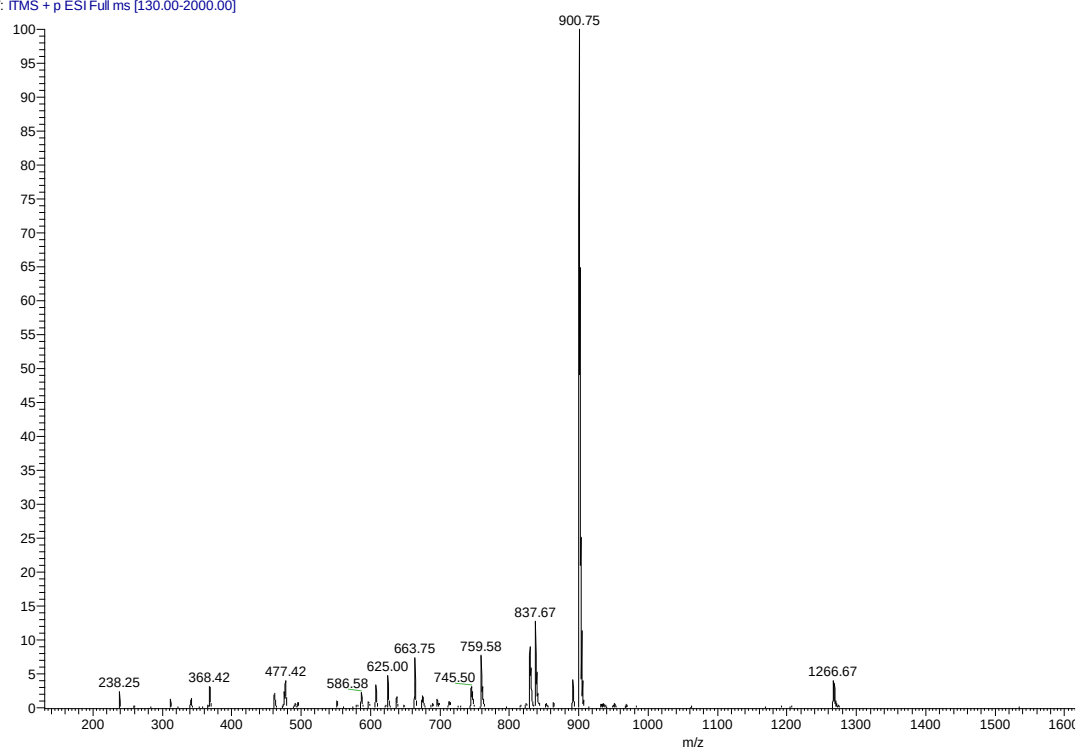


4.8.4.4 3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''':5''',2''''-sexithiophene]-5,5''''-dicarbaldehyde (**8b**)



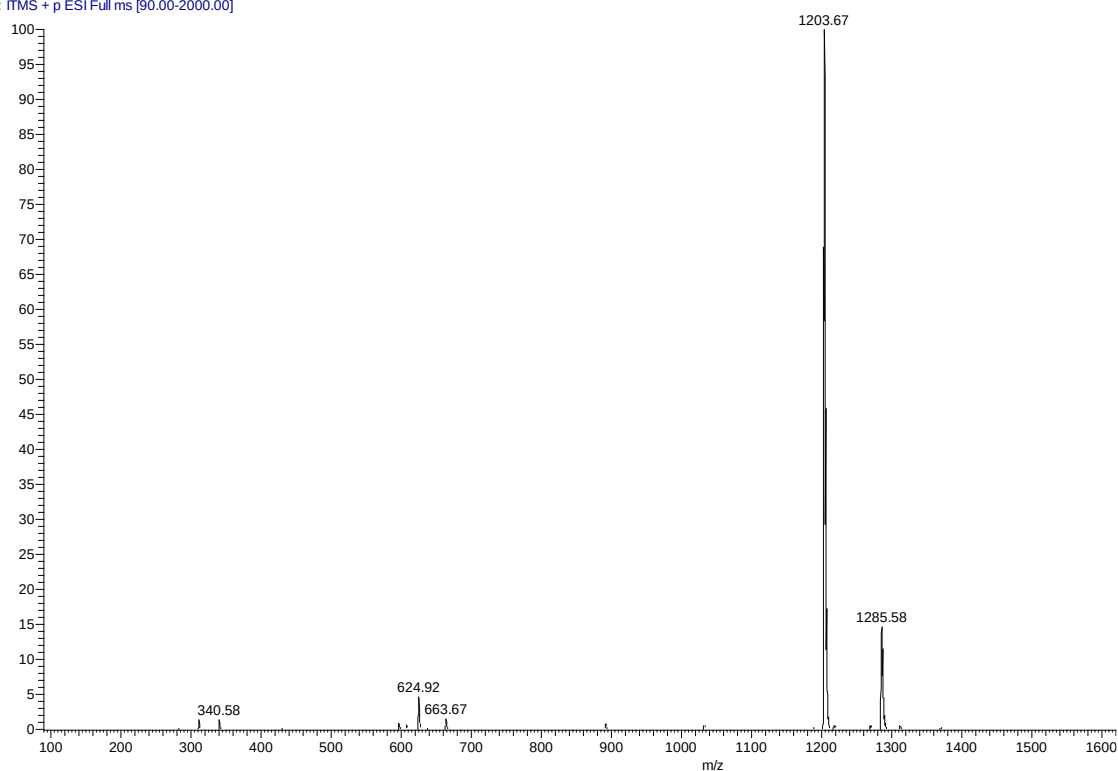
4.8.4.5 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile (**MN5T⁶**)

MSS-14-07-2015-AZ_23_FJ #1-4 RT: 0.00-0.03 AV: 4 NL: 3.36E4
T: ITMS + p ESI Full ms [130.00-2000.00]



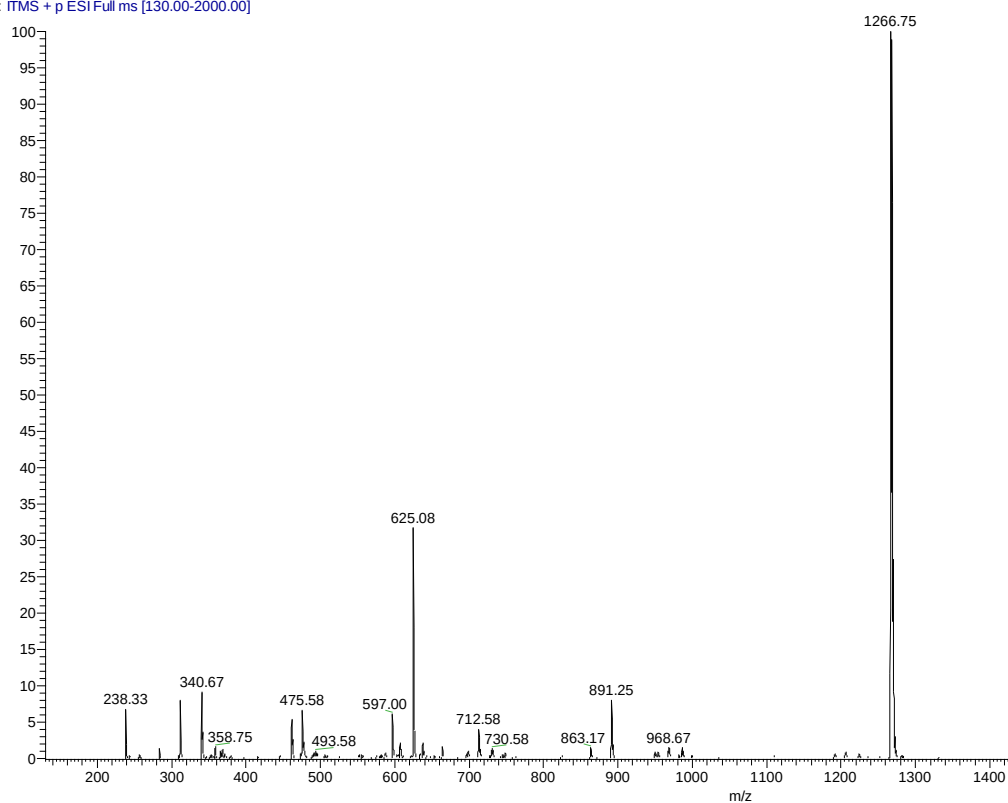
4.8.4.6 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR5T⁶**)

MSS-14-07-2015-AZ_26_FJ #1-5 RT: 0.00-0.03 AV: 5 NL: 1.13E5
T: ITMS + p ESI Full ms [90.00-2000.00]

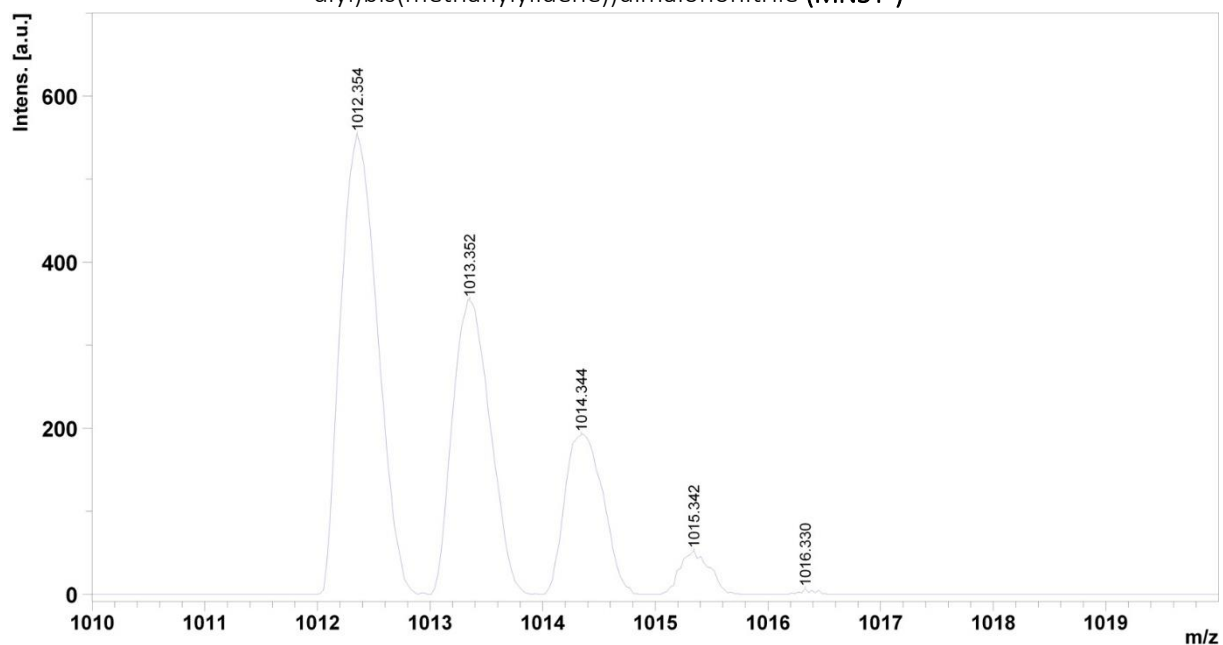


4.8.4.7 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR5T⁶**)

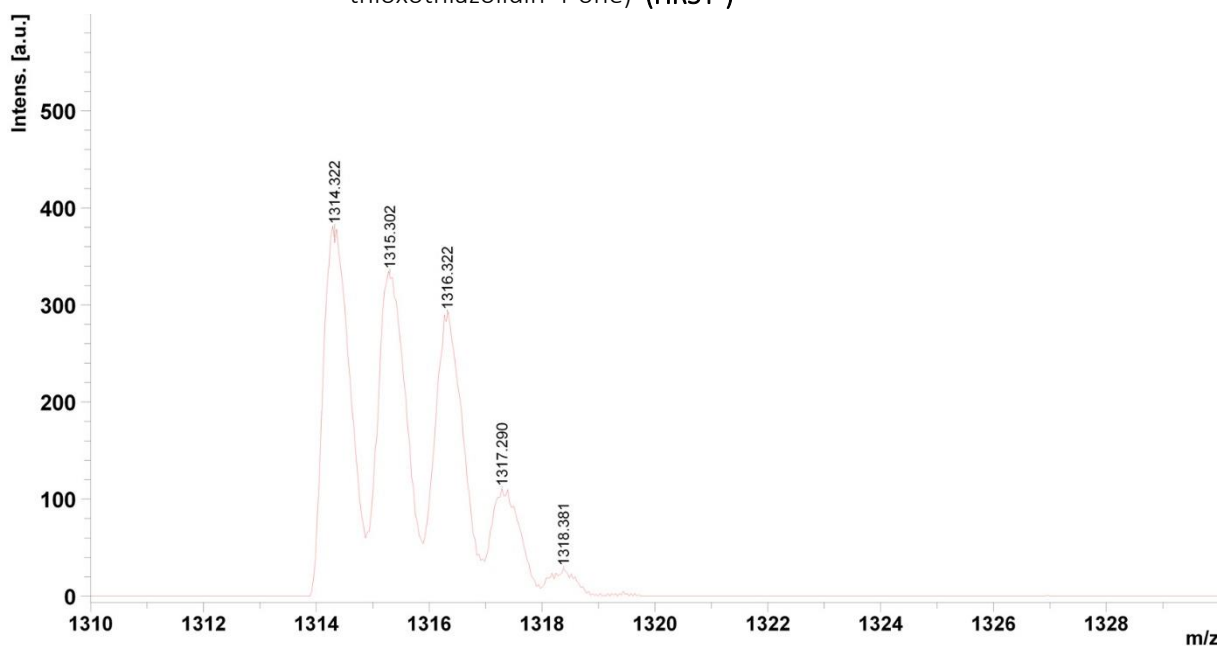
MSS-14-07-2015-AZ 22 FJ #1-4 RT: 0.00-0.03 AV: 4 NL: 1.53E4
T: ITMS + p ESI Full ms [130.00-2000.00]



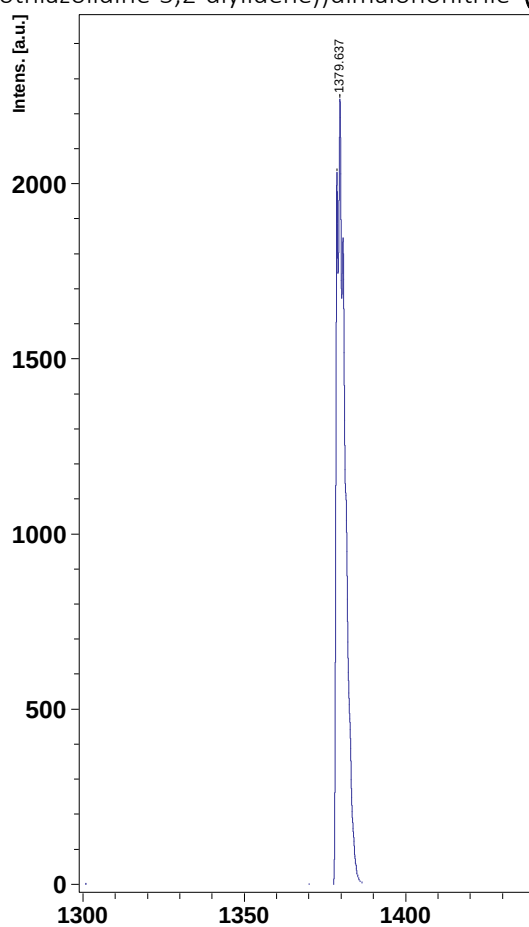
4.8.4.8 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinguethiophene]-5,5''''-diyl)bis(methanylylidene))dimalononitrile (**MN5T⁸**)



4.8.4.9 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''-quinquethiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR5T⁸**)

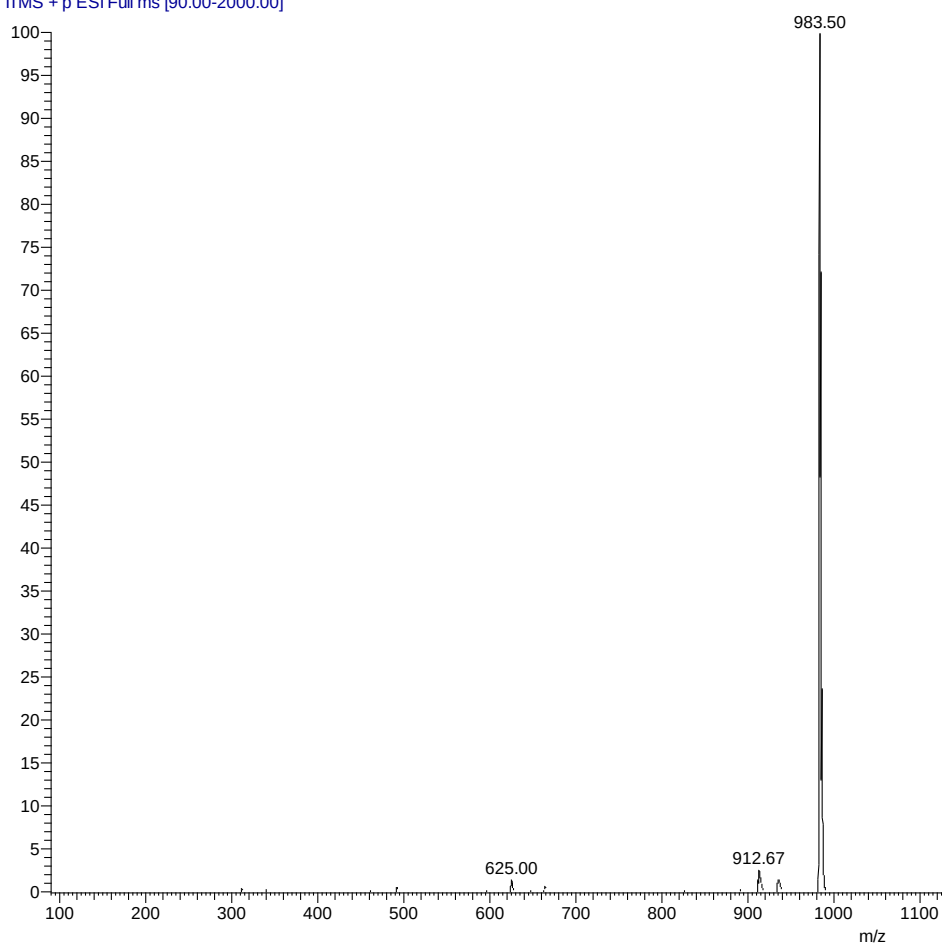


4.8.4.10 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2'''-quinquethiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR5T⁸**)



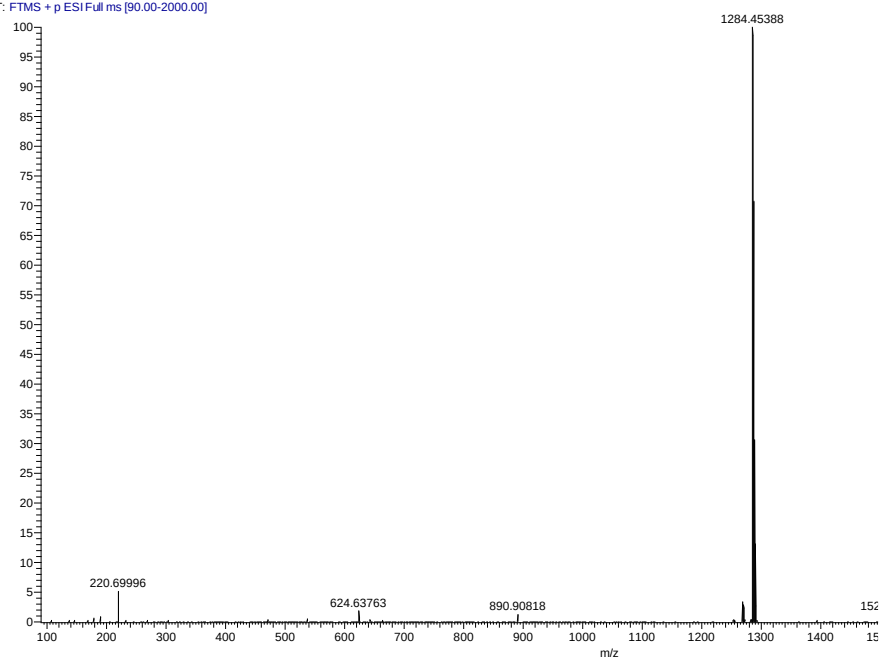
4.8.4.11 2,2'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (MN6T⁶)

MSS-14-07-2015-AZ_24_FJ #1-5 RT: 0.00-0.03 AV: 5 NL: 1.27E5
T: ITMS + p ESI Full ms [90.00-2000.00]



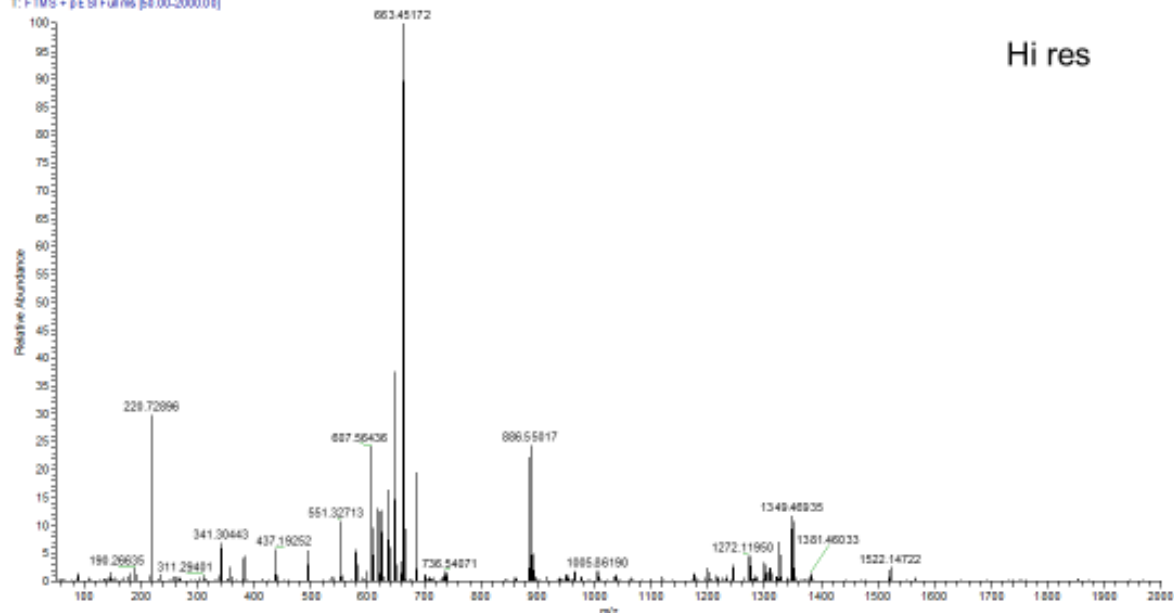
4.8.4.12 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR6T⁶**)

MSS-14-07-2015-AZ_25FT_FJ #1-9 RT: 0.01-0.14 AV: 9 NL: 2.06E6
T: FTMS + p ESI Full ms [90.00-2000.00]

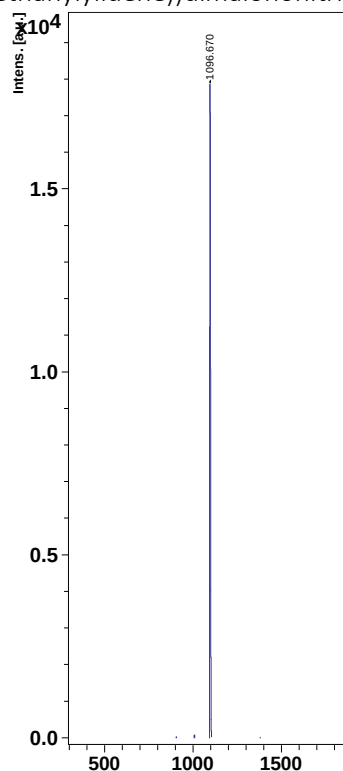


4.8.4.13 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR6T⁶**)

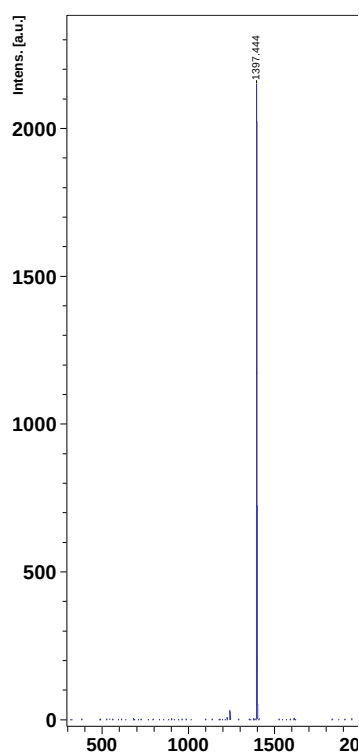
MSS-16-08-2016-AZ_32FT_FJ #1-20 RT: 0.01-0.30 AV: 20 NL: 1.67E6
T: FTMS + p ESI Full ms [50.00-2000.00]



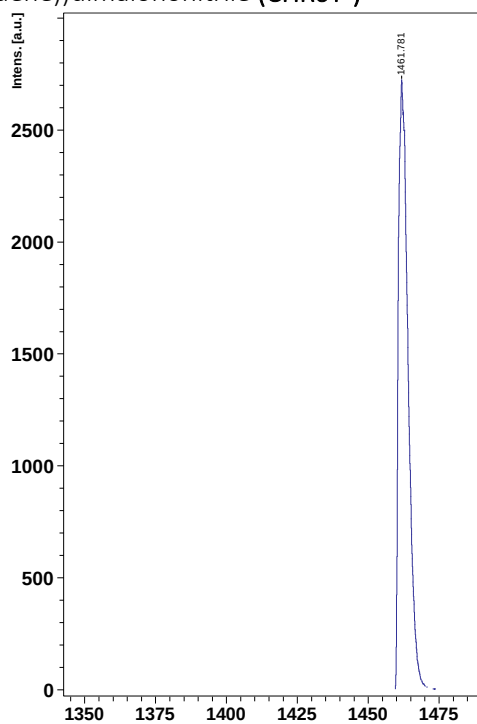
4.8.4.14 2,2'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))dimalononitrile (**MN6T⁸**)



4.8.4.15 (5Z,5'Z)-5,5'-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5'''-diyl)bis(methanylylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) (**HR6T⁸**)



4.8.4.16 2,2'-((5Z,5'Z)-((3',3'',4'',4'''-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-hexathiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-hexyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (**CHR6T⁸**)



4.8.5 Thermogravimetric analysis

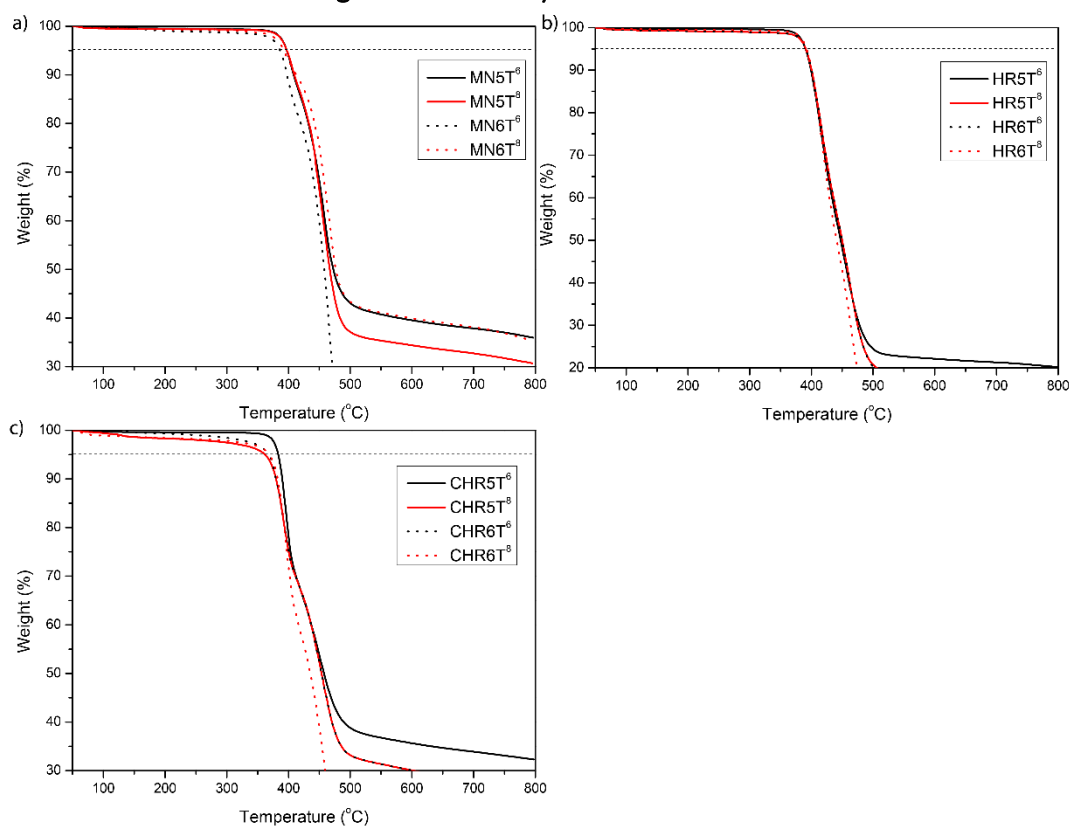


Figure 4-12: TGA thermograms of the oligothiophene materials with a) MN-, b) HR- and c) CHR- end-group acceptors.

Table 4: Thermal decomposition temperatures for the oligothiophene materials

Oligothiophene	T _{Decomp} (5% weight) °C
MN5T ⁶	395
MN5T ⁸	395
MN6T ⁶	383
MN6T ⁸	389
HR5T ⁶	388
HR5T ⁸	389
HR6T ⁶	388
HR6T ⁸	391
CHR5T ⁶	381
CHR5T ⁸	351
CHR6T ⁶	363
CHR6T ⁸	361

4.8.6 DSC thermograms

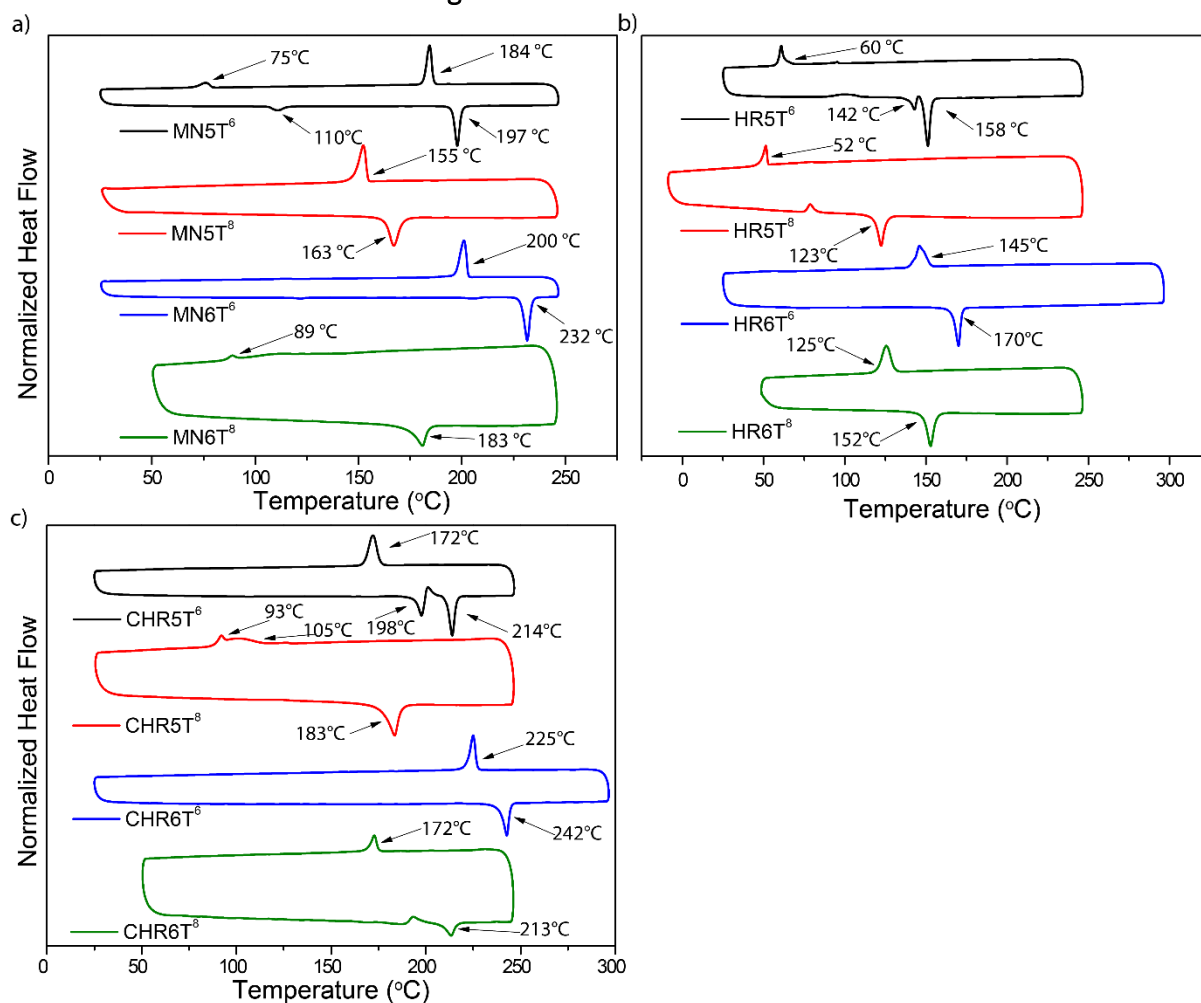


Figure 4-13: Normalized DSC thermograms for our oligothiophene materials with a) MN-, b) HR- and c) CHR- end-group acceptors with labelled phase transition temperatures.

Table 5: Melting point temperatures for our oligothiophene materials.

Oligothiophene	Melting Point
MN5T ⁶	197
MN5T ⁸	163
MN6T ⁶	232
MN6T ⁸	183
HR5T ⁶	158
HR5T ⁸	130
HR6T ⁶	170
HR6T ⁸	152
CHR5T ⁶	214
CHR5T ⁸	183
CHR6T ⁶	242
CHR6T ⁸	213

4.8.7 Cyclic voltammetry

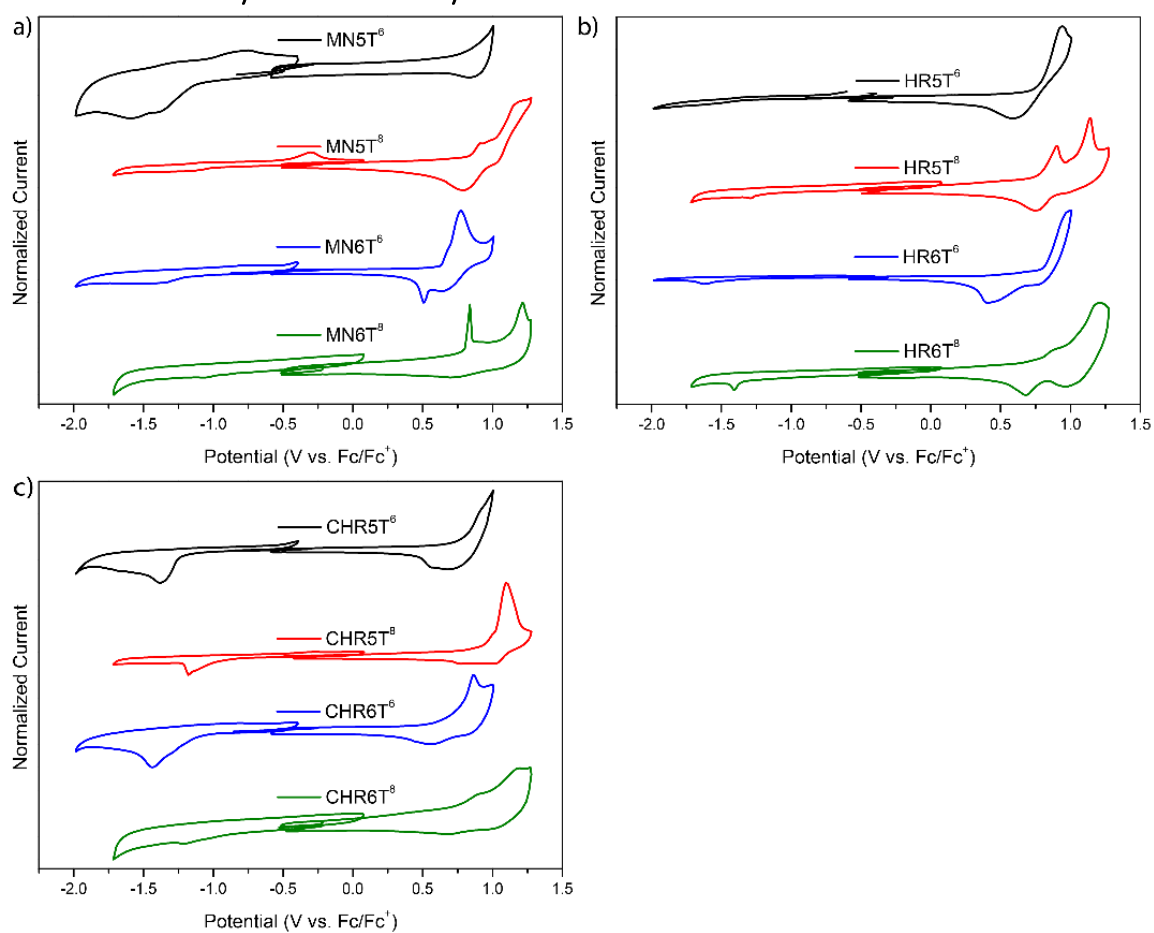


Figure 4-14: Normalized thin film cyclic voltammograms of our oligothiophene materials with a) MN-, b) HR- and c) CHR- end-group acceptors.

4.8.8 GIWAXS linecuts and scattering pattern data

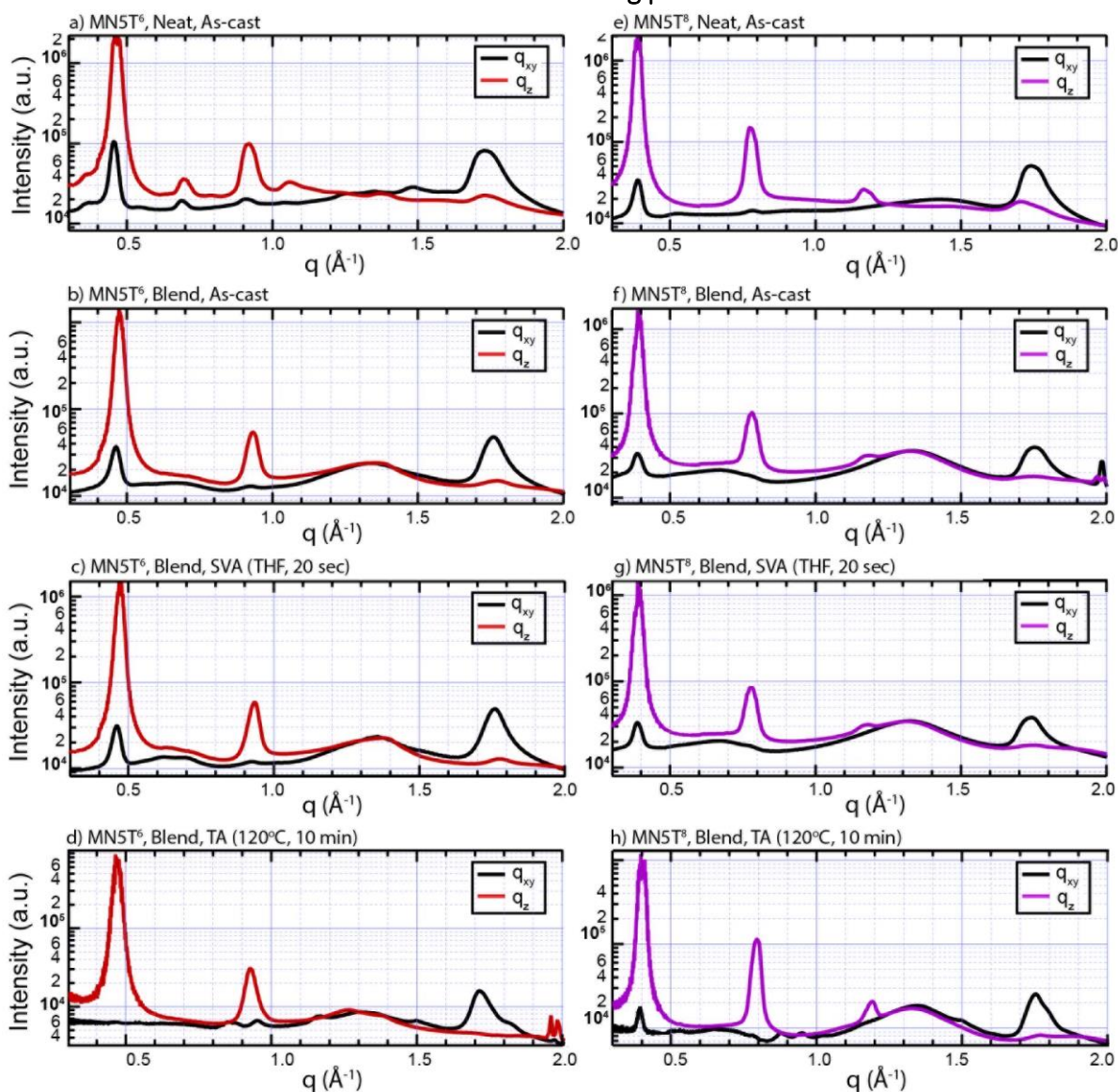


Figure 4-15: Linecuts of the GIWAXS scattering patterns for the MN5T⁶ (a-d) and MN5T⁸ (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table 6: MN5T^x scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
MN5T ⁶	Neat, As-Cast	19.1	1.36	0.36	MN5T ⁸	Neat, As-Cast	24.7	1.62	0.36
	Blend, As-Cast	22.3	1.33	0.36		Blend, As-Cast	24.1	1.61	0.36
	Blend, SVA (THF)	24.2	1.33	0.36		Blend, SVA (THF)	24.6	1.60	0.36
	Blend, TA	22.1	1.36	0.37		Blend, TA	25.6	1.59	0.36

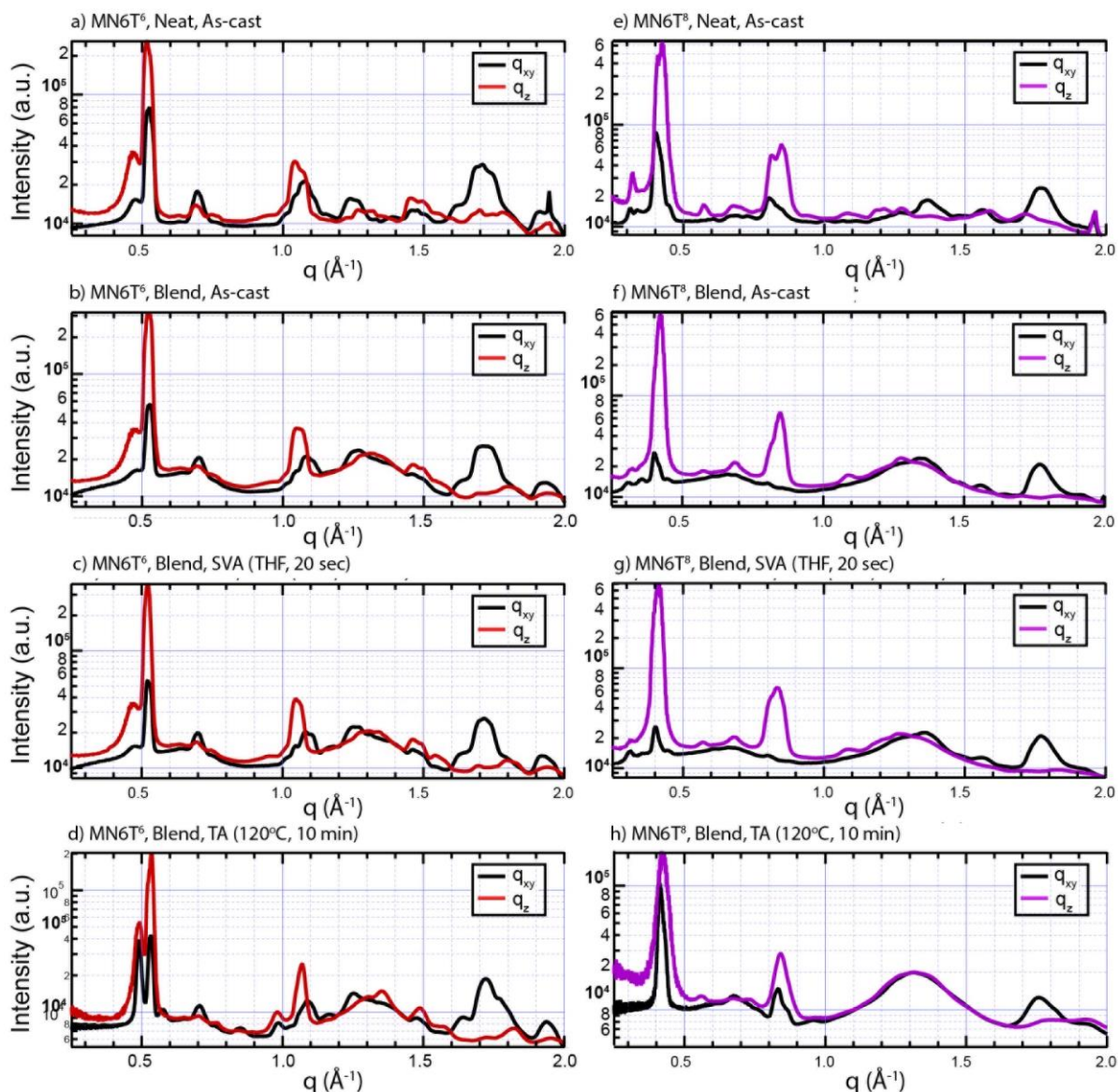


Figure 4-16: Linecuts of the GIWAXS scattering patterns for the MN6T⁶ (a-d) and MN6T⁸ (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table 7: MN6T^x scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
MN6T ⁶	Neat, As-Cast	23.2	1.21	0.37	MN6T ⁸	Neat, As-Cast	27.9	1.47	0.35
	Blend, As-Cast	24.6	1.20	0.37		Blend, As-Cast	26.0	1.48	0.36
	Blend, SVA (THF)	30.2	1.18	0.37		Blend, SVA (THF)	26.5	1.53	0.36
	Blend, TA	30.9	1.12	0.37		Blend, TA	17.8	1.49	0.36

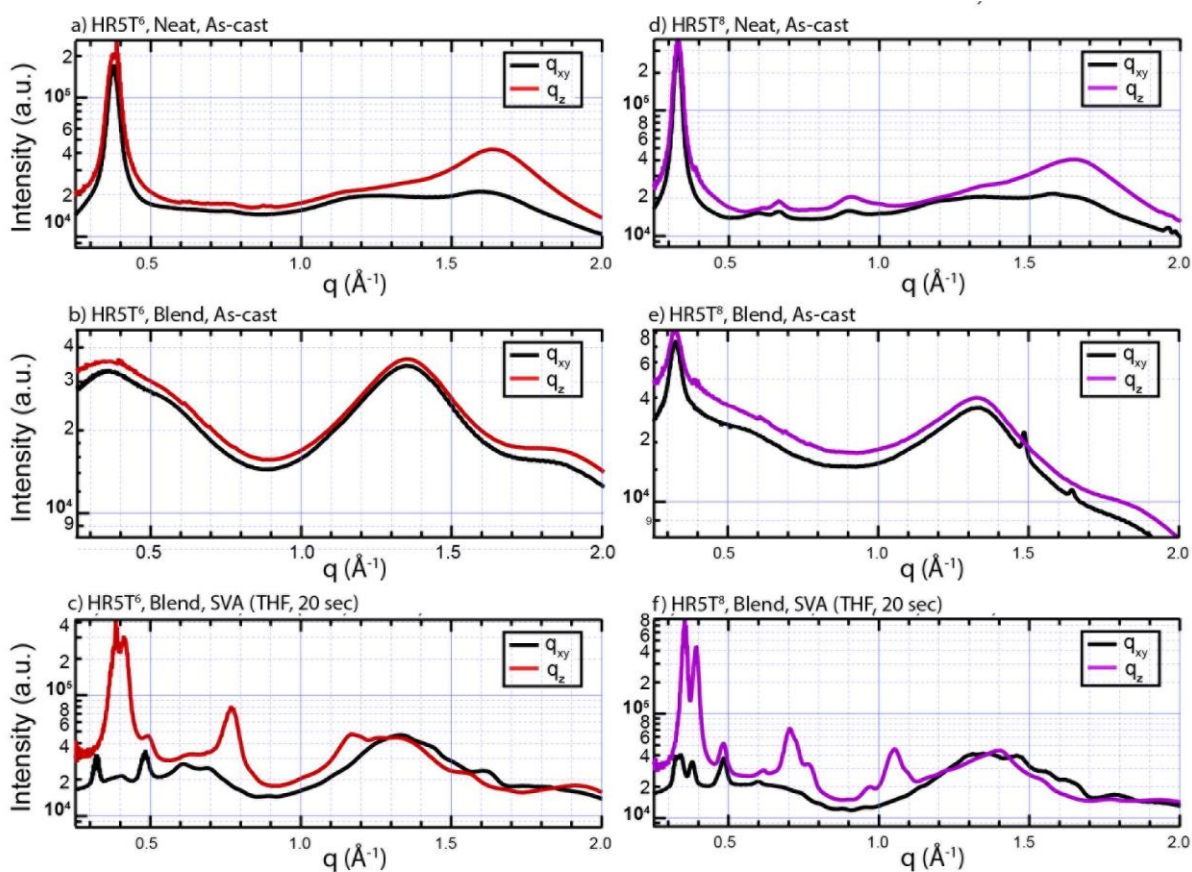


Figure 4-17: Linecuts of the GIWAXS scattering patterns for the HR5T⁶ (a-c) and HR5T⁸ (d-f) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table 8: HR5T^x scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
HR5T ⁶	Neat, As-Cast	14.5	1.66	0.38	HR5T ⁸	Neat, As-Cast	21.8	1.91	0.38
	Blend, As-Cast	1.17	1.70	N/A		Blend, As-Cast	11.4	1.96	N/A
	Blend, SVA (THF)	27.1	1.64	0.38		Blend, SVA (THF)	36.1	1.78	0.38

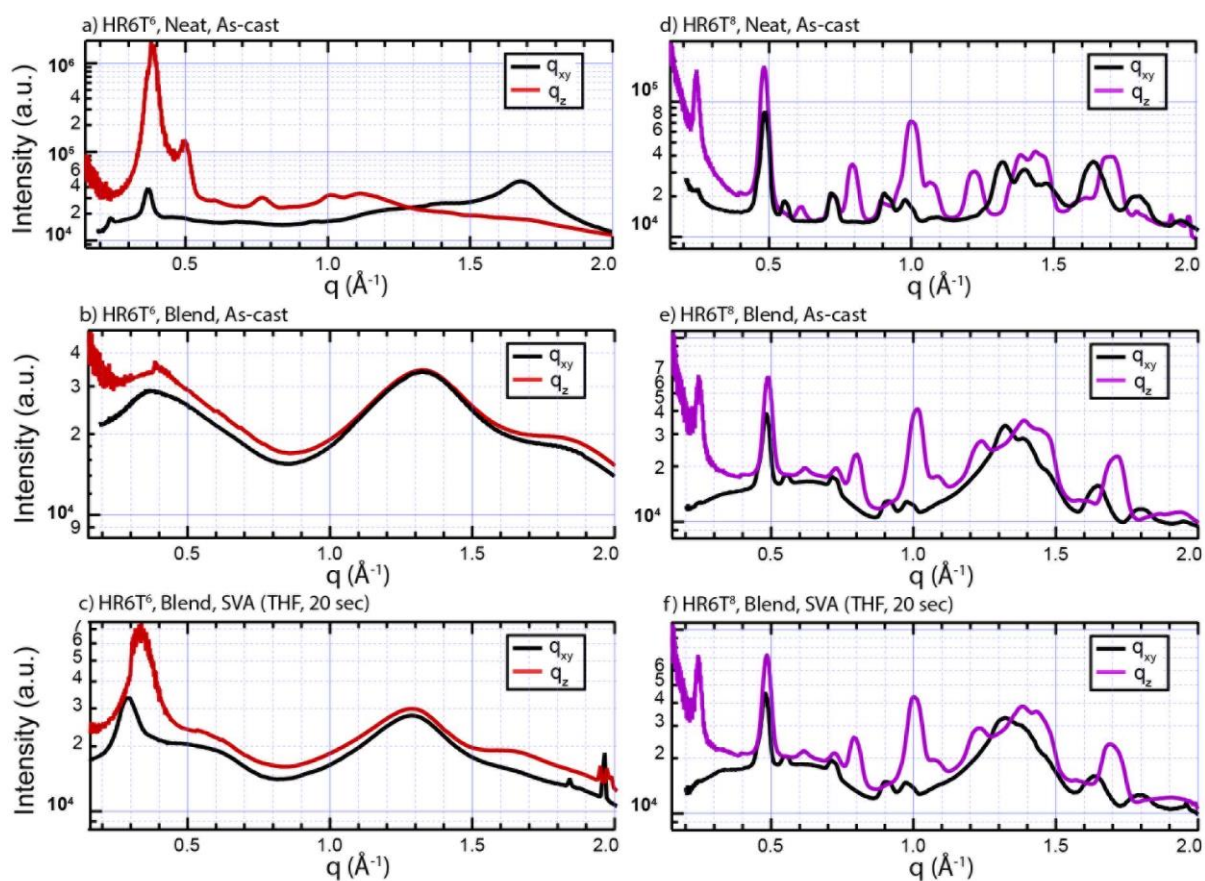


Figure 4-18: Linecuts of the GIWAXS scattering patterns for the HR6T⁶ (a-c) and HR6T⁸ (d-f) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table 9: HR6T^x scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
HR6T ⁶	Neat, As-Cast	18.7	1.63	0.37	HR6T ⁸	Neat, As-Cast	23.6	1.31	0.38
	Blend, As-Cast	3.28	1.59	N/A		Blend, As-Cast	21.1	1.29	0.37
	Blend, SVA (THF)	8.2	1.52	0.38		Blend, SVA (THF)	21.6	1.30	0.37

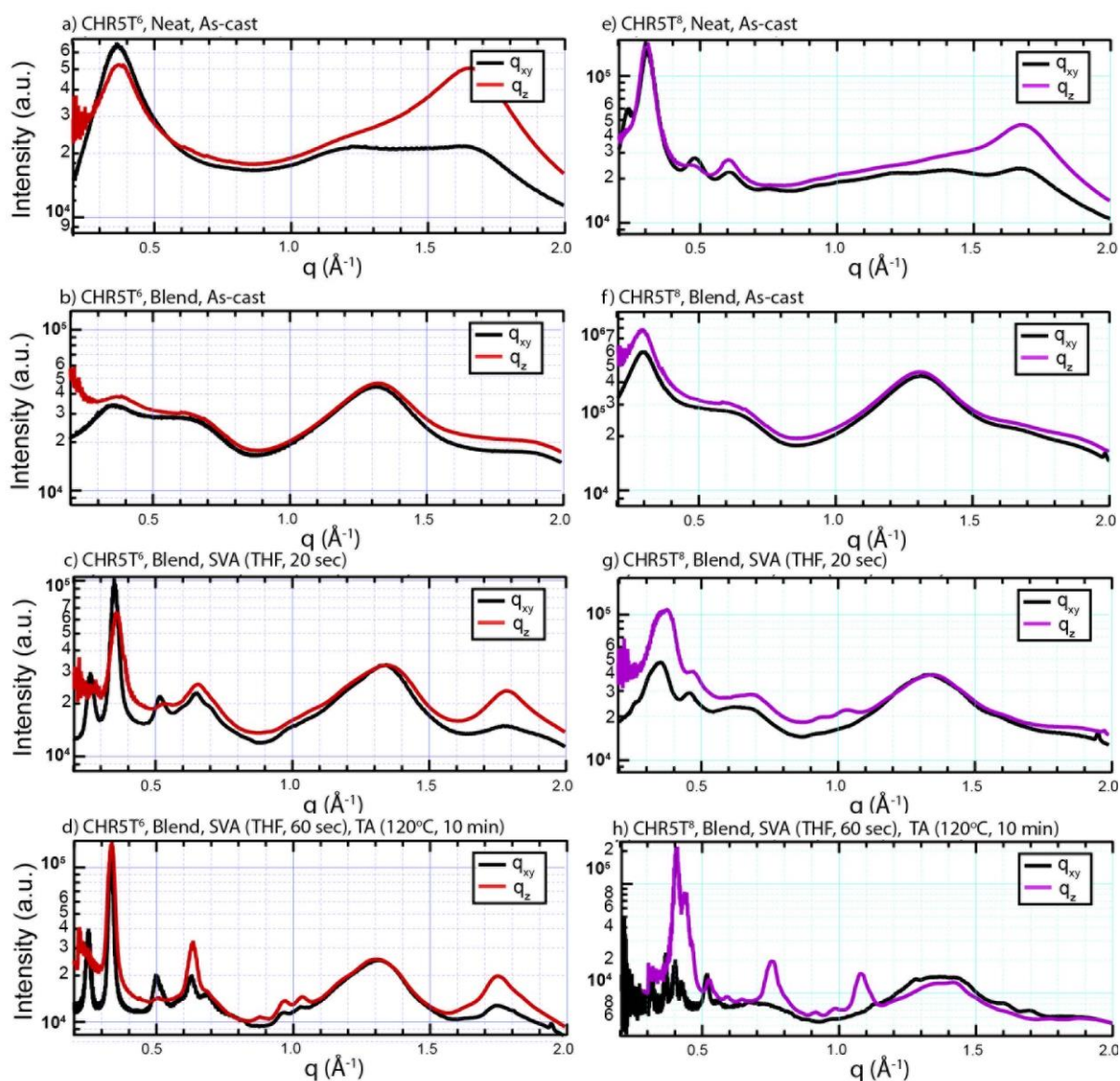


Figure 4-19: Linecuts of the GIWAXS scattering patterns for the CHR5T⁶ (a-d) and CHR5T⁸ (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table 10: CHR5T^x scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
CHR5T ⁶	Neat, As-Cast	10.25	1.72	0.38	CHR5T ⁸	Neat, As-Cast	12.8	1.87	0.36
	Blend, As-Cast	3.12	1.72	N/A		Blend, As-Cast	8.0	1.87	N/A
	Blend, SVA (THF)	22.9	1.81	0.36		Blend, SVA (THF)	10.3	1.81	N/A
	Blend, TA	37.8	1.87	0.36		Blend, TA	32.3	1.75	N/A

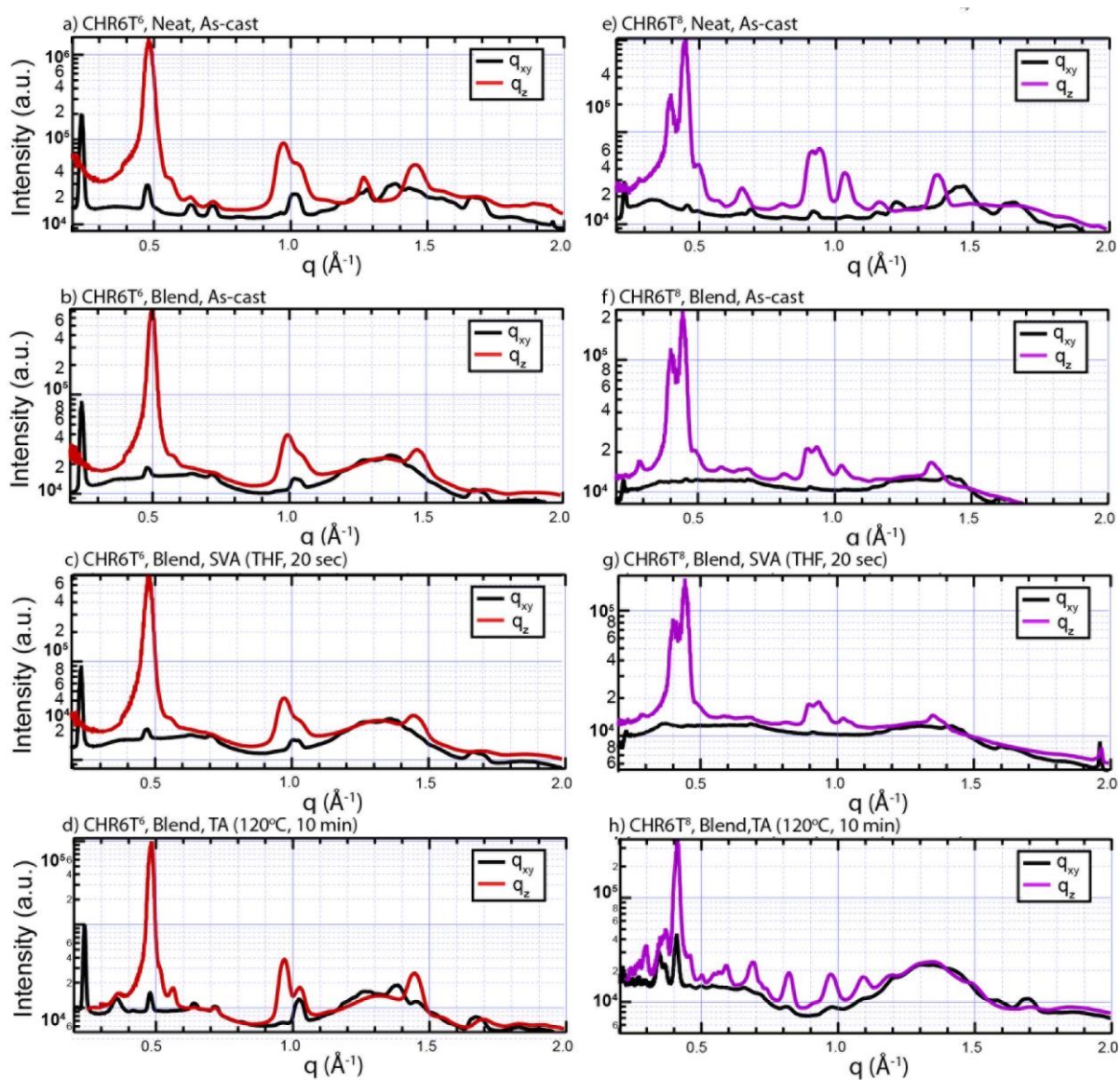


Figure 4-20: Linecuts of the GIWAXS scattering patterns for the CHR6T⁶ (a-d) and CHR6T⁸ (e-h) materials of peak intensity along the horizontal (q_{xy}) and vertical (q_z) axes.

Table 11: CHR6T^x scattering pattern data

Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]	Sample	Processing Conditions	CCL [nm]	d (100) [nm]	d (010) [nm]
CHR6T ⁶	Neat, As-Cast	21.1	1.28	0.37	CHR6T ⁸	Neat, As-Cast	30.3	1.37	0.38
	Blend, As-Cast	25.4	1.28	0.37		Blend, As-Cast	28.1	1.40	
	Blend, SVA (THF)	22.1	1.28	0.37		Blend, SVA (THF)	27.0	1.41	0.38
	Blend, TA	35.0	1.30	0.37		Blend, TA	36.2	1.53	0.37

4.8.9 Atomic force microscopy

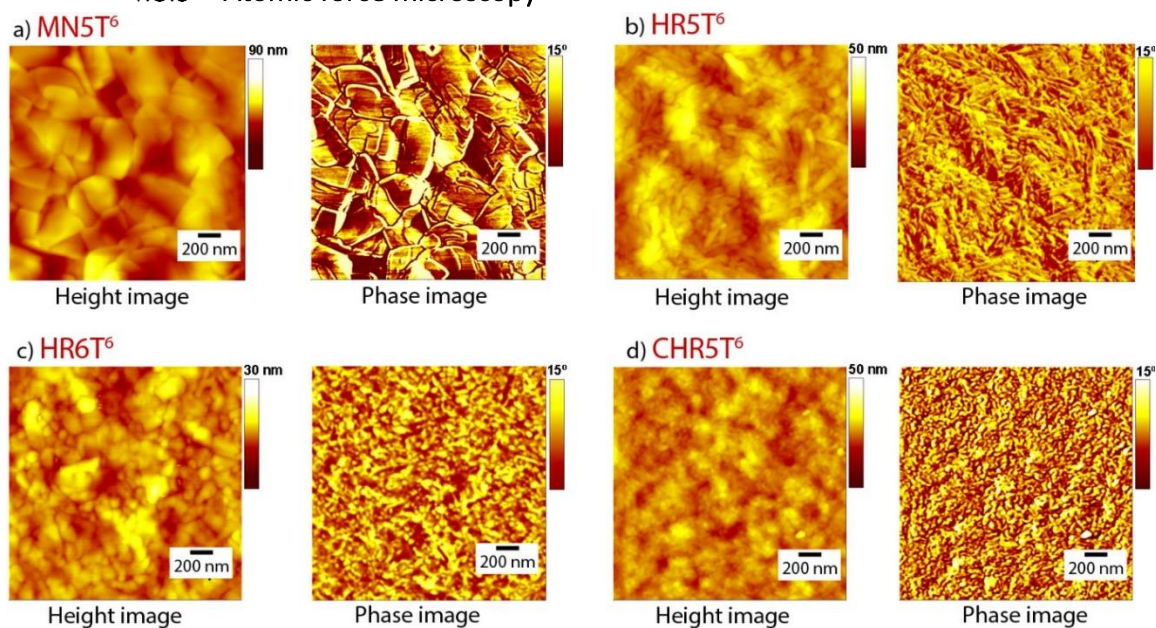


Figure 4-22: AFM images showing the surface topography of the annealed blend films of a) MN5T⁶, b) HR5T⁶, c) HR6T⁶ and d) CHR5T⁶. Annealing conditions and film blend composition are identical to those that give the best OPV device performance.

4.8.10 Crystallography

Table 12: Crystal data for MN5T⁸

Identification code	shelx	
Empirical formula	C60 H76 N4 S5	
Formula weight	1013.54	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 4.8510(10) Å	$\alpha = 86.18(3)^\circ$.
	b = 18.549(4) Å	$\beta = 87.84(3)^\circ$.
	c = 31.923(6) Å	$\gamma = 88.58(3)^\circ$.
Volume	2863.3(10) Å ³	
Z	2	
Density (calculated)	1.176 Mg/m ³	
Absorption coefficient	0.243 mm ⁻¹	
F(000)	1088	
Crystal size	0.04 x 0.03 x 0.005 mm ³	
Theta range for data collection	1.279 to 25.000°.	
Index ranges	-5 ≤ h ≤ 5, -22 ≤ k ≤ 22, -	

	37<= θ <=37	
Reflections collected	35134	
Independent reflections	9109 [R(int) = 0.1755]	
Completeness to $\theta = 25.000^\circ$	90.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9109 / 660 / 612	
Goodness-of-fit on F^2	1.686	
Final R indices [I>2 σ (I)]	R1 = 0.2094, wR2 = 0.5018	
R indices (all data)	R1 = 0.3094, wR2 = 0.5381	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.515 and -0.715 e. $\text{\AA}^{-3}$	

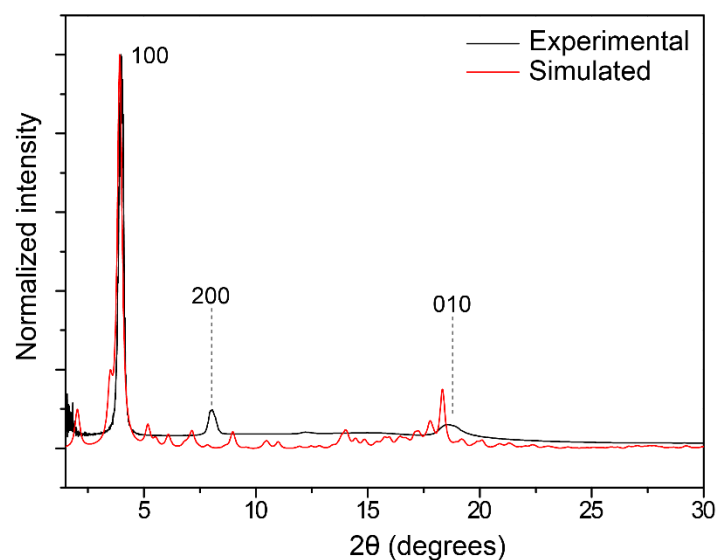


Figure 4-23: Simulated (red line) powder diffraction pattern for the MN5T⁸ structure derived from the single-crystal and experimentally-determined GIWAXS linecut (black line) of a neat, as-cast film. Wavelength used for calculations: 1.12713 Å

Chapter 5

Homopolymer design and synthesis for amphiphilic block copolymer applications

5.1 Introduction

For solution-processed OPV devices, controlling the self-assembly of active-layer blends into optimally-sized nanoscale domains remains an important challenge to overcome. As previously discussed in Chapter 1, once photogenerated the coulombically-bound exciton must diffuse to the interface between the p-type and n-type semiconductors to overcome the coulomb attraction holding the free charges together. The energetic offset between the two semiconductors provides the driving force for charge separation, allowing the electron and hole to segregate into the acceptor and donor material, respectively. These excitons possess relatively short lifetimes before recombination and decaying back into the ground state, and typical diffusion distances within this lifetime are generally held to be around 10 nm.^[203] Yet once these charges are separated, if sufficient distance is not maintained between them there exists the possibility of geminate free charge recombination which further limits charge harvesting,^[204] with an optimum separation size found to be around 16 nm.^[205] As such, to establish a balance between these two loss mechanisms and to maximize exciton harvesting, the active layer morphology should contain donor and acceptor domains which are ideally between 16-20 nm in size. To further complicate the morphology, as these charges need to be harvested at the device electrodes there is also a requirement for the active layer to feature continuous crystalline pathways allowing these charges to percolate to the electrodes. For both small-molecular and polymer-based materials with bulk heterojunction active layer architectures, achieving this fine morphological control remains difficult (as seen from the previous chapters) and aside from molecular design efforts, generally relies on approaches involving either film annealing to achieve partial phase separation or the introduction of additives to control crystallinities, both of which have to be optimized for different materials and can be challenging to reproduce.^[47]

However even after an optimal morphology has been established, long-term stability issues for solution-processed OPVs mean that maintaining this morphology is another significant problem. A study of high-performance small molecular materials, for example, have found them to undergo an exponential decay of performance by 30-60% in the first thousand hours of operation, due to a sharp decrease in J_{SC} and FF.^[206] Recent years have seen a growing interest in this field, and significant efforts have turned towards

understanding the underlying causes for this degradation.^[206-207] It has been found that this degradation proceeds via a two-stage process – a relatively rapid exponential decay known as the ‘burn-in’, and a longer, linear decay period.^[208] BTR itself has been found to undergo photodegradation-induced changes in its molecular conformation during this burn-in period, with a reduced dihedral angle of the core substituent suggested to affect charge recombination and transport.^[209] When controlling for other factors however, it has also been found that thermally-assisted morphological changes are a key contributor to this degradation. Solution-processed OPV active layer blends are typically deposited as a kinetically-trapped, metastable state that over time can diffuse into unfavourable morphologies. For example, it has been found in both small molecular and polymer solar cells that thermally-assisted degradation (where cells were held at a standard OPV operating temperature of 70°C) occurs due to the rearrangement of molecules allowing the a) phase-separation of donor and acceptor materials into larger and purer domains that reduce the interfacial region and promote exciton recombination, and b) molecular diffusion into charge extraction barriers at the active layer/interlayer interfaces, with this problem exacerbated by lower molecular weight molecules.^[206, 210] One strategy to overcoming this degradation has suggested utilizing either heavier molecular weight molecules or cross-linking smaller molecules in active layers, however these are evidently not practical to implement for many molecular substrates.

Block copolymers (BCPs) are a well-established class of materials that have found a variety of commercial uses due to their potential for complex architectures, and involve covalently binding two or more distinct homopolymer ‘blocks’ together along the chain of the polymer backbone. Though most of BCP research has been performed on non-conjugated materials, recently they have gained popularity in the OPV field as they have been found to facilitate both the specific morphology required for efficient charge-harvesting and partially resolve the long-term stability issue.^[211] This is due to their ability to thermodynamically self-assemble into specific thin-film morphologies as a function of the polymer structure (microphase separation), but are prevented from diffusing apart entirely (macrophase separation) due to their covalent linkage.^[212] These can grant regularly sized, alternating donor and acceptor domains with large interfacial regions. BCPs for organic electronic applications have only been known since 1996,^[213] and were initially limited to blocks of p-type materials, i.e. poly(3-hexylthiophene)-*b*-poly(3-(2-ethylhexyl)thiophene) and poly(3-butylthiophene)-*b*-poly(3-octylthiophene) and despite their relatively similar monomer structures were found to phase-separate into lamellar layers through AFM imaging.^[214]

It is only recently that BCPs composed of both p- and n-type segments have been developed, which can be in part attributed to the development of non-fullerene acceptor alternatives. Here the diblock copolymer architecture is of greatest interest to the OPV field, where a p-type and an n-type homopolymer are covalently linked together to form a single donor-acceptor system (see Figure 5-1a). While more complex architectures such as triblock copolymers are known in the literature,^[215] the added synthetic difficulty in an already challenging field has limited their usage. These blocks themselves may be fully conjugated along the

backbone (rod-type polymers) or comprised of pendant semiconducting entities on a non-conjugated backbone (coil-type polymers), with BCPs potentially composed of any combinations of these (i.e. rod-rod, coil-rod or coil-coil).^[212] Though early donor-acceptor BCPs were generally either coil-coil or coil-rod type polymers, presumably due to the well understood nature of coil-type polymer self-assembly from research efforts in non-conjugated polymer materials,^[216] these have the inherent problem of lower charge mobilities due to the inclusion of insulating alkyl chains and the lack of overlapping pi-orbitals, relative to the fully conjugated rod-like polymers.^[214b] Though their inherent rigidity limits the phase-separated architecture accessible, rod-like polymers maximize chromophore density and form structures that facilitate charge conduction, and are thus of greater relevance to the OPV field.^[217] In this chapter, unless otherwise specified all references to BCPs refer exclusively to diblock rod-rod copolymers.

The self-assembly of rod-rod BCPs is determined by two key factors – isotropic Flory-Huggins interactions (given by the Flory-Huggins parameter χ) which describe the tendency for blocks to phase separate, and anisotropic Maier-Saupe interactions (given by the Maier-Saupe parameter ω), which describe the tendency for rod-rod blocks to align and are of particular significance as this affects the degree of intra- and intermolecular charge transport.^[218] The balancing of these two factors in terms of the $\omega:\chi$ ratio determines the type of structure formed during self-assembly.^[212] The Maier-Saupe attraction stabilizes parallel arrangements of neighbouring molecules, and generally the strength of these interactions are such that the unique architectures seen in classical coil-coil polymers are not observed, instead resulting in various types of liquid-crystalline like morphologies with planar lamellar domains when $\omega:\chi$ ratios are close to or above one (Figure 5-1b).^[219] The size of these domains are primarily controlled by the degree of polymerization of each homopolymer block, thus necessitating fine control over polymerization conditions to achieve the optimal 16-20 nm domain widths. Though it is not within the scope of the research in this chapter, it is worthwhile to note that polymer orientation relative to the substrate is equally as important here as it is in small molecular systems. The lamellar domains should ideally be oriented with their interfaces perpendicular to the substrate, so as to allow vertically pi-stacked layers and charge percolation pathways to the electrodes. Existing research has shown that substrate modification can allow the preferential selectivity of one polymer block over another, allowing control over the orientation of the nanoscale domains formed.^[220]

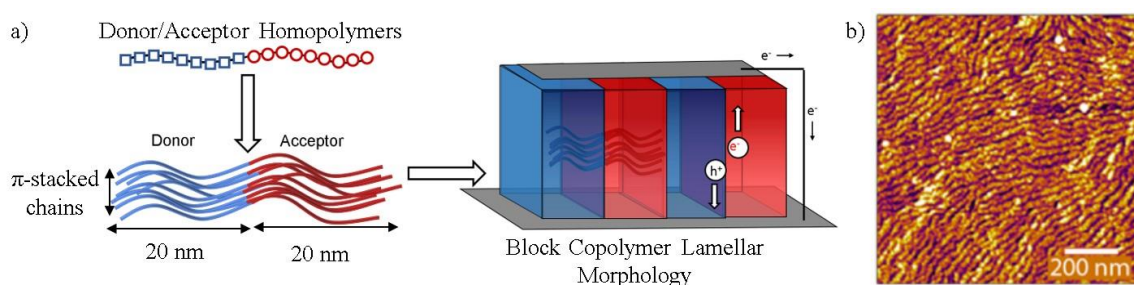


Figure 5-1: a) Schematic for idealized rod-rod diblock copolymer self-assembly into a lamellar morphology orientated with respect to the substrate; b) Surface morphology of a block copolymer film showing clear lamellar domains. Reprinted (adapted) with permission from Mitchell et al.^[221] Copyright (2017) American Chemical Society.

Yet due to the conjugated nature of the rod-rod homopolymers, the crystallization induced by π - π stacking interactions has been observed to dominate the morphology when there is a high amount of intermixing between the donor/acceptor homopolymer blocks (that is, when χ is low) and can hinder the self-assembly of BCPs into the desired lamellar domains, a phenomenon known as ‘break-out’ crystallization.^[218b, 222] As such, a certain degree of Flory-Huggins interactions are required to ensure phase-separation into these domains. The Flory-Huggins parameter χ for two given monomers, A and B, describes an interplay between the free energies of homogenous interaction (ϵ_{AA} , ϵ_{BB}) and heterogenous interaction (ϵ_{AB}).^[218b] For chemically distinct non-polar polymers the energies of heterogenous association outweigh those of homogenous association ($\chi > 0$) and there is a greater driving force for phase-separation, while for chemically-similar polymers the opposite is true ($\chi < 0$) and these tend towards miscibility and isotropic, disordered morphologies.^[223] It should be noted, however, that greater homopolymer lengths can impart a higher enthalpic cost relative to the entropic favourability for intermixing, and phase separation can still occur even for small values of χ . Generally speaking, most BCPs for OPV applications synthesized to date consist of two or more hydrophobic blocks, thus increasing their chemical similarity and homopolymer miscibility.^[224]

5.2 Amphiphilic Block Copolymers

Amphiphilic BCPs, where the different homopolymer blocks contain either hydrophobic or hydrophilic solubilizing moieties to create thermodynamically incompatible entities, possess an additional driving force for phase separation and self-assembly. This also confers solubility in both non-polar and polar media to the BCP, increasing its industrial relevancy by allowing processing in less toxic, non-chlorinated solvents such as THF or various alcohols. There are however only a few examples of these designed for OPV or organic electronics applications in the literature.^[225] Of these, many are rod-coil type polymers which incorporate either conjugated or non-conjugated hydrophilic pendant groups (pyridine or acrylic acid functional groups are fairly ubiquitous) alongside a fully conjugated block.^[226] These are more commonly used as either conductive polymers for non-OPV applications or in an interlayer/compatibilizer role to induce optimal morphologies between the main semiconducting components in the active layer,^[225b, 227] although in one recent BCP:fullerene blend the rod-coil amphiphilic BCP fulfils a dual function as both a surfactant to stabilize nanoparticles of the blend and as the p-type semiconductor.^[228] While rod-rod polymers are more suitable for all-polymer OPVs it is only recently with the development of high-performance n-type polymers that these have been utilized in this function.^[229] Early attempts to harness rod-rod amphiphilic BCPs were limited to homopolymer blocks of p-type materials, and had to incorporate separate n-type semiconductors in a blend, thus limiting the extent of morphological control possible.^[230] These generally utilize sidechain engineering to install the hydrophilic functional groups on sidechain positions non-adjacent to the conjugated backbone, as this minimizes their electronic contributions to the polymer. Commonly used hydrophilic functional groups for both rod-coil and rod-rod polymers include acrylic acids, pyridines, ethylene glycols, amines, phosphates, carboxyls, and various zwitterionic groups.^[218b, 231] One of the first amphiphilic

p-/n-type rod-rod BCPs involved a triblock donor-acceptor-donor polymer with P3HT as the p-type, hydrophobic polymer and a zwitterionic poly(pyridinium phenylene) as the hydrophilic, n-type polymer (**P3HT-*b*-PPyPh**).^[232] The reported BCPs however contained high volume fractions of the P3HT block (80-90%) which are likely the reason for the nonlamellar morphology exhibited, and though it is claimed that the BCPs showed promise as nanostructured photovoltaic materials, device data was not reported. More recently in 2016, a derivative of the best-performing block copolymer material to date was designed, which replaced hexyl sidechains with tetraethylene glycol (TEG) sidechains to impart hydrophilicity on an n-type dioctylfluorene-alt-dithienylbenzothiadiazole (PFTBT) block, which was then appended to a hydrophobic p-type P3HT block (**P3HT-*b*-PF_{TEG}T6BT**).^[225c] AFM measurements were utilized to show self-assembly into optimal lamellar domains of around 20 nm, however poor OPV performances of >0.03% were produced, which were attributed to low electron mobilities in the hydrophilic acceptor block. Lastly, to demonstrate the effectiveness of utilizing chemical disparity to ensure phase separation, semifluorinated alkyl sidechains were appended to an n-type carbazole-alt-dithienylbenzothiadiazole block coupled to a P3HT block. Although not strictly an amphiphilic BCP, it outperformed similar analogues with no sidechains or nonfluorinated sidechains (albeit only achieving a low PCE of ~1%), from which phase separation was not observed.^[229a]

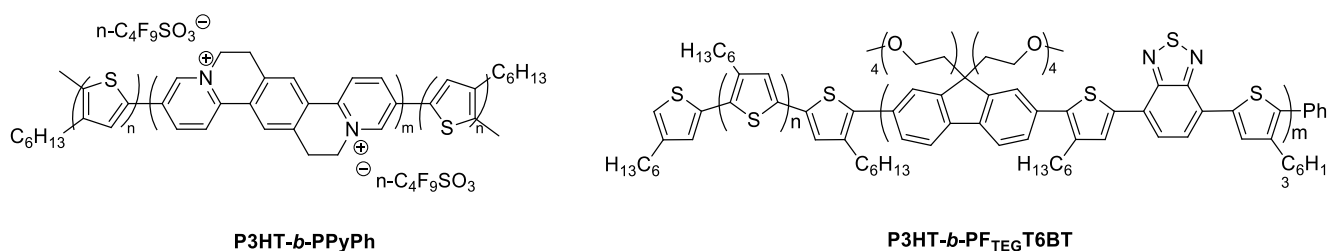


Figure 5-2: Chemical structure for examples of donor-acceptor amphiphilic block copolymers discussed in the text.

5.3 Obstacles facing block copolymer materials for OPV applications

Despite the obvious morphological benefits conferred by the unique molecular architecture, the OPV performances of BCPs remain low. The best-performing all-polymer BCP device -based on a non-amphiphilic P3HT-*b*-PFTBT polymer- features a relatively low PCE of 3.1%.^[233] Previous accounts in the literature have partially blamed these low performances on the choices of the semiconductor substrates selected having more to do with their synthetic versatility, as opposed to first choosing good polymer candidates for OPV applications and then designing a synthetic pathway.^[212] Another factor detracting from the development of high-performance BCP materials is that of the synthetic challenges in obtaining a controlled block copolymer of a high purity. Recent advances in synthetic techniques allow chain-growth polymerizations for conjugated polymers, where an individual monomer is functionalized to incorporate a group capable of initiating a controlled polymerization, ultimately resulting in a macroinitiator homopolymer end-capped with this same functional group (from which subsequent homopolymers may be grown to yield the BCP). Various catalyst-transfer reactions (ie. Kumada, Suzuki, Stille and Negishi catalyst transfer polymerizations), as well as zinc-activated or monomer deactivation reactions are all examples of polymerizations available for the

development of certain conjugated polymers,^[234] however these reactions are heavily substrate-dependant, and in particular few electron-deficient monomers have been demonstrated to be compatible with these reactions.^[235] For this reason, step-growth polycondensations are the most common approach for forming homopolymers, in which multiple chains come together in an uncontrolled fashion to form higher molecular weight polymers.^[212] Besides the high polydispersity of the resultant polymers, one of the major problems of this approach however, is that of poor end group control. End-group control is crucial and can strongly influence the suitability of the polymer for organic electronics applications through factors such as charge mobilities and photochemical stabilities. This control becomes even more inherently important when considering the synthesis of more complex polymeric architectures such as block copolymers. To attain the push-pull structures needed for high-performance polymers, most routes utilize the copolymerization of two or more symmetrically-functionalized monomers, which then results in copolymers with a mixture of end-caps (e.g. AA-, AB- and BB-capped homo-copolymers for a two-monomer reaction) as seen in Figure 5-3a. These homopolymers are usually inseparable due to the molecular weight difference between the polymer chains and the reactive terminal groups and are thus carried through to the formation of the block copolymer. This subsequently results in a mixture of homo-, di-, and triblock copolymers being formed and previous diblock copolymer materials have been demonstrated to contain as much of 42% by weight of the unreacted homopolymer and 16% of triblock contaminants,^[236] and these have been shown to be detrimental to device efficiencies through the formation of varied self-assembled morphologies and both new charge-transfer states and charge trapping sites.^[237] Though the amphiphilic nature of recent block copolymers have been exploited to facilitate purification,^[225c] this is still not a perfect strategy able to obtain block copolymers of a purity required for OPV applications. As such, it seems prudent to design a bottom-up strategy to attain this purity where fine end-group control is established to prevent triblock contaminants from forming at all.

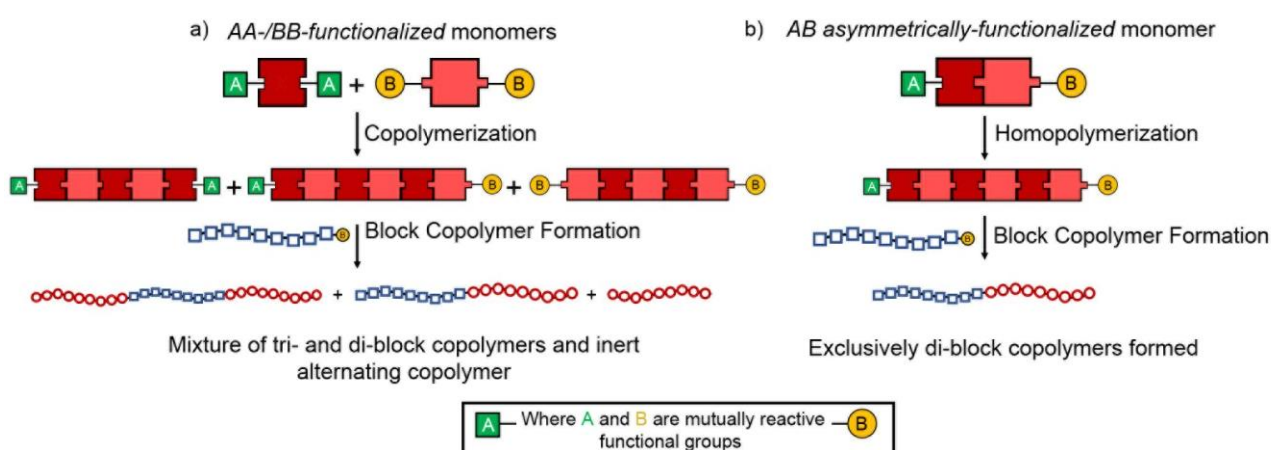


Figure 5-3: Idealized schematic of a) copolymerization using symmetrically-functionalized monomers resulting in poor end-group control and b) homopolymerization using a single asymmetrically-functionalized monomer with good end-group control

5.4 Heterobifunctional AB monomers

A more rational monomer design represents one approach to this strategy. Heterobifunctional AB-type monomers are a single monomer unit that feature two asymmetrically-functionalized end groups which are mutually reactive. While these types of monomers have been utilized to great extent in the literature for the controlled synthesis of non-conjugated polymers,^[238] their use in conjugated polymer synthesis is much more limited due to significant synthetic challenges.^[239] These monomers have mainly been used in Negishi- or Kumada-type catalyst-transfer chain-growth polymerizations,^[240] and to a lesser extent Suzuki-type chain- and step-growth polycondensations.^[241] In the small pool of AB-functionalized conjugated molecules available, the vast majority of these monomers generally consist of single structural elements such as thiophenes, fluorenes or phenylenes. Amongst these, only a handful of monomers have been developed that are inherently comprised of the push-pull architecture common to high-performing polymer materials.^[236b] Examples of some of these AB-type monomers (both single and multi-chromophore) can be seen in Figure 5-4. AB-functionalized monomers with mutually-reactive end-groups are able to polymerize to a single conjugated block with distinct end-groups. Subsequently, upon grafting to another asymmetrically-functionalized homopolymer, a deblock copolymer will be exclusively formed (Figure 5-3b).

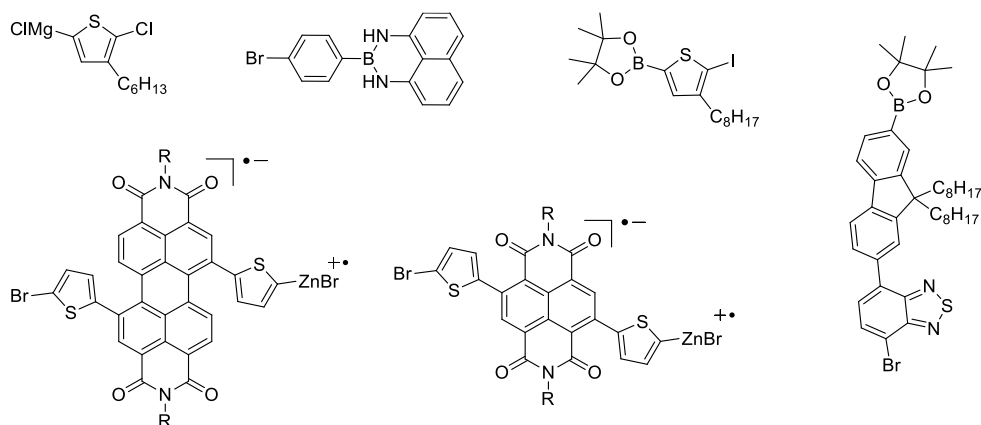


Figure 5-4: Examples of existing heterobifunctional monomers

5.5 Proposed amphiphilic block copolymer design

One of the key findings behind the **P3HT-*b*-PF_{TEG}T6BT** amphiphilic BCP was that its low electron mobility could be attributed to charge trapping by the TEG sidechains on the n-type homopolymer block. Inspiration for the work in this chapter came from the theory that if similar hydrophilic oxygenated sidechains were instead appended on the hole-transporting p-type homopolymer block, then higher electron charge mobilities could be achieved. Bearing this in mind, along with the need for a) high-performance components and b) a synthetic route that would minimize contaminant formation, two new amphiphilic BCPS (**P1** and **P2**) were designed. These both utilized a hydrophobic isoindigo-based push-pull homopolymer at the cutting edge of n-type semiconductor research, as well as a novel synthetic route to this homopolymer that proceeded through an asymmetrically-functionalized monomer to grant fine end-group control. The isoindigo-based

polymers were to be coupled to analogues of P3HT as the p-type block, which were appended with sidechains of increasing oxygen content as ether linkages to install the hydrophilic functionality (Figure 5-5).

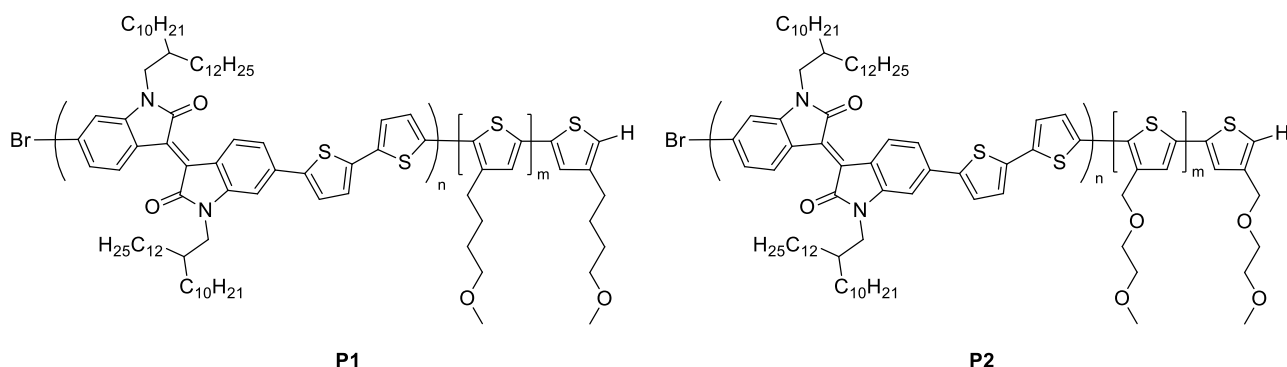
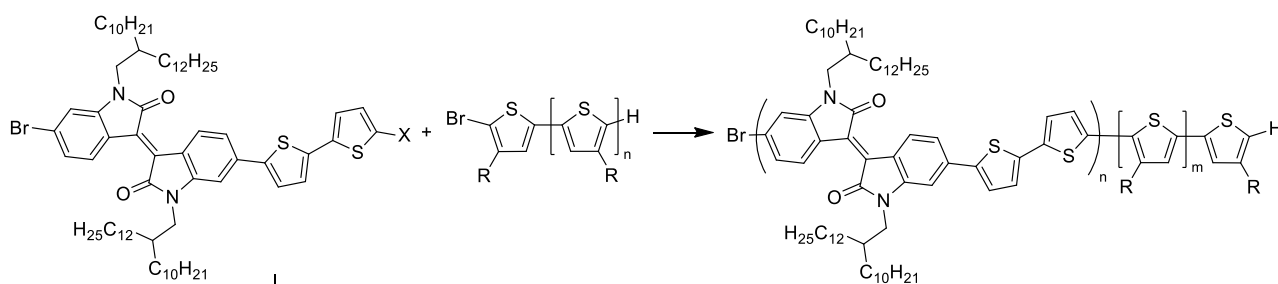


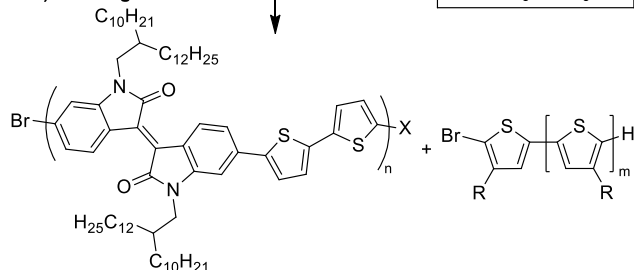
Figure 5-5: Proposed structures of the novel P3HT-*b*-isoindigo amphiphilic block copolymers

Previous studies have shown that incorporating ether linkages into polymeric thiophene sidechains have not shown any detrimental effects on its charge-transport properties, and so theoretically this is an ideal route to achieve amphiphilicity without comprising device performance.^[242] The isoindigo n-type block is functionally identical the well-known polymer P(il-T2) from the literature, and was selected for both its high hole mobility, complementary spectral coverage with P3HT and the inherent asymmetric nature of its synthesis.^[243] To synthesize our isoindigo block it was envisaged that the isoindigo -bithiophene monomer would be asymmetrically functionalized and installed with terminal Br-/X- groups, where X could be a boryl, stannyl or hydrogen moiety. Through routes such as Suzuki or Stille polycondensations or direct heteroarylation polymerizations (DHAP), the isoindigo monomer would then either a) utilize the asymmetric Br-/H-terminated P3HT analogue as a macroinitiator for chain-extension reactions, or b) form a homopolymer and be grafted onto the P3HT analogue (Figure 5-4).

a) Macroinitiator route



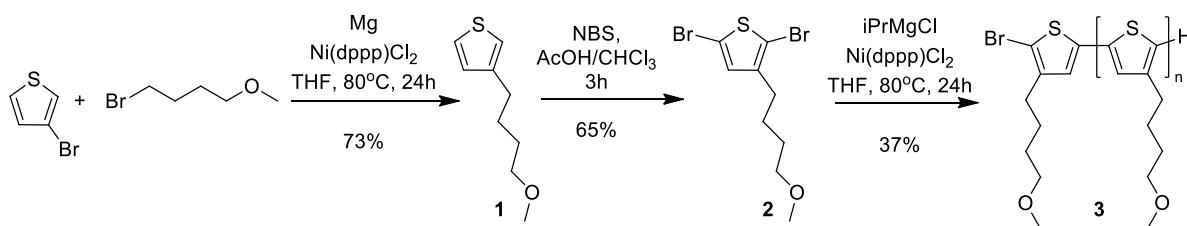
b) Grafting route



Scheme 5-1: Two proposed routes towards formation of the block copolymer as described in the text

5.6 Synthesis of the hydrophilic p-type homopolymer block

For this study two separate P3HT based monomers with either one (compound **2**) or two (compound **5**) oxygens as ether linkages within the alkyl sidechains were selected, which kept an overall combined sidechain length of six carbon or oxygen repeat units in order to capitalize on the optimized hexyl length for P3HT. The synthesis of the unreported mono-oxygenated polymer (Scheme 5-2) began with a Kumada coupling between the commercially available 3-bromothiophene **1** and freshly prepared (4-methoxybutyl)magnesium bromide in a 1.3-fold excess, which yielded the target alkylated thiophene **2** after purification via distillation in yields of ~70%. In preparation for polymerization the thiophene was then dibrominated using *n*-bromosuccinimide (NBS) to afford the target monomer **3** after purification via silica column chromatography in yields of ~60%. This was then polymerized via the chain-growth Kumada catalyst transfer polycondensation (KTCP) developed by the McCullough and Yokozawa groups, which could theoretically confer a narrow polydispersity and fine end-group control.^[227, 244] A specific molar ratio of 0.95 eq. of the isopropylmagnesium chloride (iPrMgCl) solution was used to form the active Grignard reagent from **3**, this ensuring the complete consumption of iPrMgCl and the formation of exclusively Br-/H- endcapped polymers, as described by the Yokozawa group.^[244] Regioregularity of the polymer was also established, with a small portion of the active Grignard species quenched via HCl prior to addition of the nickel catalyst and analysed via ¹H NMR to ensure selective insertion of the magnesium metal at the unhindered 2-position on the thiophene (see Figure 5-6a). Prior to formation of the polymer, based on prior studies of P3HT in the literature it was calculated that roughly 100 repeat units of the thiophene monomer (equalling a molecular weight of 16.8 kg/mol) would result in the targeted solid-state domain sizes of 20 nm.^[221] A 0.01 mol% of the nickel (1,3-diphenylphosphinopropane) catalyst was found, after purification via successive Soxhlet extractions in methanol, acetone, hexanes and chloroform to result in a polymer close to the target weight with a *M_n* of 17.7 kg/mol and a PDI of 1.26, however a relatively low yield of 37% was obtained. MALDI mass-spec analysis confirmed a large majority of Br-/H- end-capped polymers relative to the functionally inert H-/H- polymers.

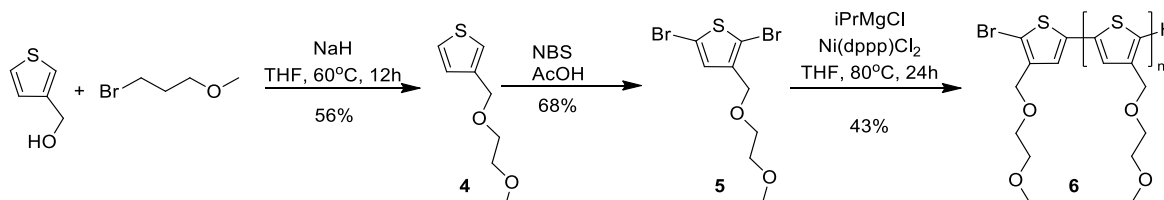


Scheme 5-2: Mono-oxygenated P3HT analogue synthetic pathway

The synthesis of the previously reported di-oxygenated polymer began by employing a modified procedure from the literature to afford the monomer.^[245] This utilized sodium hydride to deprotonate 3-thiophenemethanol which was then quenched with 1-bromo-2-methoxyethane to form the di-oxygenated thiophene **4** in a yield of 56%. After this, formation of the polymer proceeded along a similar route to **3**, with the monomer **5** formed after a di-bromination using NBS and the target polymer **6** formed through a KTCP

reaction. 0.005 mol% of the nickel catalyst afforded, after purification, a polymer with a M_n of 17.7 kg/mol and a PDI of 1.7 in a yield of 43%, close to our target molecular weight of 17.0 kg/mol.

Unfortunately, ^1H NMR analysis of the quenched Grignard reagent (Figure 5-6b) revealed that oxidative insertion into the Br-C bond occurred in a 1:1 ratio between the 5- and the desired 2-position on the thiophene, a ratio far higher than the 1:4 observed in the literature for both P3HT and the mono-oxygenated analogue.^[246] This was theorized to be due to the close proximity of the oxygen atom on the sidechain stabilizing the magnesium insertion at the otherwise unfavourable 2-position. This mixture of active Grignard species predicted the subsequent formation of regio-irregular polymers comprised of random head-to-head and head-to-tail orientations. This was confirmed via ^1H NMR analysis of the polymer itself, which exhibited two different sets of peaks in the alkyl region that we assigned to these two monomer orientations. This also further suggests that the catalytic selectivity observed by the McCullough group (where the 20% of the 2-magnesiumbromide thiophene active Grignard species formed were functionally inert to oxidative insertion of the nickel catalyst) is not in operation here, and presumably the steric repulsion experienced by the nickel catalyst is in competition with a stabilizing effect from the adjacent oxygen atom.^[246] This is an agreement with the ^1H NMR spectrum published by McCullough of the di-oxygenated polymer, which appears to exhibit the same ‘twin’ set of peaks in the alkyl region corresponding to the two regioisomers, although this is hard to confirm due to the lack of assigned chemical shifts from this spectrum.^[247] The only other published article that reports this polymer has also not reported any in-depth analytical data.^[248]



Scheme 5-3: Di-oxygenated P3HT analogue synthetic pathway

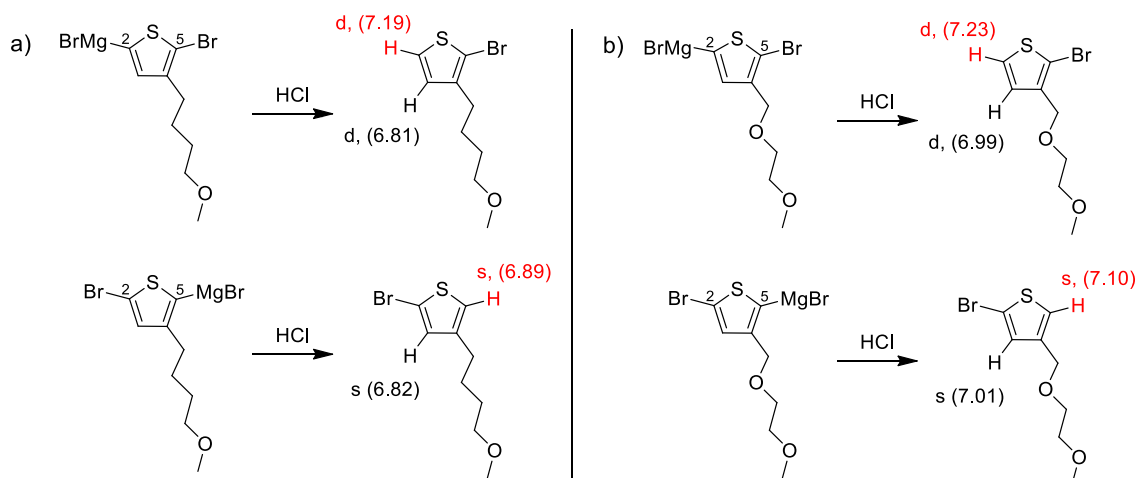
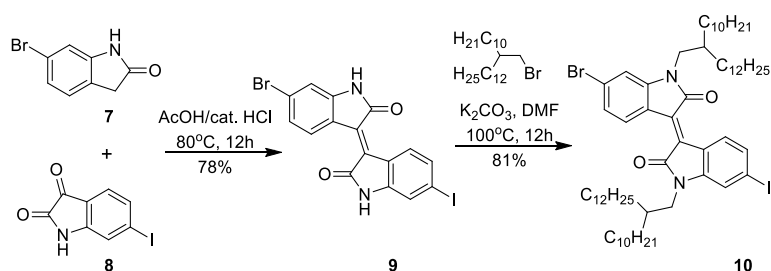


Figure 5-6: Peak types and chemical shifts (ppm) of the quenched Grignard species used for ^1H NMR analysis

5.7 Synthesis of the hydrophobic n-type homopolymer block

In this study several synthetic routes towards a heterobifunctionalized isoindigo monomer were investigated that could ultimately polymerize to the well-known semiconducting polymer **P(il-T2)**.^[243a, 249] As previously mentioned it was envisaged that this monomer be comprised of an electron-poor isoindigo (**il**) and an electron-rich bithiophene (**T2**) unit. All synthetic routes to this polymer to date however, utilize symmetrically-functionalized monomers, and therefore no end-group control has been reported. Here the overarching design strategy for all routes investigated involved assembling the monomer from components that were themselves asymmetrically functionalized.

For example, it was quickly established that the inherently asymmetric nature of the isoindigo core assembly could be harnessed (Scheme 5-4). A commonly-used route in the literature proceeds through the condensation between oxindole and indole-dione moieties, however these are typically both brominated, with the condensation yielding a dibrominated species that offers no selectivity. In this study on the other hand, the 5-bromooxindole **7** and 5-iodoisatin **8** couple together to produce the asymmetrically-halogenated core **9** in a high yield, conferring a molecule that does possess an asymmetric functionality. Curiously, despite the significant potential offered by this molecule and that both **7** and **8** are commercially-available reagents, this represents an unprecedented, novel reaction in the literature. Subsequently, the isoindigo core was alkylated under basic conditions using 1-bromo-2-decyltetradecane to yield **10**.



Scheme 5-4: Isoindigo core synthetic pathway

Following this, three unsuccessful, separate routes were attempted to obtain the target asymmetrically functionalized n-type isoindigo homopolymer **P(il-T2)**, as outlined in Scheme 5-5, and are worth a brief discussion as to why these were ultimately considered to be not feasible.

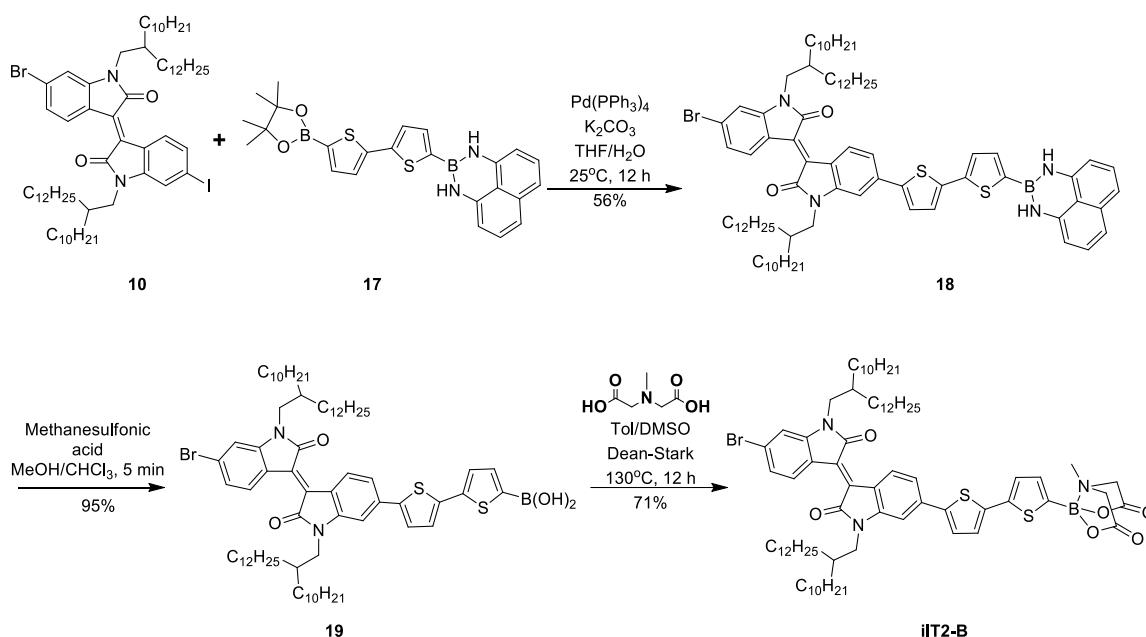
The first route sought to utilize a synthetically simple isoindigo monomer with Br-/H- terminal moieties **12**, which was assembled via Suzuki coupling with a mono-borylated bithiophene **11** that was itself asymmetrically-functionalized. Here the first-generation Suzuki coupling catalyst Pd(PPh₃)₄ and low reaction temperatures of 25°C were utilized in an effort to slow the rate of oxidative addition and to increase the selectivity between the different halides, with the ultimate goal of preferential oxidative addition into the C-I bond. Despite also forming the doubly-coupled product, after column chromatographic purification a relatively low yield of ~40% of product **12** was obtained, with no trace of the H-/I-functionalized material. This is indicative of the preferential selectivity of the Pd catalyst for insertion into the C-I bond, however the

formation of relatively high levels -around 20 mol% of **10**- of the doubly-substituted isoindigo core suggests that a 'ring-walking' mechanism is in effect, where the Pd catalyst remains coordinated to the electron-deficient aryl centre of the isoindigo moiety after reductive elimination and subsequently undergoes intramolecular oxidative addition into the C-Br bond.^[250] Once **12** had been obtained, it was to be polymerized using a DHAP reaction utilizing conditions modified from a similar reaction in the literature (which instead utilized two symmetrically-functionalized AA/BB type monomers),^[251] however it was found that this route resulted in poor control over the degree of polymerization and provided poor end-group control when grafted onto the similarly-functionalized Br/H-terminated p-type polymer.

Following this, the second attempted reaction proceeded through an iridium catalysed C-H activation to install a boronic acid pinacol ester (Bpin) functional group onto **12** in preparation for a Suzuki polycondensation,^[252] however the reaction was found to be low yielding even at long (>12h) reaction times. This was believed to be due to the electron-poor nature of the isoindigo substrate which is known to be problematic for C-H activations.^[253] Another attempt was made to obtain the borylated monomer **13** through the novel asymmetrically-functionalized bithiophene **14**, which was itself synthesized through a procedure modified from the asymmetrization of a thiophene from the literature.^[254] Here a stannyl moiety was introduced to allow coupling of the bithiophene under Stille coupling conditions which would render the borylated moiety inert, however unlike the reported purification of the thiophene compound from the literature, the asymmetrized bithiophene was unable to be purified via recrystallization and so had to be carried through as the crude material. This, in conjunction with the formation of the bis-substituted product during the Stille coupling to **13** in yields of around 10-20% (again through the chain-walking mechanism), meant that there was a non-trivial quantity of impurities present. Unfortunately, it was quickly found that the Bpin moiety on **13** was prone to deborylation under standard purification conditions (including but not limited to silica and alumina column chromatography), and as high monomer purity was required in order to ensure high homopolymer purity, this rendered the synthetic route non-viable. As such, a new boryl moiety was required that exhibited a high tolerance to purification conditions.

For this, the N-methyliminodiacetic acid (MIDA) ligand was chosen. Developed by Gillis and Burke, MIDA-protected boronate esters are known to be compatible with chromatographic conditions, indefinitely stable under ambient conditions and easily deprotected under mild aqueous basic conditions. The guiding principle for the design of the new bithiophene component was the need for a diborylated species that could be asymmetrically and reversibly protected against Suzuki coupling conditions, to allow for the sequential coupling of 1) the MIDA-functionalized bithiophene to the isoindigo core, then 2) each monomer to the next to yield the target polymer.

microwave conditions resulted in increased doubly-functionalized isoindigo core formation or trace amounts of the B(DAN)-/I-functionalized material. The deprotection of the B(DAN) moiety was carried out to restore Suzuki-coupling capability to the monomer. Dilute methanesulfonic acid (1 v/v %) was used to treat **18** in a 0.7 mM solution of 10:1 chloroform:methanol. Following the reaction by NMR analysis of the crude solution it was found that at these concentrations deprotection could be carried out to 95% completion within 5 minutes at room temperature, at which point deborylation started to occur. The liberated DAN was then removed from the reaction mixture by washing with dilute acid, leaving the free boronic acid-functionalized **19**. At this point, the isoindigo moiety was capable of undergoing polymerization, however amongst the organoboranes, the boronic acid moiety is known to be particularly unstable to both column chromatography conditions and long-term storage and so as the facile purification of the monomer was deemed to be a required property the MIDA ligand was installed. Coordination of the MIDA ligand was performed by refluxing the crude boronic acid-functionalized compound **19** and an excess of the MIDA ligand in a 10:1 solvent mixture of toluene:DMSO in a Dean-Stark apparatus, and the MIDA-protected monomer **iIT2-B** isolated after silica column chromatography with a reaction yield of 71%.



Scheme 5-7: Asymmetric isoindigos monomer synthetic pathway

With the monomer obtained a proof-of-principle Suzuki polycondensation was performed. As the in-situ deprotection of the MIDA boronate required two equivalents of base to form the free boronic acid in addition to that required for the Suzuki catalytic cycle, five equivalents of K_2CO_3 was utilized alongside a $Pd_2(dba)_3/P(o\text{-tolyl})_3$ catalyst/ligand combination in a THF/ H_2O mixture. After 24 hours at 60 °C, the resulting polymer was first filtered through a thin pad of silica, and then purified via sequential Soxhlet extractions with methanol, hexanes, acetone and dichloromethane. The polymer was then collected via dissolution in boiling chloroform and precipitation in methanol to yield the polymer **P(iIT2)** with an M_n of 24,000 and a PDI of 1.39 in 70% yield. MALDI-TOF mass spectrometry studies was utilized to perform an end-group analysis on the low-molecular

weight chains of the resulting polymer (See S5.9.2.3), as it was found that the higher-weight chains did not ionize readily. The masses of the major peaks present were found to follow the formula $(1096.78)n + 81.77$ - where 1096.78 is the mass for the **iIT2** repeat unit- which was identified as the $[M+H]^+$ mass for the growing polymer chain end-capped by Br-/H- moieties. No peaks were identified with a mass corresponding to a polymer end-capped by Br-/B(OH)₂ moieties. This indicates that, as expected, the B(OH)₂ moiety did not survive the purification process but was instead replaced by a hydrogen atom after deborylation, and suggests that if block copolymerization occurs through the grafting route described in Scheme 5-1b, it would have to do so in-situ and prior to homopolymer purification.

5.8 Chapter conclusion

The work in this chapter details the synthesis of the two homopolymer blocks for amphiphilic block copolymer OPV applications, with a particular focus on achieving fine end-group control to minimize polymer contaminants. Two H-/Br-terminated hydrophilic P3HT analogues were successfully synthesized using a KTCP reaction to their targeted molecular weights, however the bulk of the research efforts in this chapter went to establishing an asymmetrization route that utilized a selective combination of orthogonal boron protecting groups to yield a push-pull heterobifunctional isoindigo monomer. The resulting monomer is stable to ambient conditions as well as silica column chromatography and can thus be purified to a high degree prior to polymerization. The monomer can be easily deprotected under basic conditions and subsequently undergo Suzuki polymerization in a one-pot reaction, and was able to achieve the target molecular weight of 20,000 Da. These efforts serve as an ideal proof-of-concept to show that end-group control for block copolymers is accessible through a rational synthetic approach. While the synthesis of the block copolymer itself is outside the scope of the work in this thesis, nonetheless these results showcase ideal homopolymer components and represent a strong foundation on which future amphiphilic BCP syntheses may be based on.

5.9 Experimental and supporting information

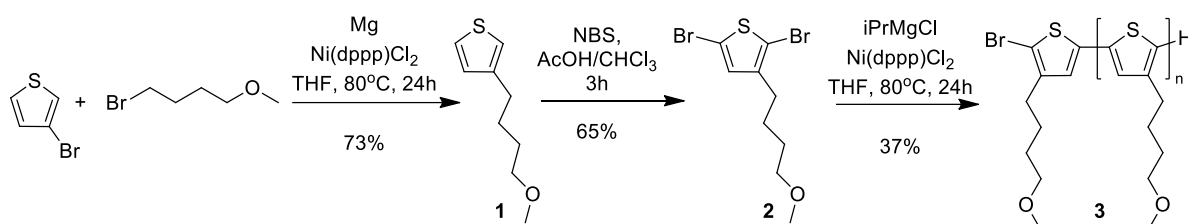
5.9.1 Materials and methods

Unless noted, all materials were reagent grade and used as received without further purification. Anhydrous solvents were prepared by drying HPLC grade solvents using freshly activated molecular sieves. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-Vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. ¹H NMR and ¹³C NMR spectra were carried out on a 400 MHz or 600 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet). MALDI-TOF mass spectrometry was performed on a Bruker microflex instrument, using chloroform as solvent and DCTB or

terthiophene as the assisted matrix. ESI mass spectrometry was performed on a Thermo Scientific Q Exactive Plus Orbitrap LC-MS/MS instrument, using 50% acetonitrile/ 0.1% formic acid as the solvent. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) on an Exeter Analytical CE-440 elemental analyzer.

5.9.2 Synthesis

The synthesis of the polythiophene analogues **4**, **5** and **6** have been previously reported.^[256] Here a modified synthetic route to these compounds are used. The synthesis of the bithiophene intermediate **11** has also been reported.^[254] The synthesis of the bithiophene intermediate **14** has been modified from a procedure in the literature for a similar compound.^[254]



5.9.2.1 3-(4-methoxybutyl)thiophene (**1**)

Magnesium chips (5.1 g, 210 mmol) were flame-dried under vacuum in a three-necks flask. Anhydrous THF (200 mL) was introduced into the flask and stirred for 30 minutes. 4-methoxybutane (33.4 g, 200 mmol) was added dropwise at a rate sufficient to keep a gentle reflux. After addition, the Grignard reagent was introduced dropwise to a solution of 3-bromothiophene (24.4 g, 150 mmol) and nickel (diphenylphosphinopropane) dichloride (5 mol%, 3.96 g, 7.45 mmol) in anhydrous THF (200 mL). The reaction was left to stir overnight at room temperature. The crude oil was distilled to yield a colourless oil (18.7 g, 109.5 mmol, 73%). and utilized in the next step without further purification. ¹H-NMR (400 MHz; CDCl₃): δ 7.24 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.93 (s, 1H), 3.41 (t, J = 6.1 Hz, 2H), 3.33 (s, 3H), 2.66 (t, J = 7.4 Hz, 2H), 1.22 (m, 4H). ¹³C NMR (CDCl₃, 151 MHz) δ 142.73, 128.19, 125.13, 119.96, 72.60, 58.55, 30.06, 29.29, 27.10. IR = 2930, 2860, 1457, 1386, 1116, 947, 857, 769, 684 cm⁻¹. MS (ESI) calculated for C₉H₁₄OS: 170.08; Found: [M+2Na]⁺: 213.15.

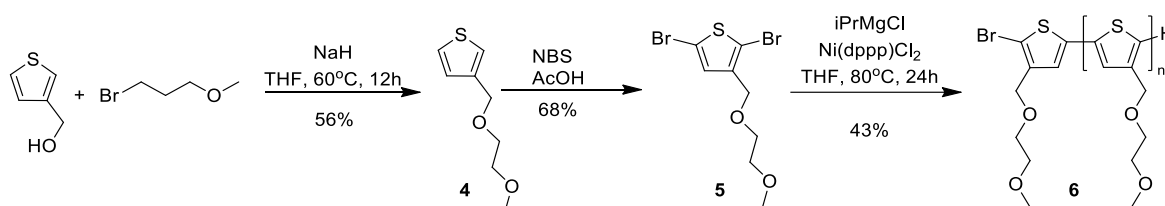
5.9.2.2 2,5-dibromo-3-(4-methoxybutyl)thiophene (**2**)

1 (9 g, 53 mmol) was dissolved in a 1:1 solution of chloroform: glacial acetic acid (50 mL) in a 2-neck flask. To this, n-Bromosuccinimide (23.5 g, 132.5 mmol) in a dropping funnel containing a 1:1 solution of chloroform: glacial acetic acid (100 mL) was slowly added. The reaction was left to stir for 3 hours at room temperature in the dark. The reaction was poured into ice water, and extracted with diethyl ether. The solvent was removed under rotary evaporation, and the product purified via column chromatography (silica, 1:1 petroleum spirits: chloroform) to yield a yellow oil (11.3 g, 34.5 mmol, 65%). ¹H-NMR (400 MHz; CDCl₃): δ 6.71 (s, 1H), 3.38 (t, J = 6.1 Hz, 2H), 3.33 (s, 3H), 2.54 (t, J = 7.2 Hz, 2H), 1.22 (m, 4H). ¹³C NMR (CDCl₃, 151

MHz) δ 142.51, 130.88, 110.41, 108.10, 77.19, 76.98, 76.77, 72.36, 58.58, 29.19, 29.04, 26.18. IR = 2923, 2861, 1541, 1456, 1417, 1386, 1185, 1116, 999, 932, 825, 753 cm^{-1} . MS (ESI) calculated for $\text{C}_9\text{H}_{12}\text{Br}_2\text{OS}$: 327.90; Found $[\text{M}+\text{DMSO}+\text{H}]^+$: 407.91.

5.9.2.3 Mono-oxygenated P3HT analogue (3)

2 (1 g, 3.1 mmol) and anhydrous THF (20 mL) were combined under a dinitrogen atmosphere. An isopropylmagnesium chloride solution in THF (1.62 M, 1.93 mL, 2.95 mmol) was added dropwise via syringe. The solution was stirred at room temperature for 20 hours. The catalyst $\text{Ni}(\text{dppp})\text{Cl}_2$ (17 mg, 0.031 mmol) was added and the solution stirred for an additional 3 hours. The reaction was then quenched with 10 mL of 5 M HCL. The product was precipitated in cold methanol and purified via soxhlet extraction with petroleum spirits (40-60°C), acetone and finally dichloromethane to afford the product. The resulting dark purple solid (194 mg, 37% yield) and shown by GPS analysis to have a Mw of 18.9 kg/mol, a Mn of 17.7 kg/mol, and a PDI of 1.26. ^1H -NMR (400 MHz; CDCl_3): δ 6.99 (s, 1H), 3.44 (t, J = 6.1 Hz, 2H), 3.35 (s, 3H), 2.84 (t, J = 7.4 Hz, 2H), 1.86 – 1.65 (m, 4H). ^{13}C -NMR (101 MHz; CDCl_3): 139.44, 133.65, 130.68, 128.64, 72.53, 58.59, 29.49, 29.17, 27.13. IR = 2931, 2861, 1450, 1386, 1117, 825 cm^{-1} .



5.9.2.4 3-((2-methoxyethoxy)methyl)thiophene (4)

A solution of sodium hydride (1.26 g, 52.5 mmol) and anhydrous THF (50 mL) was made up, and cooled to 0°C under a dinitrogen atmosphere. Thiophen-3-ylmethanol (2 g, 17.5 mmol) was added dropwise and the mixture allowed to stir for 15 minutes. The solution was then allowed to warm to room temperature, and 1-bromo-2-methoxyethane (3.6 g, 26.25 mmol) added dropwise. The solution was refluxed at 60°C overnight, and then quenched with cold H_2O . The organic phase was extracted with DCM (2 x 50 mL) and dried over MgSO_4 . The crude material was purified via column chromatography (silica, 1:4 ethyl acetate: petroleum spirits) to yield a clear oil (1.69 g, 9.8 mmol, 56%). ^1H -NMR (600 MHz; CDCl_3): δ 7.30 (m 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 4.58 (s, 2H), 3.61 (m, 2H), 3.57 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (CDCl_3 , 151 MHz) δ 139.33, 127.37, 125.90, 122.89, 71.96, 69.16, 68.48, 59.04. IR = 2872, 1452, 1418, 1348, 1198, 1090, 1043, 852, 775, 690 cm^{-1} . MS (ESI) calculated for $\text{C}_8\text{H}_{12}\text{O}_2\text{S}$: 172.06; Found: $[\text{M}+\text{ACN}+\text{H}]^+$: 461.09.

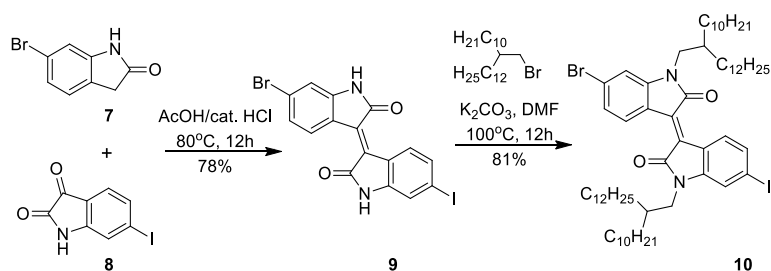
5.9.2.5 2,5-dibromo-3-((2-methoxyethoxy)methyl)thiophene (5)

3-((2-methoxyethoxy)methyl)thiophene (3.4 g, 19.7 mmol) was dissolved in glacial acetic acid (20 mL) and the solution cooled down to 0°C. n-Bromosuccinimide (8.77 g, 49.25 mmol) was added portion wise, and the solution allowed to warm to room temperature. The reaction was stirred in light-free conditions overnight under a dinitrogen atmosphere. The reaction was quenched with cold H_2O , and the organic phase extracted

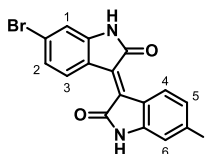
with the addition of chloroform (2 x 50 mL), then dried over MgSO_4 . The crude material was purified via column chromatography (silica, 1:1 petroleum spirits: chloroform) to yield a yellow oil (4.43 g, 13.8 mmol, 68%). ^1H -NMR (600 MHz; CDCl_3): δ 7.00 (s, 1H), 4.44 (s, 2H), 3.61 (m, 2H), 3.57 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (CDCl_3 , 151 MHz) δ 139.17, 130.87, 111.27, 110.03, 71.80, 69.51, 66.94, 59.08. IR = 2924, 2861, 1541, 1456, 1417, 1386, 1188, 1116, 1000, 932, 825, 754 cm^{-1} . MS (ESI) calculated for $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_2\text{S}$: 327.90; Found $[\text{M}+\text{DMSO}+\text{H}]^+$: 409.89.

5.9.2.6 Di-oxygenated P3HT analogue (6)

5 (1.71 g, 5.21 mmol) and anhydrous THF (20 mL) were combined under a dinitrogen atmosphere. An isopropylmagnesium chloride solution in THF (1.62 M, 3.06 mL, 4.95 mmol) was added dropwise via syringe. The solution was stirred at room temperature for 20 hours. The catalyst $\text{Ni}(\text{dppp})\text{Cl}_2$ (13.76 mg, 0.025 mmol) was added and the solution stirred for an additional 3 hours. The reaction was then quenched with 10 mL of 5 M HCL. The product was precipitated in cold methanol and purified via soxhlet extraction with petroleum spirits (40-60°C), acetone and finally dichloromethane to afford the product. The resulting dark purple solid (194 mg, 37% yield) and shown by GPS analysis to have a Mw of 18.9 kg/mol, a Mn of 17.7 kg/mol, and a PDI of 1.26. ^1H -NMR (400 MHz; CDCl_3): δ 7.29 (s, 1H), 4.50 (m, 2H), 3.63 (m, 3H), 3.58 (m, 2H), 3.39 (s, 3H). ^{13}C -NMR (101 MHz; CDCl_3): 139.49, 139.31, 136.00, 134.49, 133.09, 129.57, 128.23, 126.85, 71.89, 71.85, 69.56, 66.95, 59.08, 59.04. IR = 2871, 1450, 1349, 1241, 1196, 1086, 1040, 831 cm^{-1} .

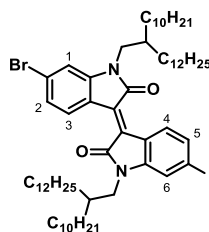


5.9.2.7 (E)-6-bromo-6'-iodo-[3,3'-biindolinylidene]-2,2'-dione (**9**)

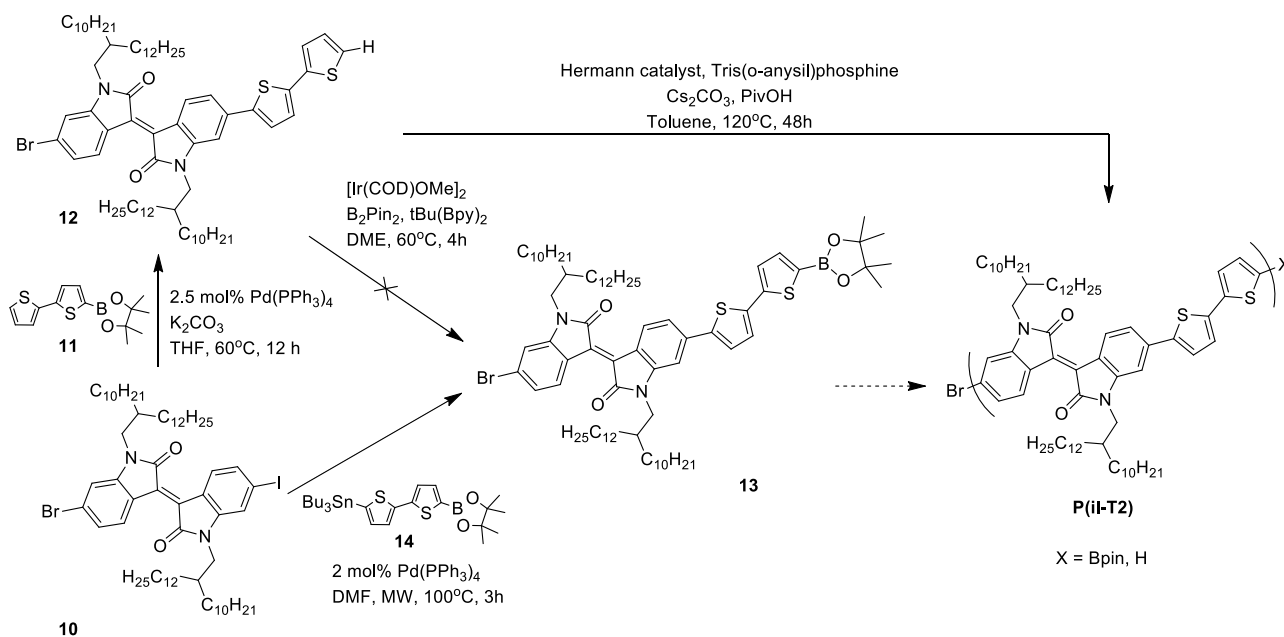


6-bromoindolin-2-one **7** (4 g, 18.86 mmol) and 6-iodoindoline-2,3-dione **8** (5.15 g, 18.86 mmol) were suspended in glacial acetic acid (200 mL). 12 M HCl (cat., 5 mL) was added and the resulting mixture refluxed for 3 hours. The solution was allowed to cool to room temperature and the resulting solid product filtered off and washed with cold methanol, water, sodium bicarbonate solution and hexane to afford the desired product as an analytically pure dark red solid (8.8 g, 14.71 mmol, 78%). ^1H -NMR (400 MHz; $\text{d}^6\text{-DMSO}$): δ 8.98 (d, J = 8.6 Hz, 1H, H-3), 8.81 (d, J = 8.5 Hz, 1H, H-4), 7.31 (d, J = 8.5 Hz, 1H, H-5), 7.14 (s, 1H, H-2), 7.11 (d, J = 8.6 Hz, 1H, H-6), 6.94 (s, 1H, H-1). IR (Neat): ν = 3170, 3110, 1694, 1602 cm^{-1} . MS(MALDI) m/z calculated for $\text{C}_{16}\text{H}_8\text{BrIN}_2\text{O}_2$: 465.88, found: 465.83 $[\text{M}^+]$.

5.9.2.8 (E)-6-bromo-1,1'-bis(2-decyltetradecyl)-6'-iodo-[3,3'-biindolylidene]-2,2'-dione (**10**)

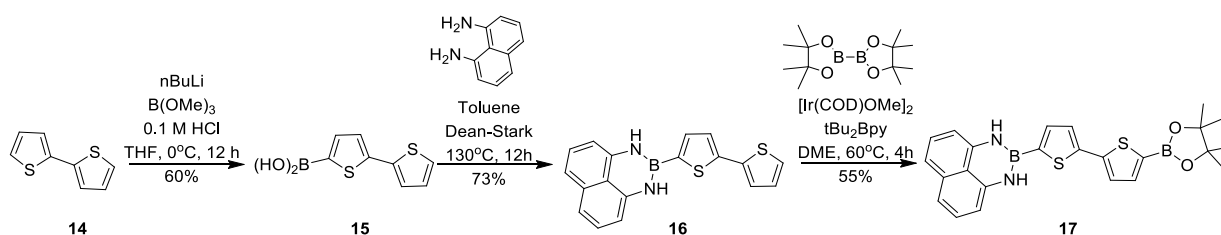


To a solution of **9** (0.5 g, 1.07 mmol) and potassium carbonate (0.89 g, 5.35 mmol) in DMF (20 mL), 1-bromo-2-decyltetradecane (0.98 g, 2.35 mmol) was added under dinitrogen. The mixture was stirred for 15 hours at 100°C, after which the reaction was quenched with water and the crude mixture extracted with DCM. The organic layer was washed with brine and dried over MgSO_4 and the solvent removed under reduced pressure. The residue was further purified by column chromatography (silica, 5:1 petroleum spirits/DCM) and dried under vacuum to yield the product as a dark red solid (0.97 g, 0.87 mmol, 81%). $^1\text{H-NMR}$ (600 MHz; CDCl_3): δ 9.08 (dd, J = 8.6, 1.9 Hz, 1H, H-3), 8.91 (dd, J = 8.6, 1.8 Hz, 1H, H-4), 7.39 (ddd, J = 8.5, 3.0, 1.6 Hz, 1H, H-5), 7.17 (ddd, J = 8.6, 2.9, 1.9 Hz, 1H, H-2), 7.10 (dd, 3.6, 1.5 Hz, 1H, H=6), 6.90 (dd, J = 3.6, 1.8 Hz, 1H, H-1), 3.62 (t, J = 8.6 Hz, 4H, N- CH_2), 1.88-1.87 (s, 2H, CH), 1.49-1.20 (m, 80 H, CH_2), 0.88 (m, 12H, CH_3). $^{13}\text{C NMR}$ (CDCl_3 , 151 MHz) δ 168.09, 167.88, 146.19, 145.83, 132.91, 132.78, 132.68, 132.55, 131.31, 130.99, 130.83, 126.67, 126.63, 125.07, 121.01, 120.98, 120.40, 120.37, 117.28, 111.52, 98.90, 98.86, 44.67, 44.59, 36.06, 36.04, 31.91, 31.89, 31.47, 29.96, 29.67, 29.63, 29.60, 29.58, 29.56, 29.34, 29.32, 26.33, 22.67, 14.10. IR (Neat): ν = 2954, 2921, 2852, 1699, 1592, 1351, 870, 814 cm^{-1} . MS(MALDI) m/z calculated for $\text{C}_{64}\text{H}_{101}\text{BrIN}_2\text{O}_2$: 1138.63, found: 1138.78 [M^+]. Elemental analysis calculated for $\text{C}_{64}\text{H}_{101}\text{BrIN}_2\text{O}_2$: C, 67.41; H, 9.19; Br, 7.01; I, 11.13; N, 2.46; O, 2.81. Found; C, 67.75; H, 9.30; N, 2.47.

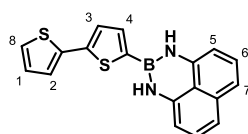


5.9.2.9 (E)-6-([2,2'-bithiophen]-5-yl)-6'-bromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (**12**)

10 (0.5 g, 0.44 mmol), **11** (0.13 g, 0.44 mmol), potassium carbonate (0.12 g, 0.88 mmol) and palladium tetra(triphenylphosphine) (11.6 mg, 2.5 mol%) were placed into a Schlenk flask and dried under vacuum for 0.5 hours. The flask was then back-filled with dinitrogen, and THF (2 mL) and distilled water (0.45 mL) were added. The mixture was then left to stir at room temperature overnight, after which the organic layer was extracted with DCM (3 x 50 mL), dried over MgSO₄ and the solvent removed under reduced pressure. The crude was further purified under column chromatography (silica, 4:1 petroleum spirits/chloroform) and dried under vacuum to yield the product as a dark purple solid (203 mg, 0.19 mmol, 43%). ¹H-NMR (600 MHz; CDCl₃): δ 9.15 (d, J = 8.5 Hz, 1H), 9.06 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 3.9 Hz, 1H), 7.26 (dd, J = 8.7, 1.8 Hz, 1H), 7.25 (d, J = 3.9 Hz, 1H), 7.23 (d, J = 8.5 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 7.16 (dd, J = 8.7, 1.8 Hz, 1H), 7.04 (t, J = 4.2 Hz, 1H), 6.88 (s, 1H), 6.85 (s, 1H), 3.66 (d, J = 7.2 Hz, 2H), 3.59 (d, J = 7.3 Hz, 2H), 1.87 (m, 2H), 1.45-1.16 (m, 80 H), 0.88 (m, 12H). ¹³C NMR (CDCl₃, 151 MHz) δ 168.46, 168.11, 145.93, 145.86, 142.39, 138.26, 137.68, 137.02, 133.01, 131.08, 130.77, 130.46, 127.95, 126.02, 125.07, 124.90, 124.85, 124.72, 124.05, 120.82, 120.58, 118.85, 111.33, 104.58, 44.60, 44.42, 36.37, 36.10, 31.92, 31.76, 31.51, 30.02, 30.00, 29.70, 29.66, 29.61, 29.36, 26.66, 26.38, 22.69, 14.12. IR = 2921, 2852, 1694, 1595, 1403, 1351, 870, 814, 760 cm⁻¹. MS(MALDI) m/z calculated for C₇₂H₁₀₉BrN₂O₂S₂: 1178.71, found: 1178.62 [M⁺].



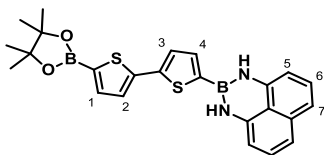
5.9.2.10 2-([2,2'-bithiophen]-5-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (**16**)



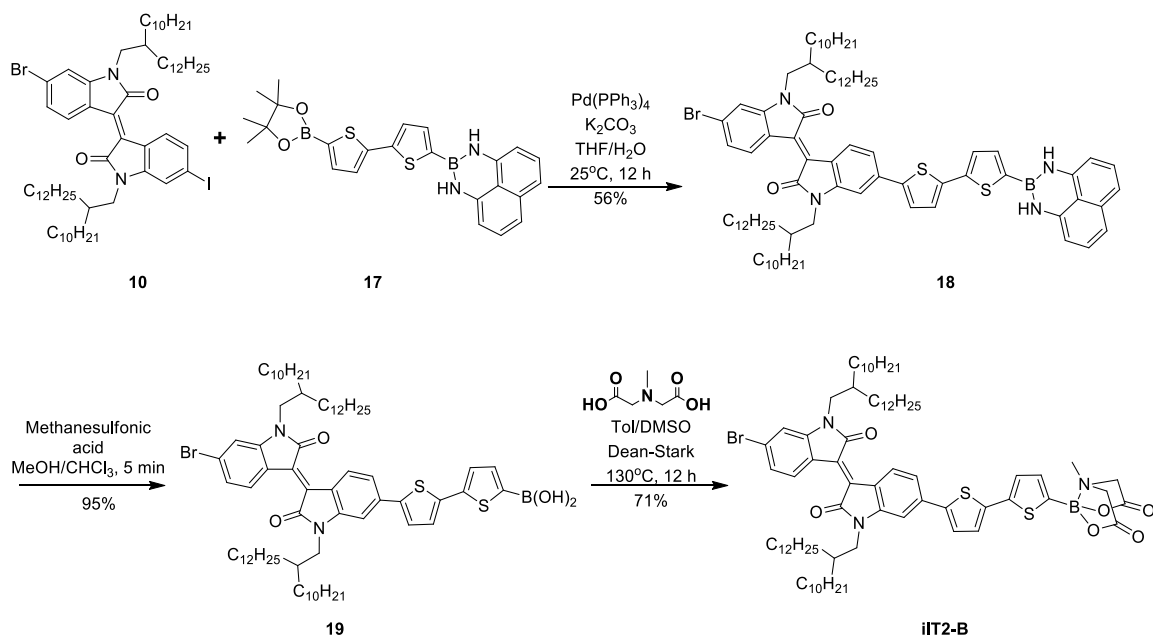
Compound **15** (3.79 g, 18.05 mmol) was utilized without purification from the previous step. The crude material was dissolved in toluene (150 mL) in a Dean-Stark apparatus and 1,8-diaminonaphthalene (4.28 g, 27.08 mmol) was added. The Dean-Stark apparatus was purged of oxygen by briefly placing the mixture under vacuum, and then back-filled with dinitrogen. The mixture was then refluxed for 12 hours, after which the solvent was removed via rotary evaporation. The crude material was purified via column chromatography (silica, 1:9 ethyl acetate/hexanes) and precipitated in hexanes to yield the product as a yellow crystalline solid (4.38 g, 13.18 mmol, 73%). ¹H-NMR (600 MHz; CDCl₃): δ 7.39 (d, J = 3.5 Hz, 1H, H-4), 7.29 (d, J = 3.5 Hz, 1H, H-3), 7.27 (d, J = 7.8 Hz, 1H, H-2), 7.26 (d, J = 7.8 Hz, 1H, H-1), 7.16-7.13 (t, J = 7.8 Hz, 2H, H-7), 7.07 (d, J

= 8.1 Hz, 2H, H-6), 7.05 (m, 1H, H-8), 6.43 (d, $J = 7.3$ Hz, 2H, H-5), 5.95 (br-s, 2H, NH). ^{13}C NMR (CDCl_3 , 151 MHz) δ 142.11, 140.59, 137.00, 136.27, 133.62, 127.93, 127.56, 125.15, 124.99, 124.32, 119.73, 118.02, 106.14. IR (Neat): $\nu = 3050, 1628, 1599\text{ cm}^{-1}$. MS(ESI) m/z calculated for $\text{C}_{18}\text{H}_{13}\text{BN}_2\text{S}_2$: 332.06, found: 333.068 $[\text{M}+\text{H}^+]$. Elemental analysis calculated for $\text{C}_{18}\text{H}_{13}\text{BN}_2\text{S}_2$: C, 65.07; H, 3.94; B, 3.25; N, 8.43; S, 19.30. Found: C, 64.87; H, 4.04; N, 8.65.

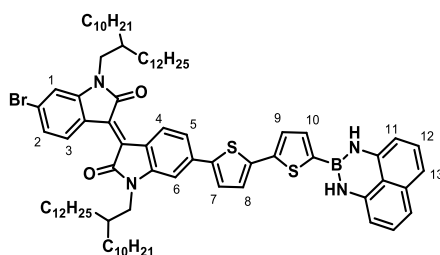
5.9.2.11 2-(5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2'-bithiophen]-5-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (**17**)



The protected bithiophene **16** (0.2 g, 0.6 mmol), B_2Pin_2 (0.08 g, 0.31 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (7.95 mg, 0.012 mmol), and tert-butylbipyridine (9.66 mg, 0.036 mmol) were placed into a Schlenk flask and dried under vacuum at 60°C for 30 minutes. Dry, degassed DME (2 mL) was added to the Schlenk flask and the reaction left to stir at 70°C for 12 hours. The solvent was then removed via rotary evaporation and the crude material redissolved in DCM and precipitated in methanol. The solid was collected via filtration to yield a green powder (151 mg, 0.33 mmol, 55%) and used in the next step without further purification. ^1H NMR (600 MHz, CDCl_3) δ 7.55 (d, $J = 3.6$ Hz, 1H, H-1), 7.39 (d, $J = 3.6$ Hz, 1H, H-4), 7.34 (d, $J = 3.5$ Hz, 1H, H-2), 7.31 (d, $J = 3.6$ Hz, 1H, H-3), 7.16 – 7.12 (m, 2H, H-7), 7.06 (d, $J = 8.3$ Hz, 2H, H-6), 6.43 (d, $J = 8.2$ Hz, 2H, H-5), 5.95 (br-s, 2H, NH), 1.36 (s, 12H, CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 143.55, 141.90, 140.56, 137.97, 136.27, 133.69, 127.55, 125.79, 125.53, 119.75, 118.05, 106.16, 84.24, 24.75. IR (Neat): $\nu = 3411, 1628, 1596, 140, 759\text{ cm}^{-1}$. MS(MALDI) m/z calculated for $\text{C}_{24}\text{H}_{24}\text{B}_2\text{N}_2\text{O}_2\text{S}_2$: 458.21, found: 458.08 $[\text{M}^+]$.

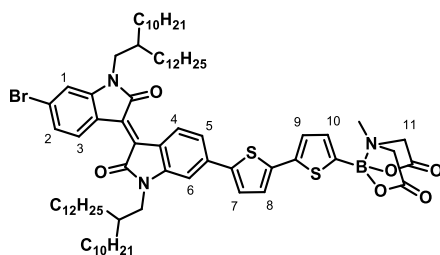


5.9.2.12 (E)-6-(5'-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-[2,2'-bithiophen]-5-yl)-6'-bromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (**18**)



The isoindigo core **10** (1.25 g, 1.1 mmol), bithiophene **17** (0.5 g, 1.1 mmol), Pd(PPh₃)₄ (31.8 mg, 0.03 mmol) and K₂CO₃ (0.30 g, 2.2 mmol) were placed under dinitrogen. Degassed THF (30 mL) and H₂O (3.3 mL) were added and the mixture stirred at room temperature for 12 hours. DCM (200 mL) was added and the organic layer extracted. After the solvent was removed via rotary evaporation, the crude material was purified via column chromatography (silica, 14:5:1 hexanes/chloroform/ethyl acetate) before precipitation in methanol yielding a purple powder (827 mg, 0.61 mmol, 56%). ¹H NMR (600 MHz, CDCl₃) δ 9.19 (d, J = 8.4 Hz, 1H, H-3), 9.07 (d, J = 8.5 Hz, 1H, H-4), 7.39 (d, J = 3.5 Hz, 1H, H-10), 7.35 (d, J = 3.8 Hz, 1H, H-7), 7.32 (d, J = 3.5 Hz, 1H, H-9), 7.28 (dd, J = 8.4, 1.7 Hz, 1H, H-5), 7.24 (d, J = 3.8 Hz, 1H, H-8), 7.17 – 7.14 (m, 1H, H-2), 7.13 (d, J = 7.2 Hz, 2H, H-13), 7.07 (d, J = 8.4 Hz, 2H, H-12), 6.94 (s, 1H, H-1), 6.87 (s, 1H, H-6), 6.41 (d, J = 7.0 Hz, 2H, H-11), 5.93 (br-s, 2H, NH), 3.68 (d, J = 7.3 Hz, 2H, N-CH₂), 3.61 (d, J = 7.5 Hz, 2H, N-CH₂), 1.92-1.88 (m, 2H, CH), 1.47 – 1.15 (m, 80H), 0.91 – 0.82 (m, 12H, CH₃). ¹³C NMR (125 MHz), CDCl₃) δ 168.48, 168.14, 145.93, 145.87, 143.11, 141.60, 140.47, 137.72, 137.48, 136.25, 133.69, 132.92, 131.25, 130.75, 130.44, 127.54, 126.09, 125.30, 125.14, 124.87, 121.00, 120.56, 119.72, 118.91, 118.09, 111.36, 106.20, 104.62, 44.58, 44.44, 36.36, 36.08, 31.91, 31.74, 31.50, 30.02, 29.99, 29.71, 29.69, 29.66, 29.64, 29.61, 29.60, 29.36, 29.34, 26.63, 26.37, 22.67, 14.10. IR (Neat): ν = 2922, 2852, 1693, 1600, 1523, 1404, 817, 760 cm⁻¹. MS(MALDI) m/z calculated for C₈₂H₁₁₆BBBrN₄O₂S₂: 1343.78, found: 1345.07 [M+H⁺]. Elemental analysis calculated for C₈₂H₁₁₆BBBrN₄O₂S₂: C, 73.24; H, 8.70; B, 0.80; Br, 5.94; N, 4.17; O, 2.38; S, 4.77. Found C, 74.93; H, 9.33; N, 4.61.

5.9.2.13 (E)-8-(5'-(6'-bromo-1,1'-bis(2-decyltetradecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)-[2,2'-bithiophen]-5-yl)-4-methyl-2,6-dioxohexahydro-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-ium-8-uide (**iIT2-B**)

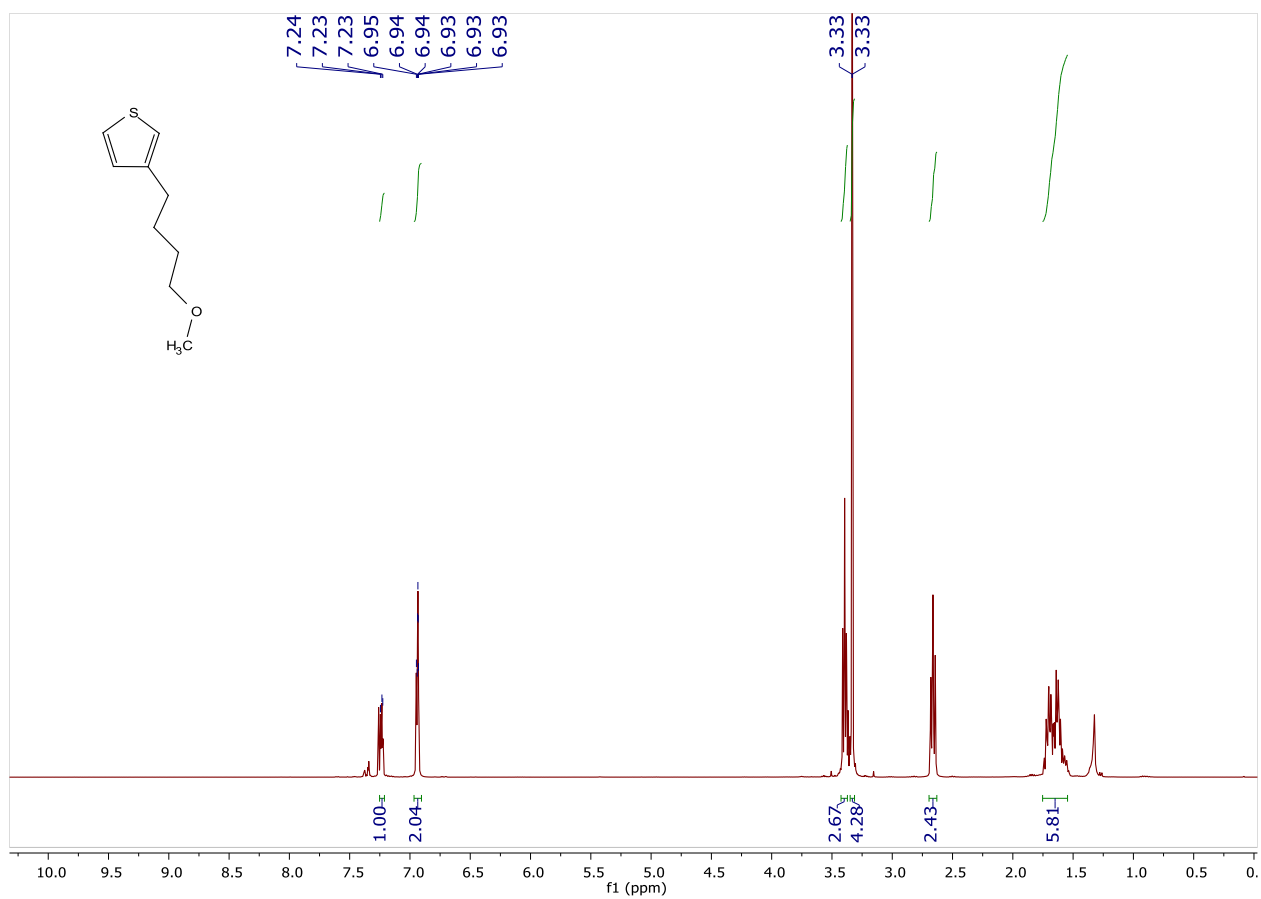
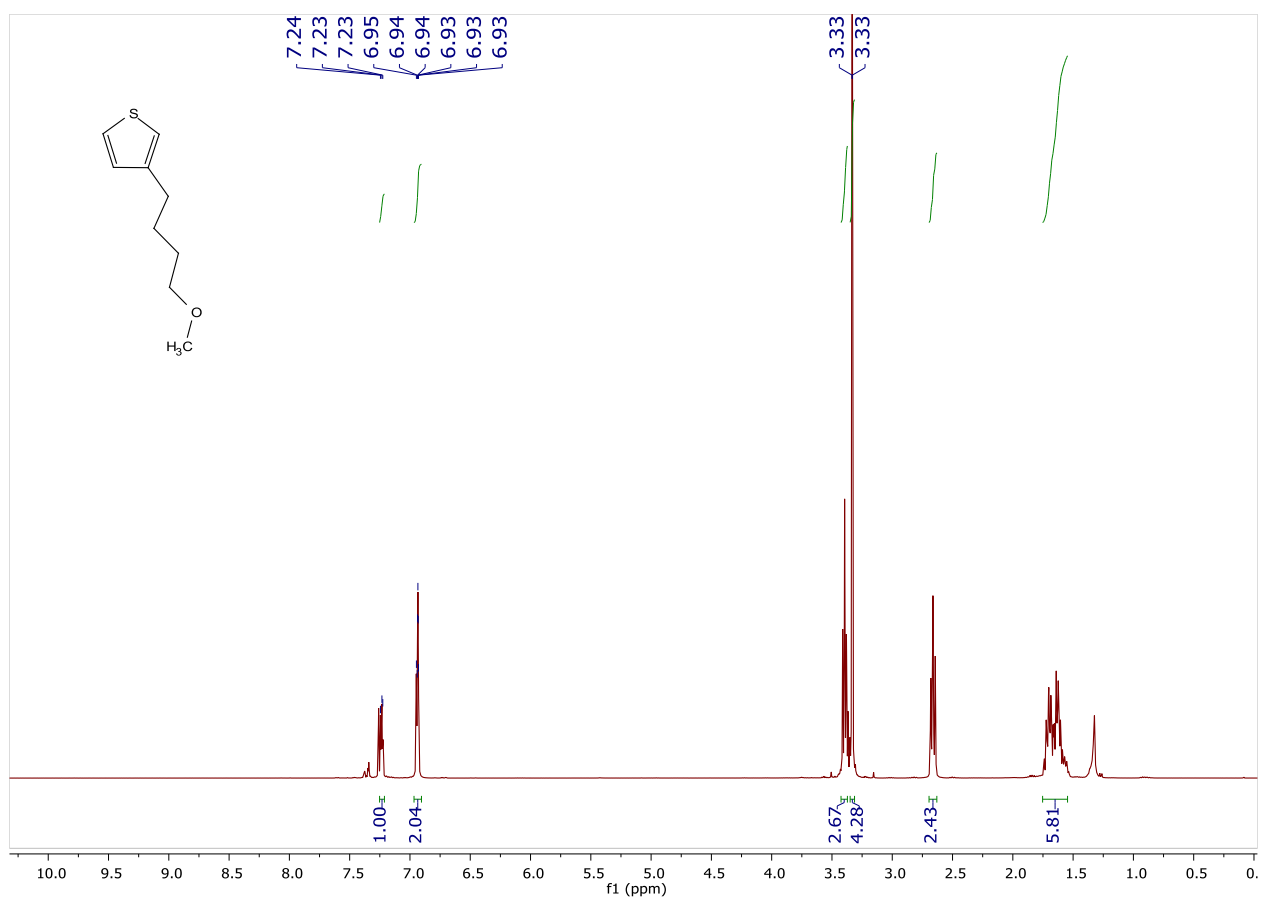


Isoindigo **18** (550 mg, 0.41 mmol) was dissolved in chloroform (500 mL) and methanol (50 mL). Methanesulfonic acid (4 mL) was added dropwise and the reaction left to stir for 5 minutes. The solvent was then removed by rotary evaporation, after which the crude material was redissolved in toluene (225 mL). A

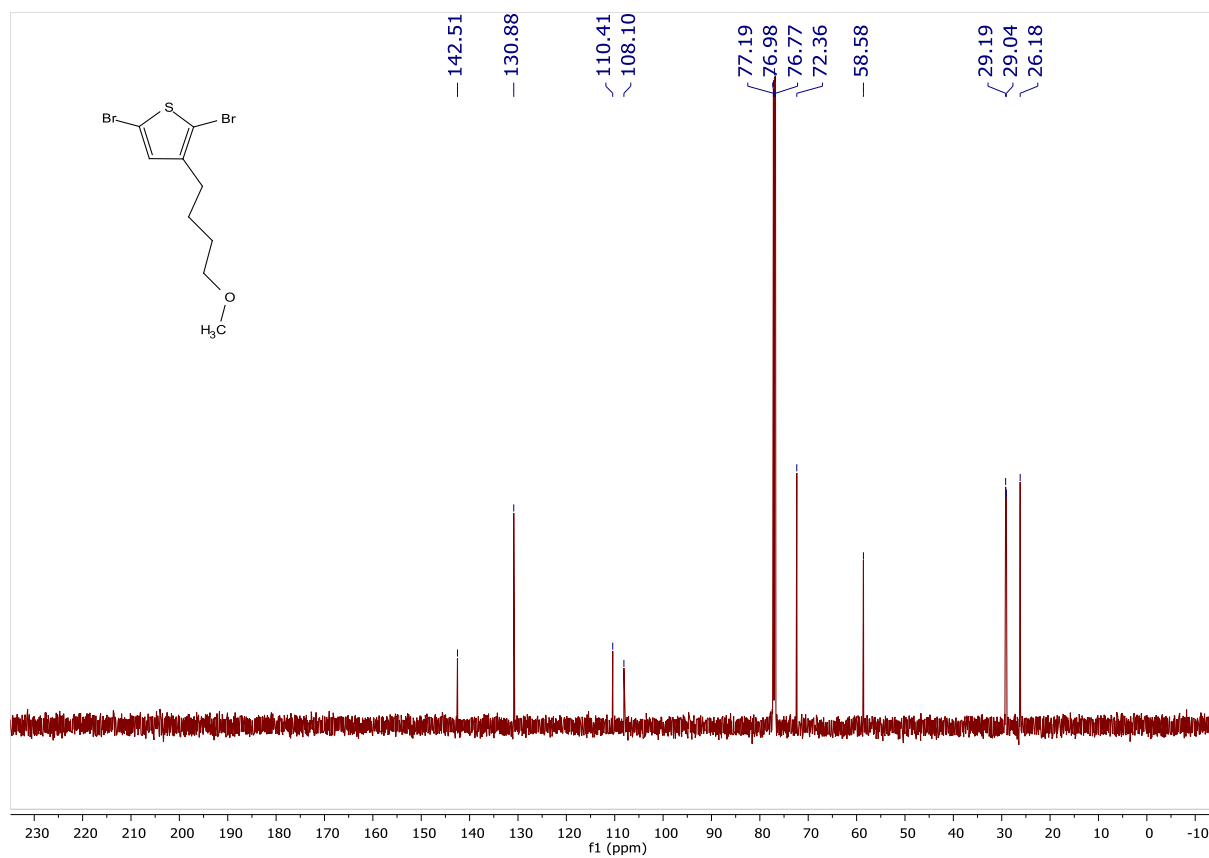
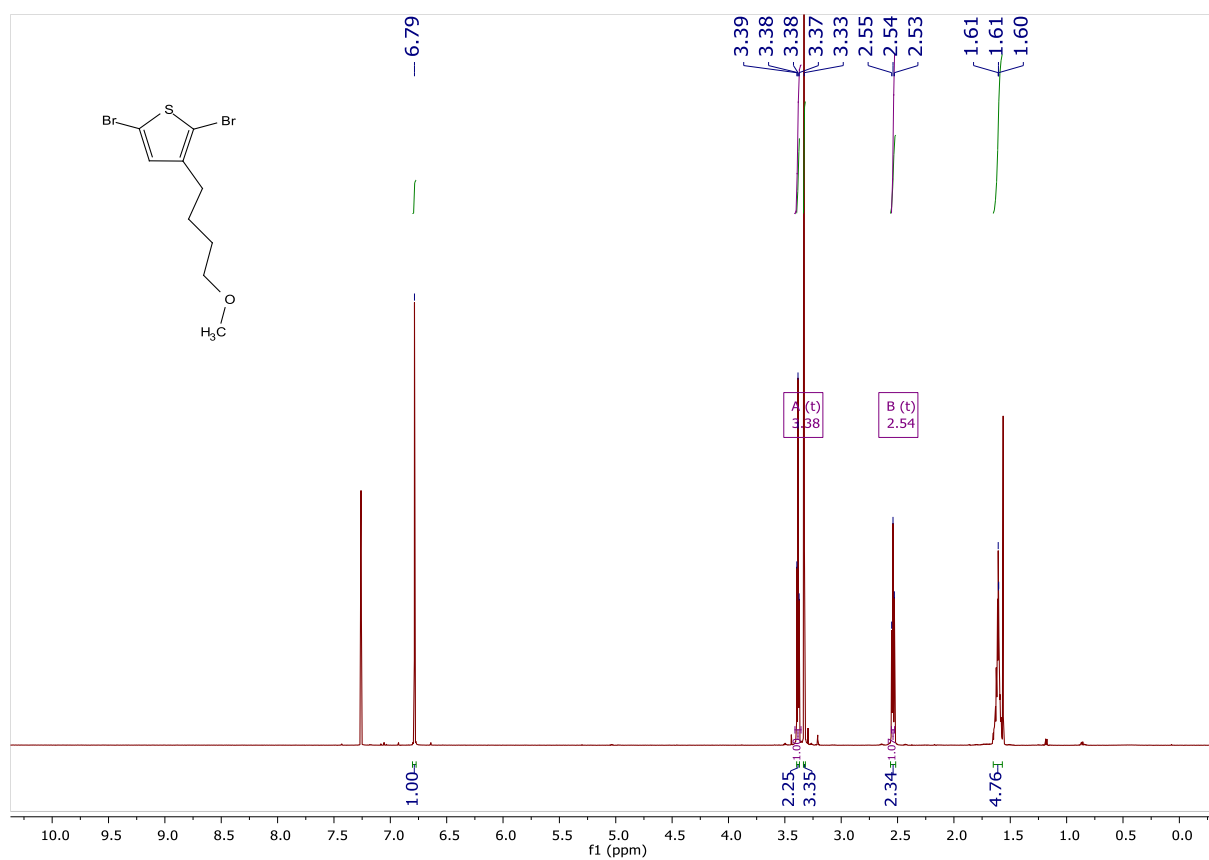
solution of methyliminodiacetic acid (121 mg, 0.82 mmol) in DMSO (25 mL) was added to this and the combined mixture placed in a Dean-Stark apparatus. The mixture was then refluxed for 12 hours, after which the solvent was removed via rotary evaporation. The crude material was purified via column chromatography (silica, 1:1:1 chloroform/ethyl acetate/hexanes) and precipitated in isopropanol to yield the product **IT2-B** as a purple crystalline solid (350 g, 0.27 mmol, 65%). ^1H NMR (600 MHz, CDCl_3) δ 9.16 (d, J = 8.4 Hz, 1H, H-3), 9.05 (d, J = 8.6 Hz, 1H, H-4), 7.31 (d, J = 3.8 Hz, 1H, H-7), 7.28 (d, J = 3.5 Hz, 1H, H-10), 7.25 (dd, J = 8.5, 18 Hz, 1H, H-5), 7.25 (d, J = 3.5 Hz, 1H, H-8), 7.20 (d, J = 3.8 Hz, 1H, H-9), 7.14 (dd, J = 8.5, 1.9 Hz, 1H, H-2), 6.90 (d, J = 1.7 Hz, 1H, H-1), 6.87 (d, J = 1.8 Hz, 1H, H-6), 3.92 (d, J = 16.4 Hz, 2H, H-11), 3.83 (d, J = 16.4 Hz, 2H, H-11), 3.68 (d, J = 7.3 Hz, 2H, N- CH_2), 3.61 (d, J = 7.5 Hz, 2H, N- CH_2), 2.77 (s, 3H, N- CH_3) 1.90-1.88 (m, 2H, CH), 1.47 – 1.15 (m, 80H), 0.91 – 0.82 (m, 12H, CH_3). ^{13}C NMR (125 MHz), CDCl_3) δ . 168.45, 168.13, 166.51, 145.97, 145.91, 142.98, 142.01, 137.70, 137.53, 134.54, 132.93, 131.25, 130.80, 130.46, 126.11, 125.50, 125.25, 125.16, 124.88, 120.97, 120.54, 118.98, 111.36, 104.60, 61.48, 47.35, 44.63, 44.51, 36.32, 36.10, 31.89, 31.67, 31.50, 29.97, 29.67, 29.65, 29.63, 29.60, 29.58, 29.34, 29.32, 26.55, 26.37, 22.66, 14.09. IR (Neat): ν = 2924, 2853, 1778, 1691, 1611, 1596, 1450, 872 cm^{-1} . MS(MALDI) m/z calculated for $\text{C}_{77}\text{H}_{115}\text{BBrN}_3\text{O}_6\text{S}_2$: 1333.60, found: 1333.45 [M^+]. Elemental analysis calculated for $\text{C}_{77}\text{H}_{115}\text{BBrN}_3\text{O}_6\text{S}_2$: C, 69.35; H, 8.69; B, 0.81; Br, 5.99; N, 3.15; O, 7.20; S, 4.81 Found: C, 69.05; H, 8.90; N, 3.35; S, 5.04.

5.9.1 ^1H and ^{13}C NMR spectra of unpublished materials

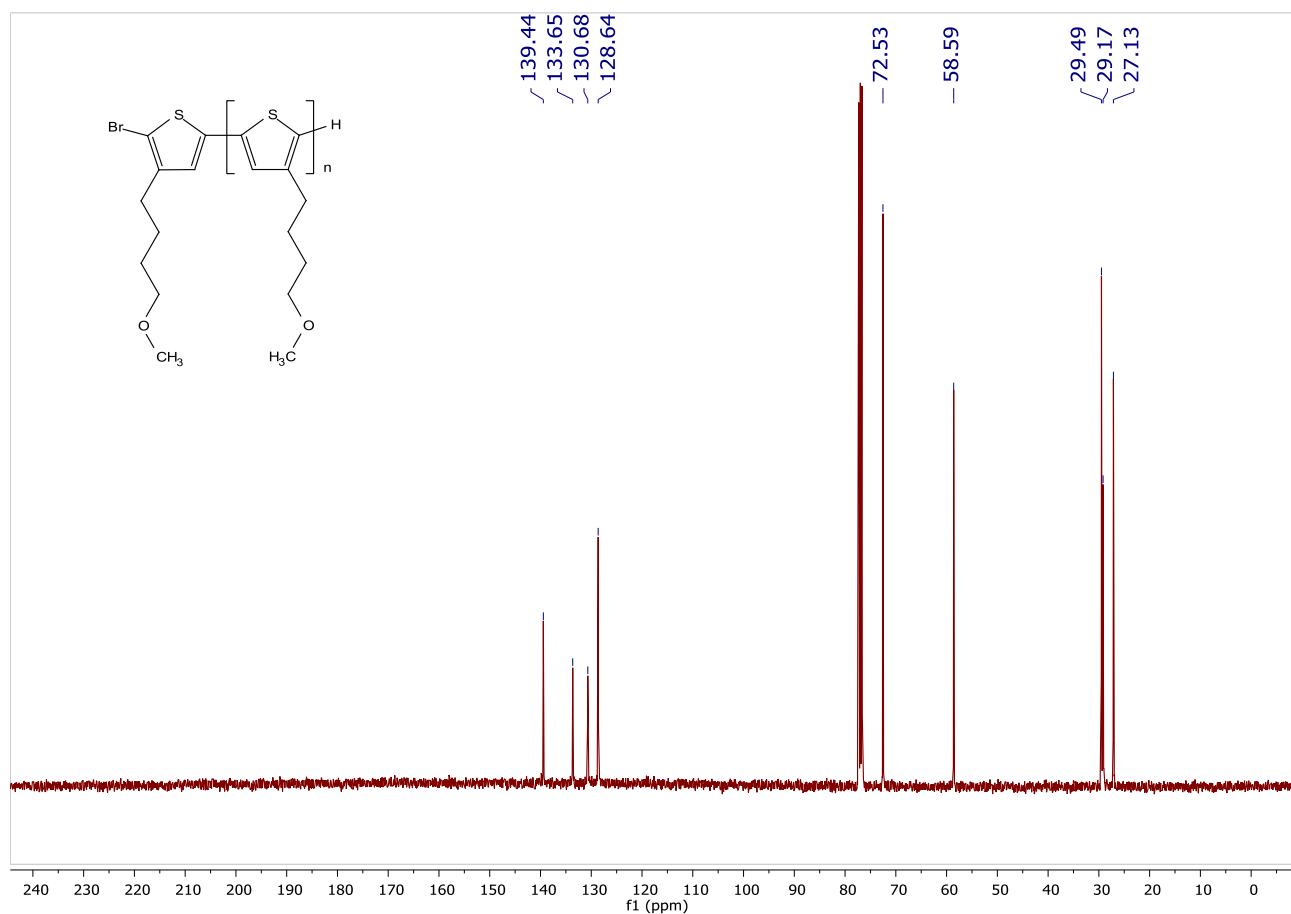
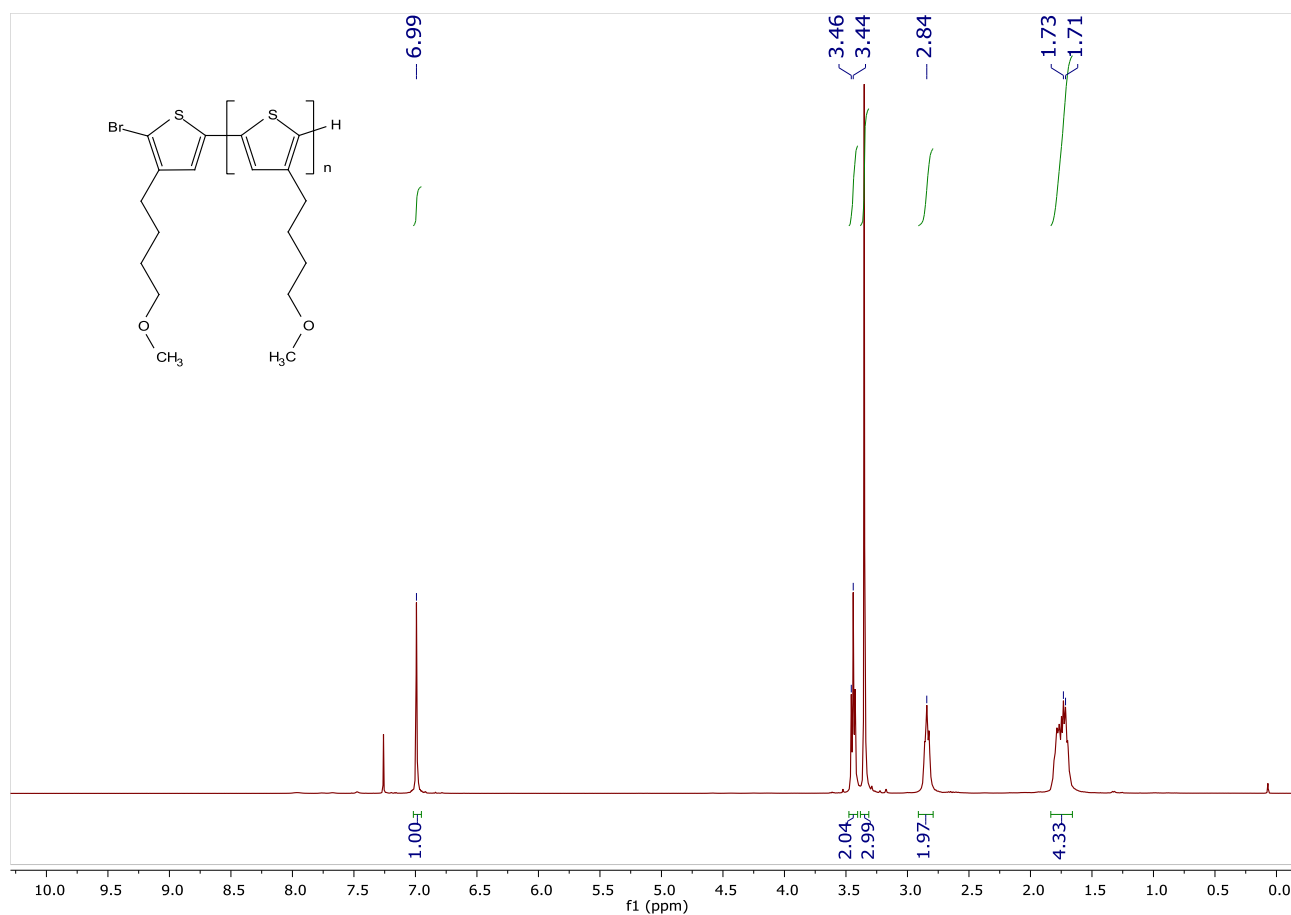
5.9.1.1 3-(4-methoxybutyl)thiophene (**1**)



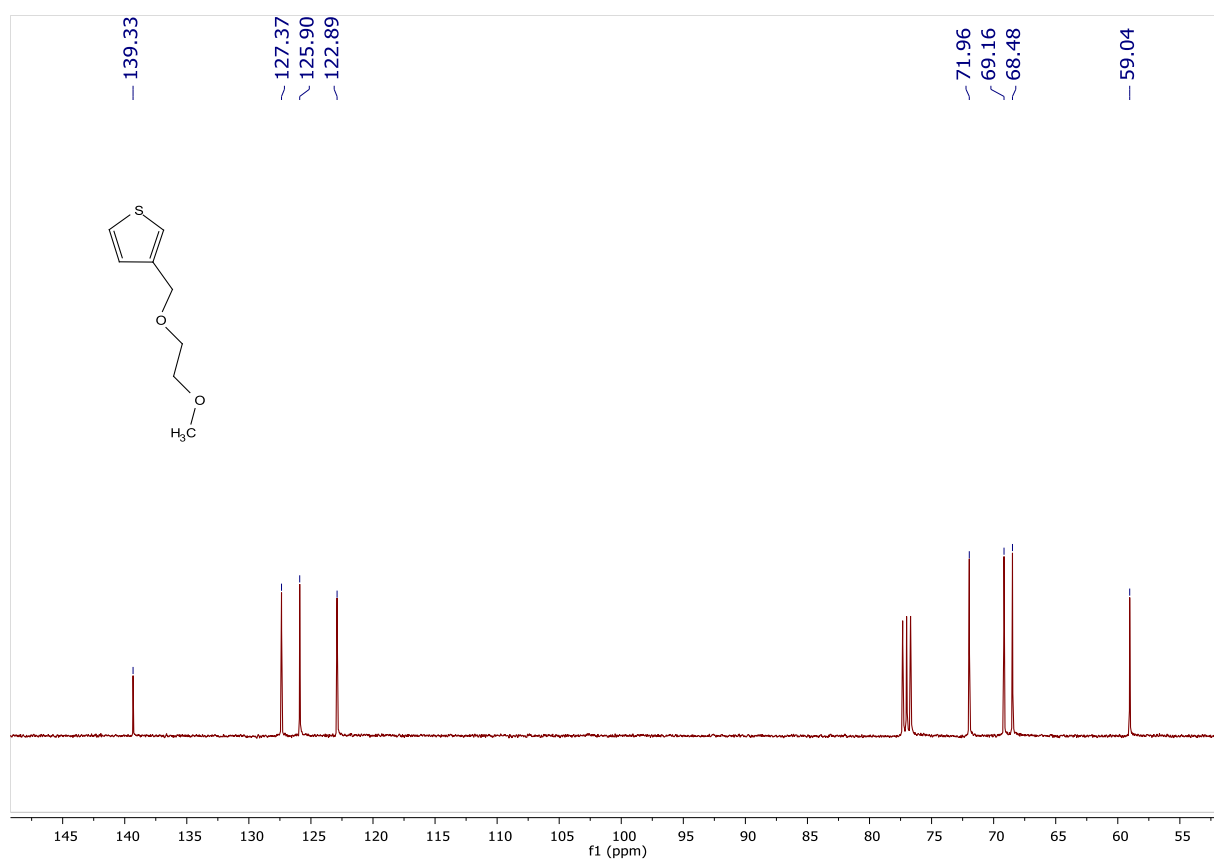
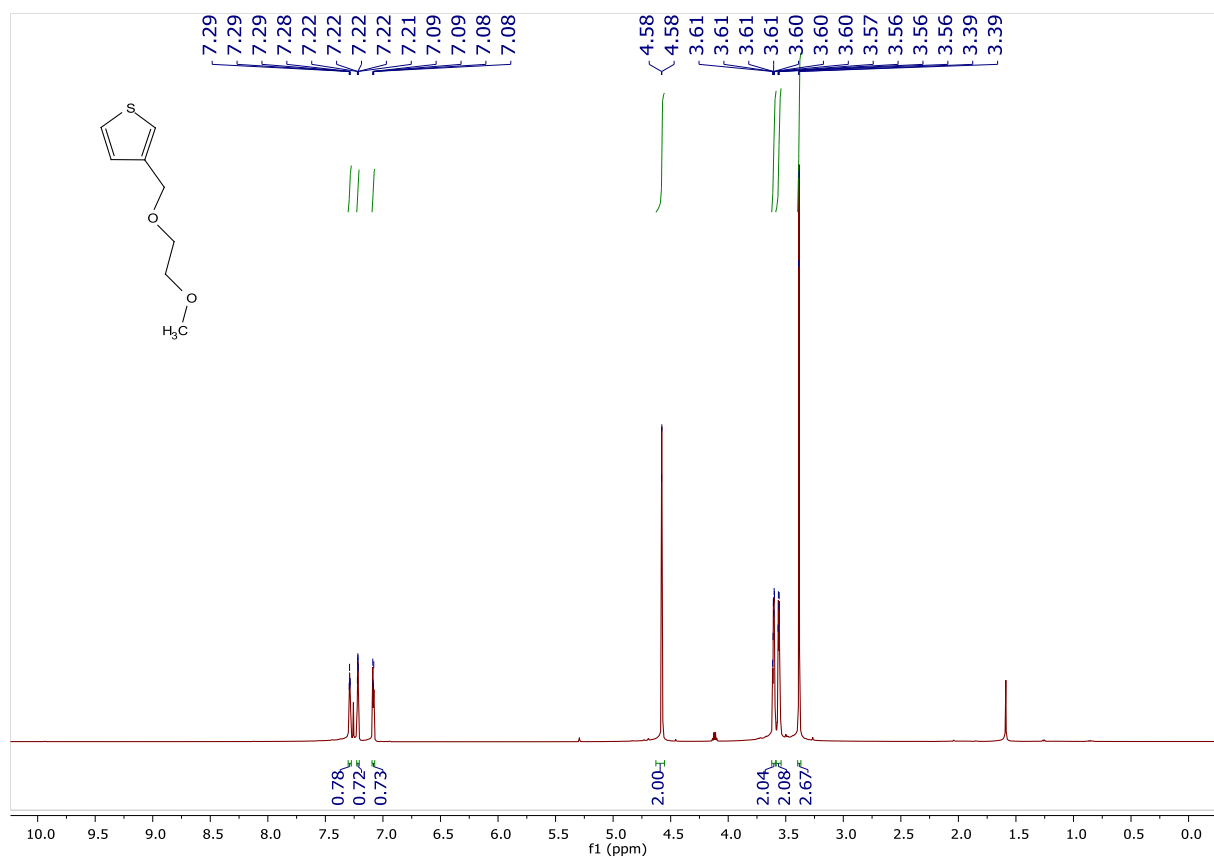
5.9.1.2 2,5-dibromo-3-(4-methoxybutyl)thiophene (2)



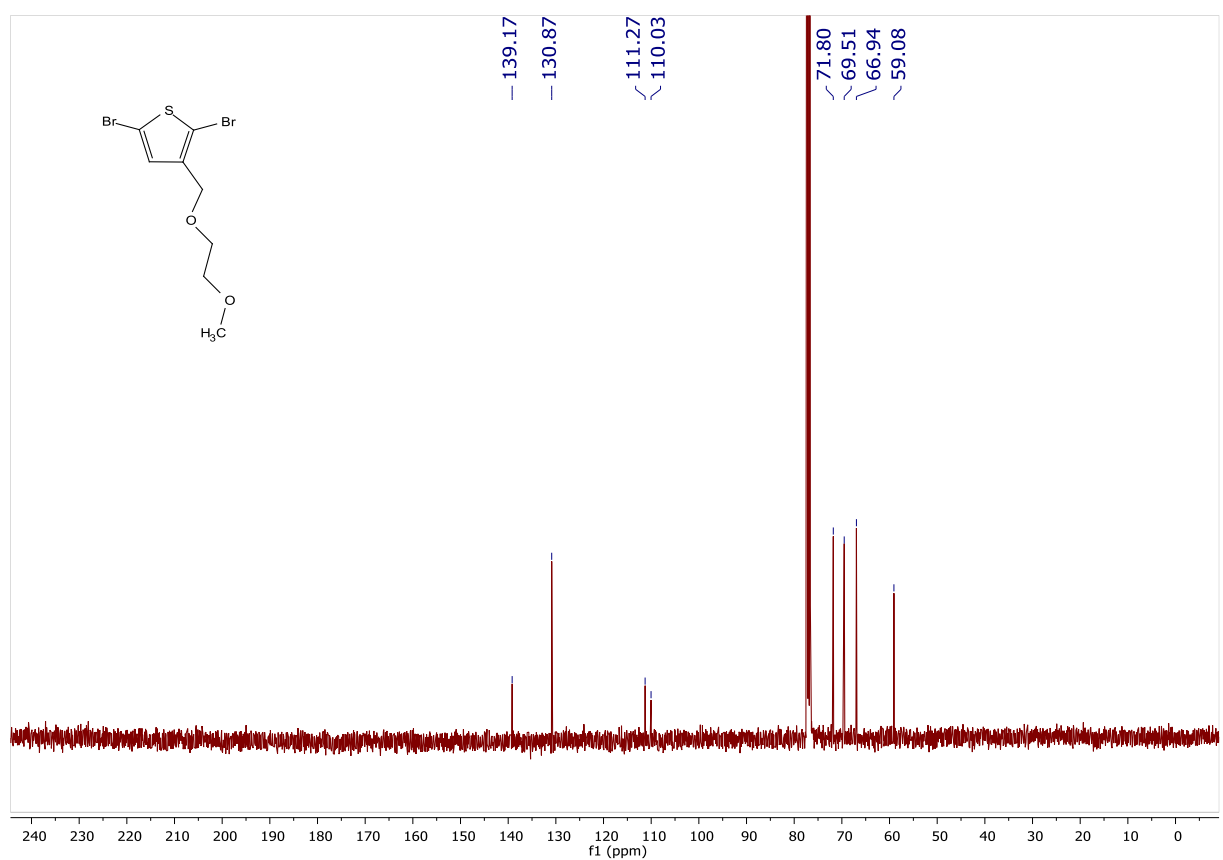
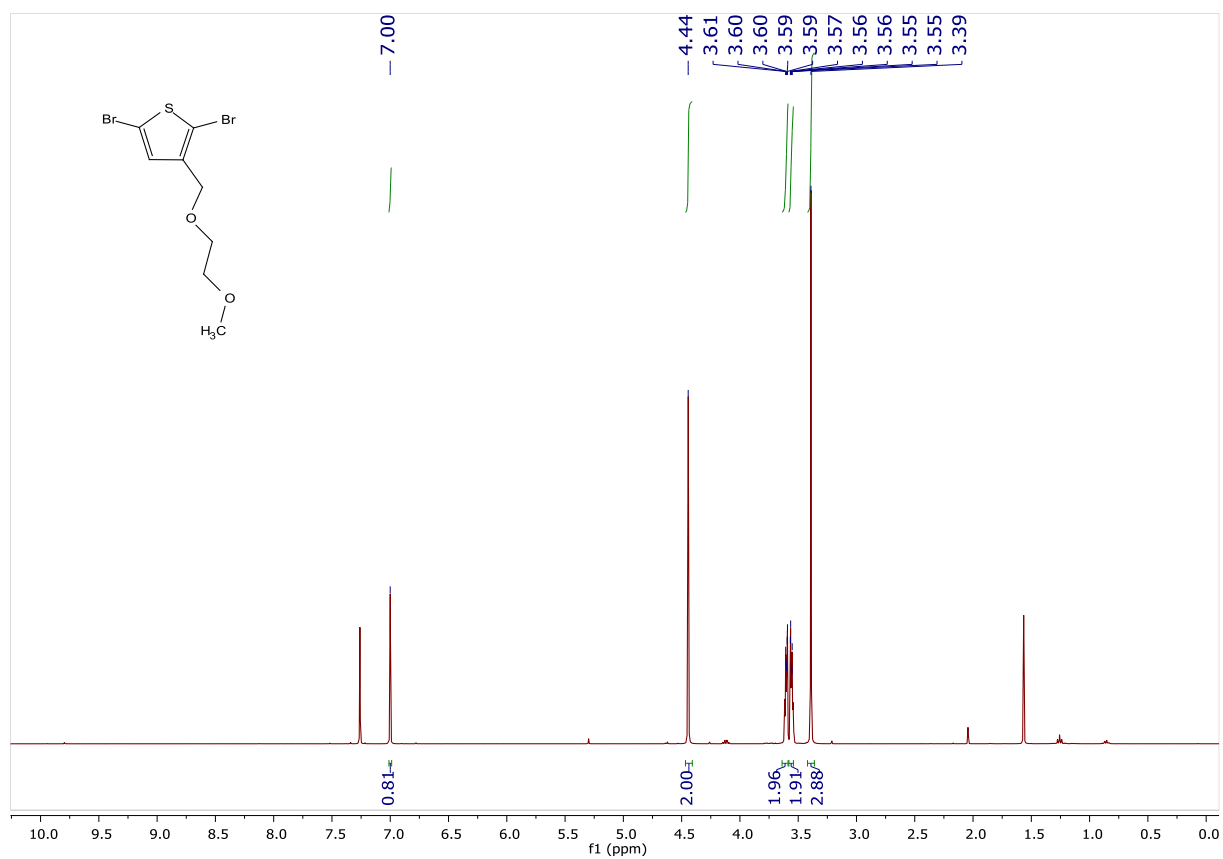
5.9.1.3 Mono-oxygenated P3HT analogue (3)



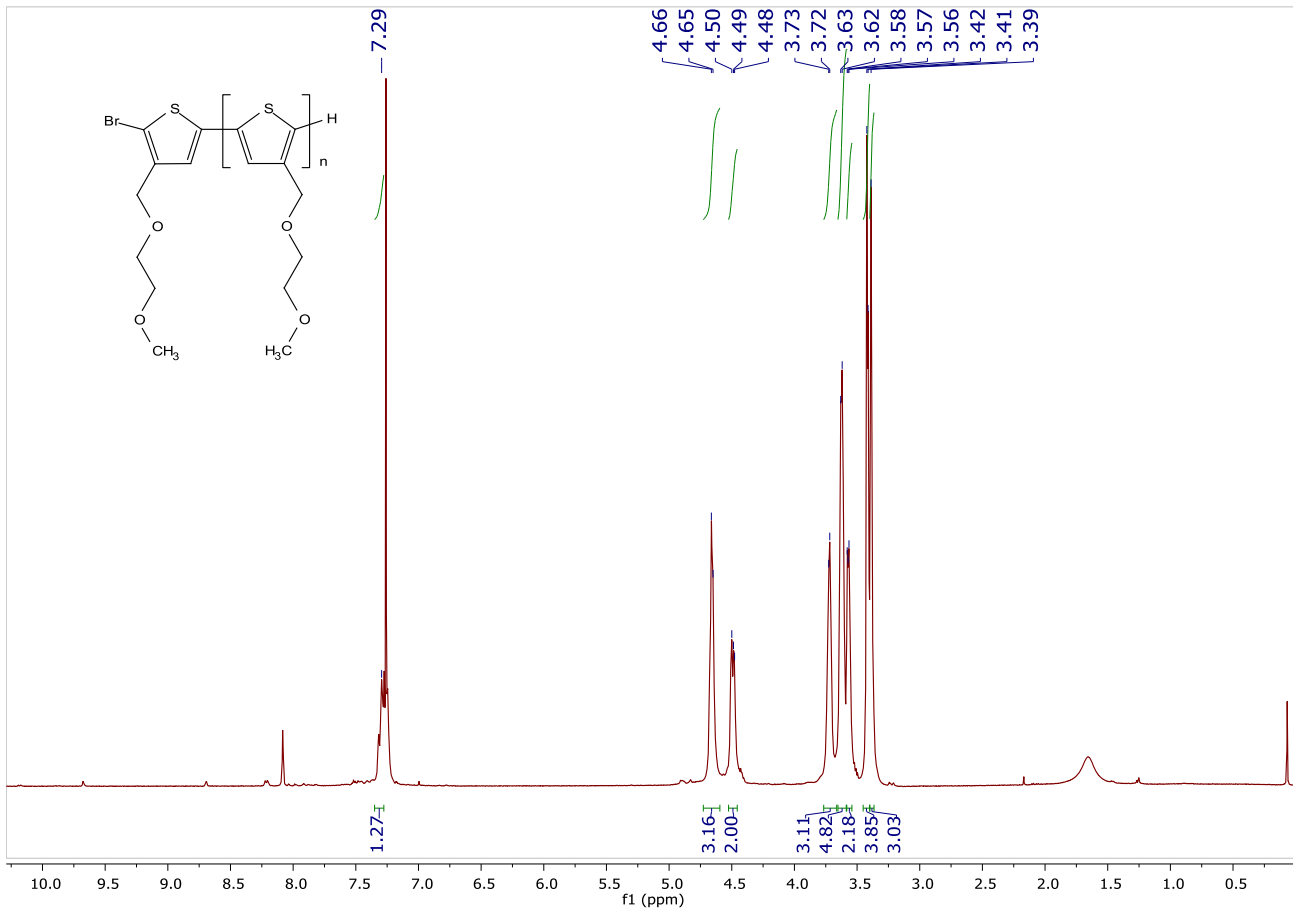
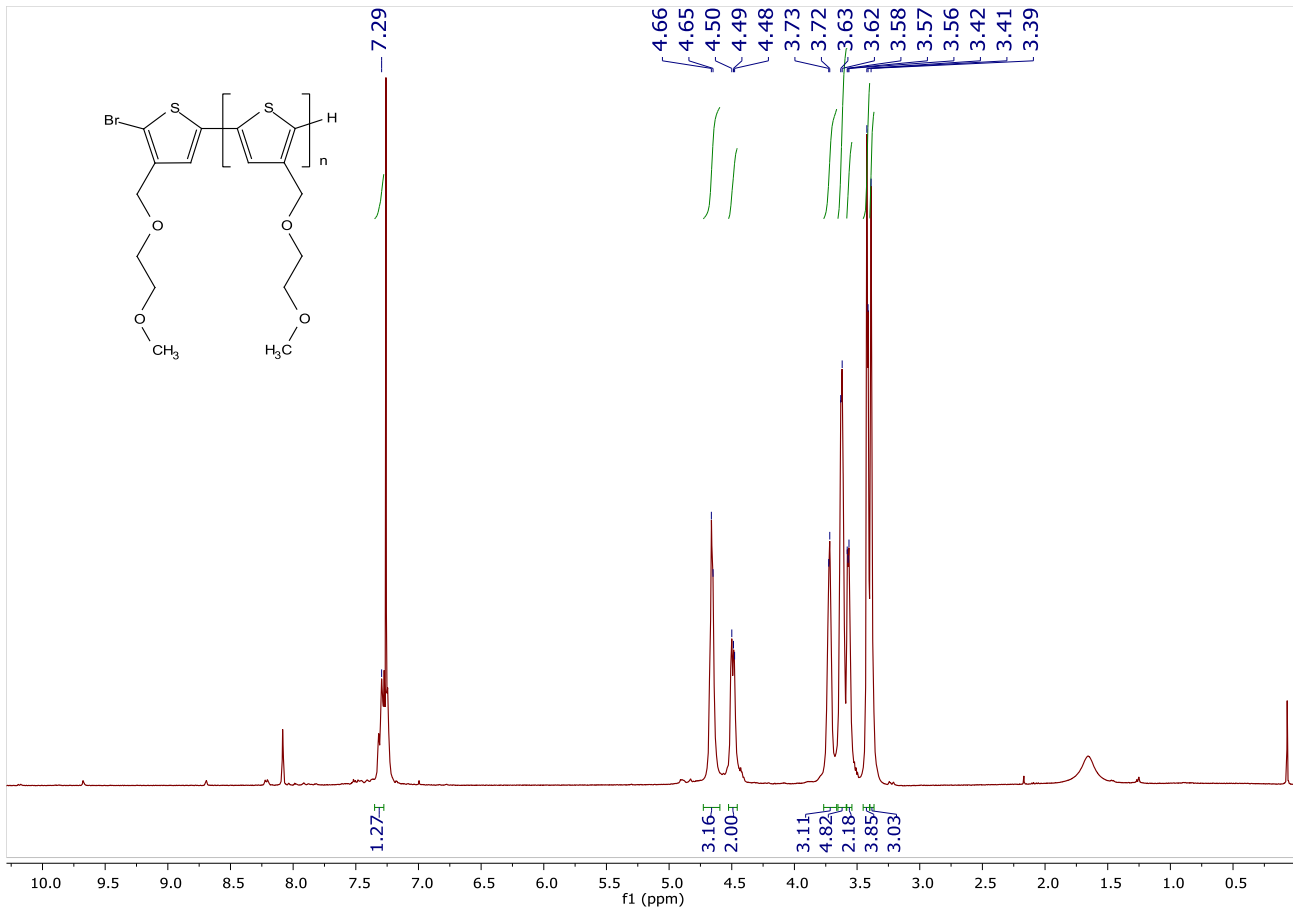
5.9.1.4 3-((2-methoxyethoxy)methyl)thiophene (4)



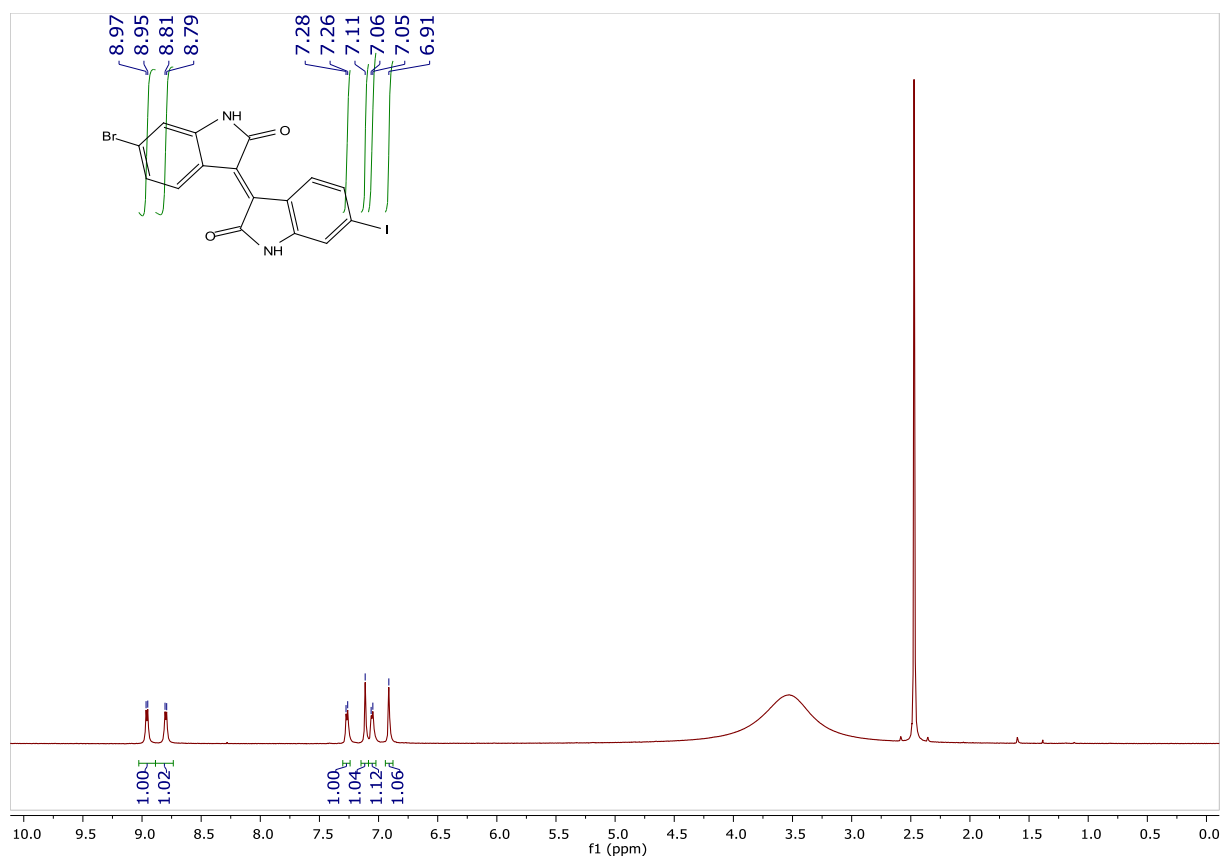
5.9.1.5 2,5-dibromo-3-((2-methoxyethoxy)methyl)thiophene (5)



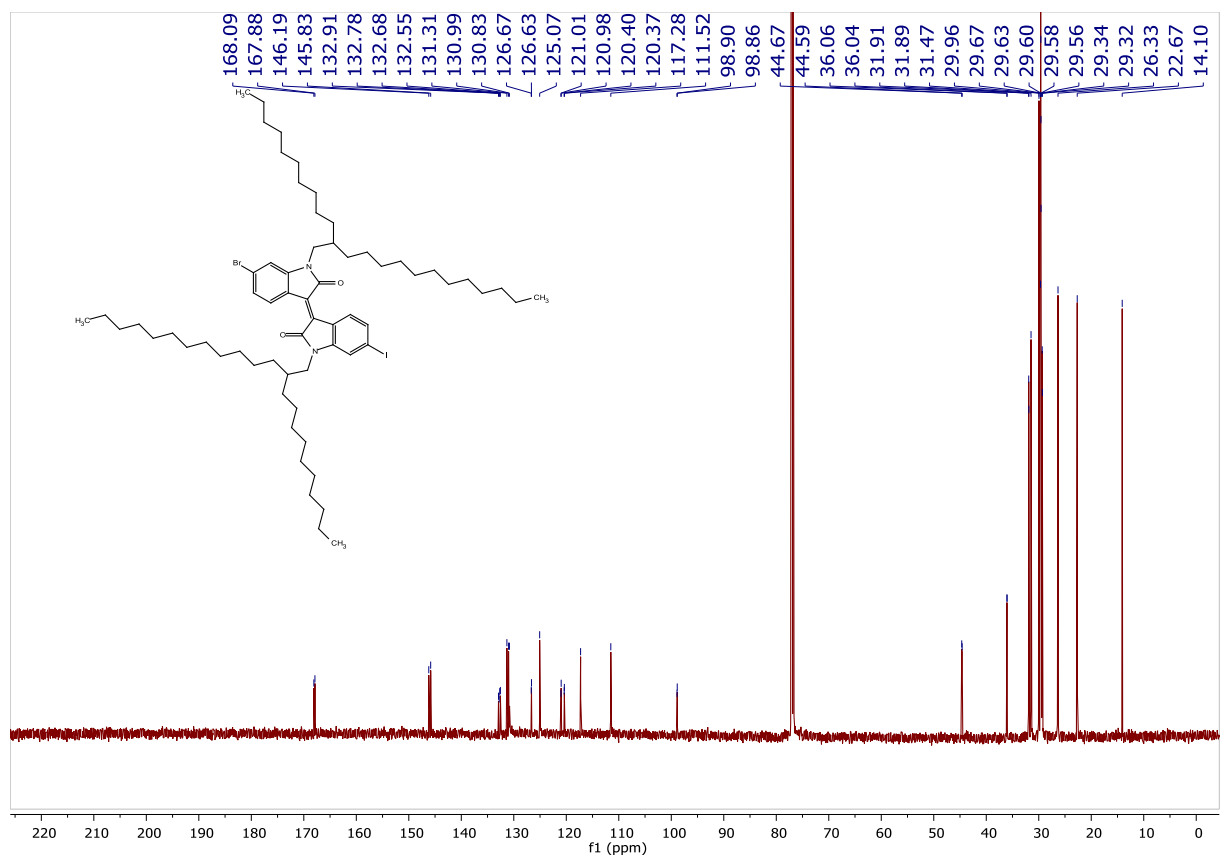
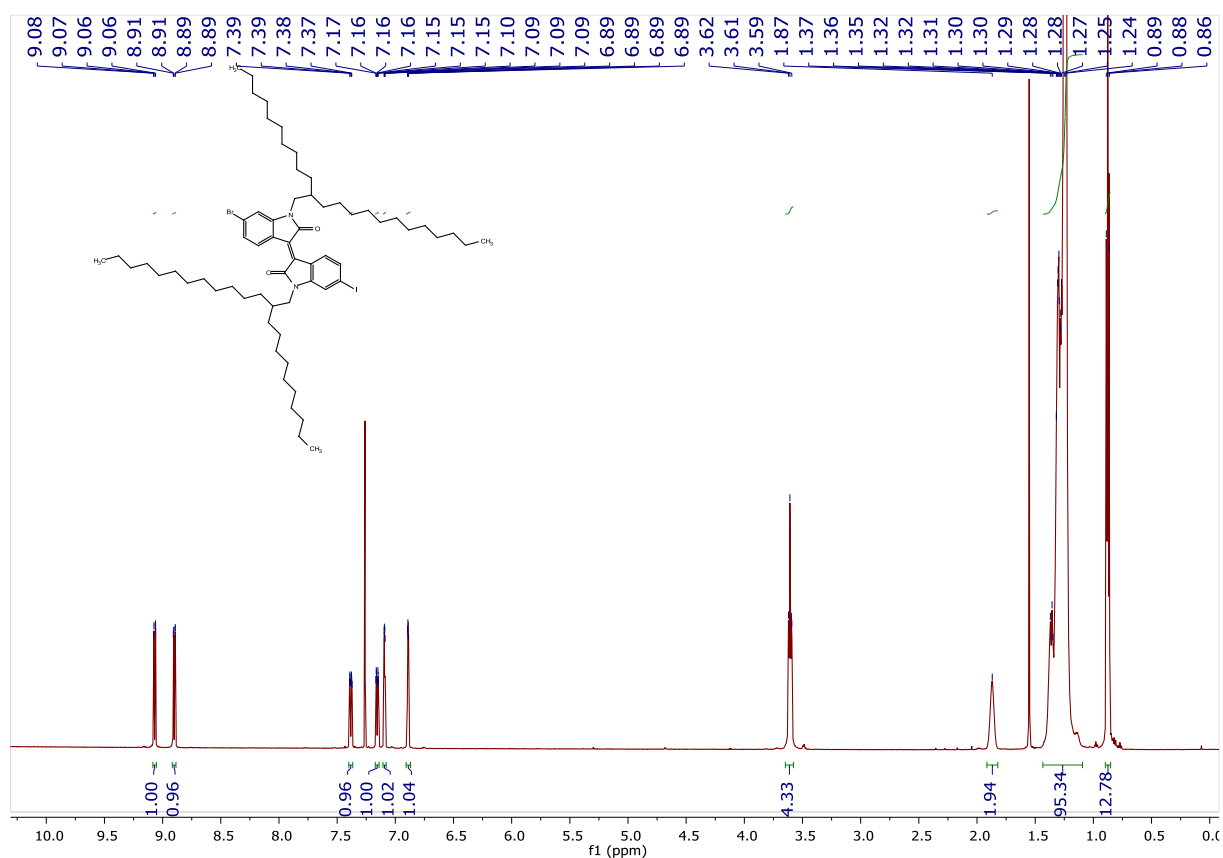
5.9.1.6 Di-oxygenated P3HT analogue (6)



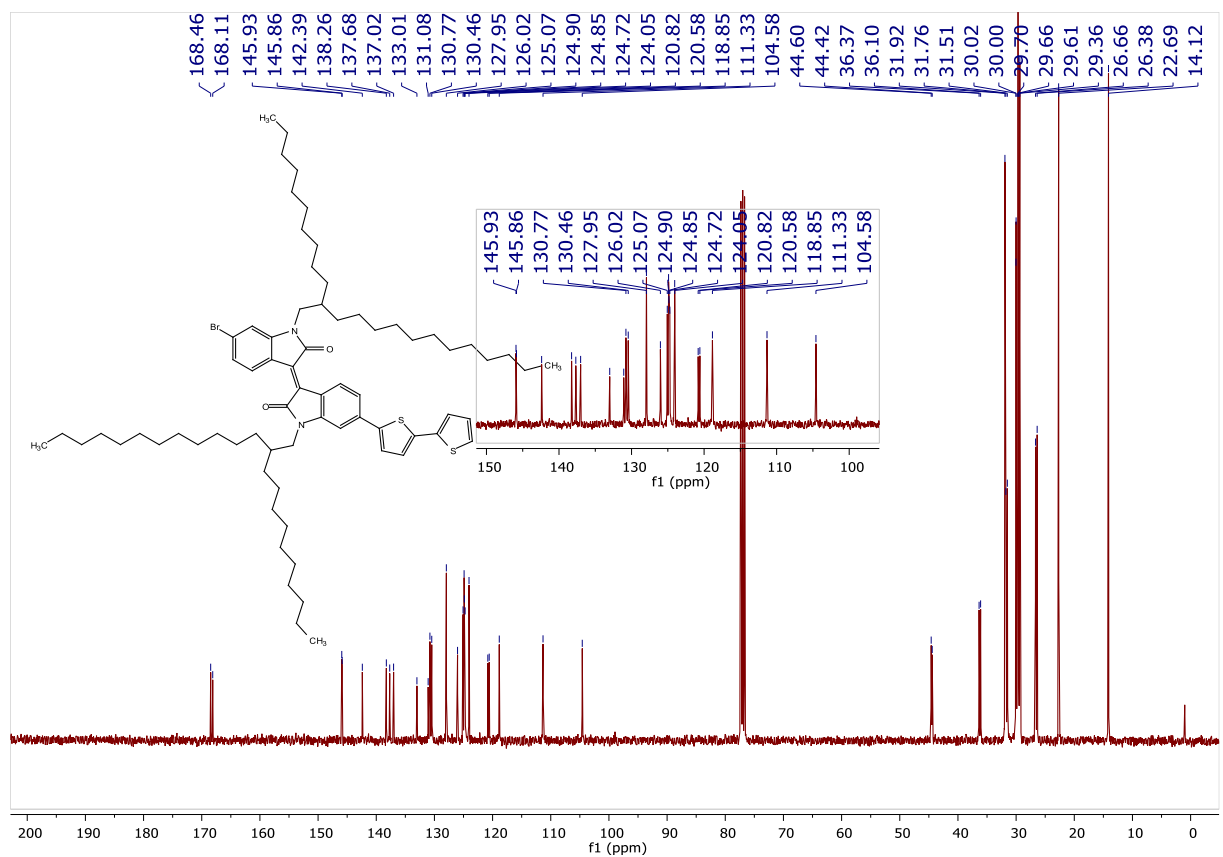
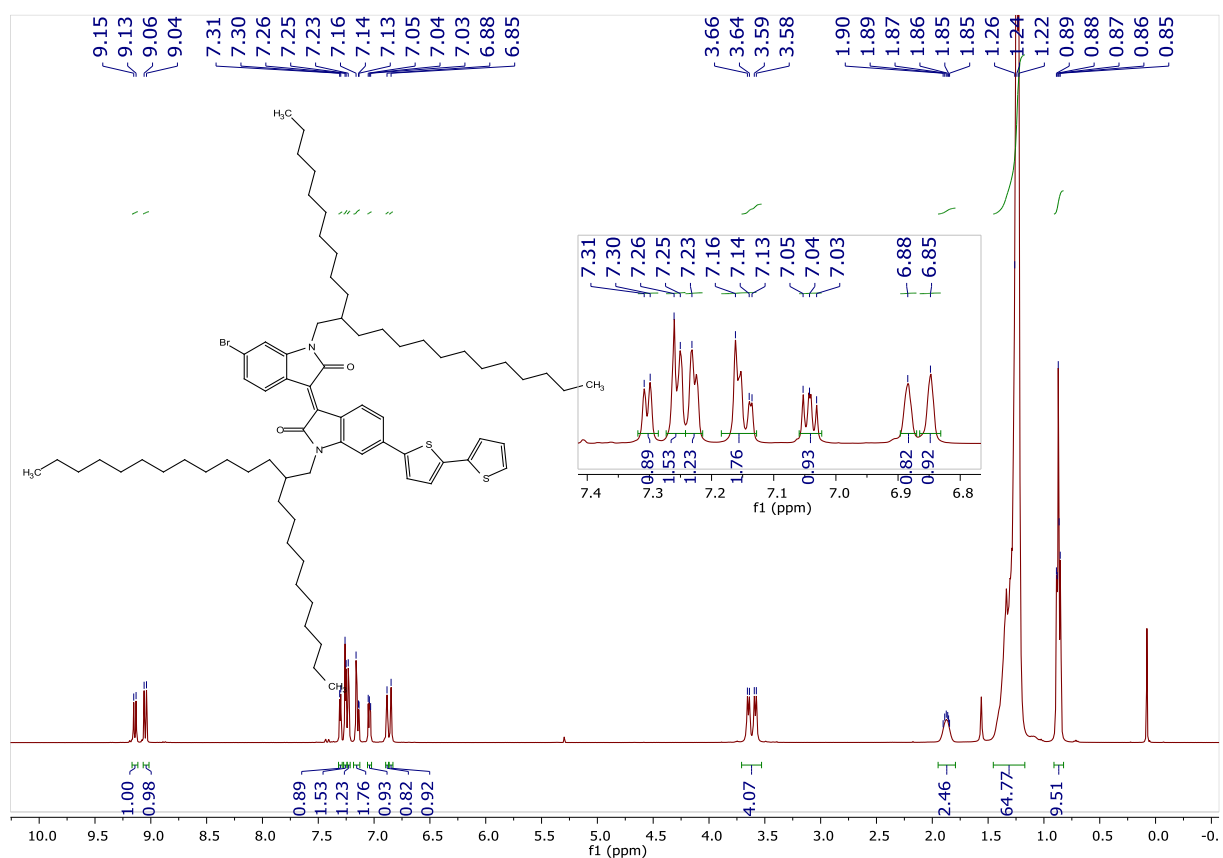
5.9.1.7 (E)-6-bromo-6'-iodo-[3,3'-biindolinylidene]-2,2'-dione (9)



5.9.1.8 (E)-6-bromo-1,1'-bis(2-decyltetradecyl)-6'-iodo-[3,3'-biindolylidene]-2,2'-dione (10)

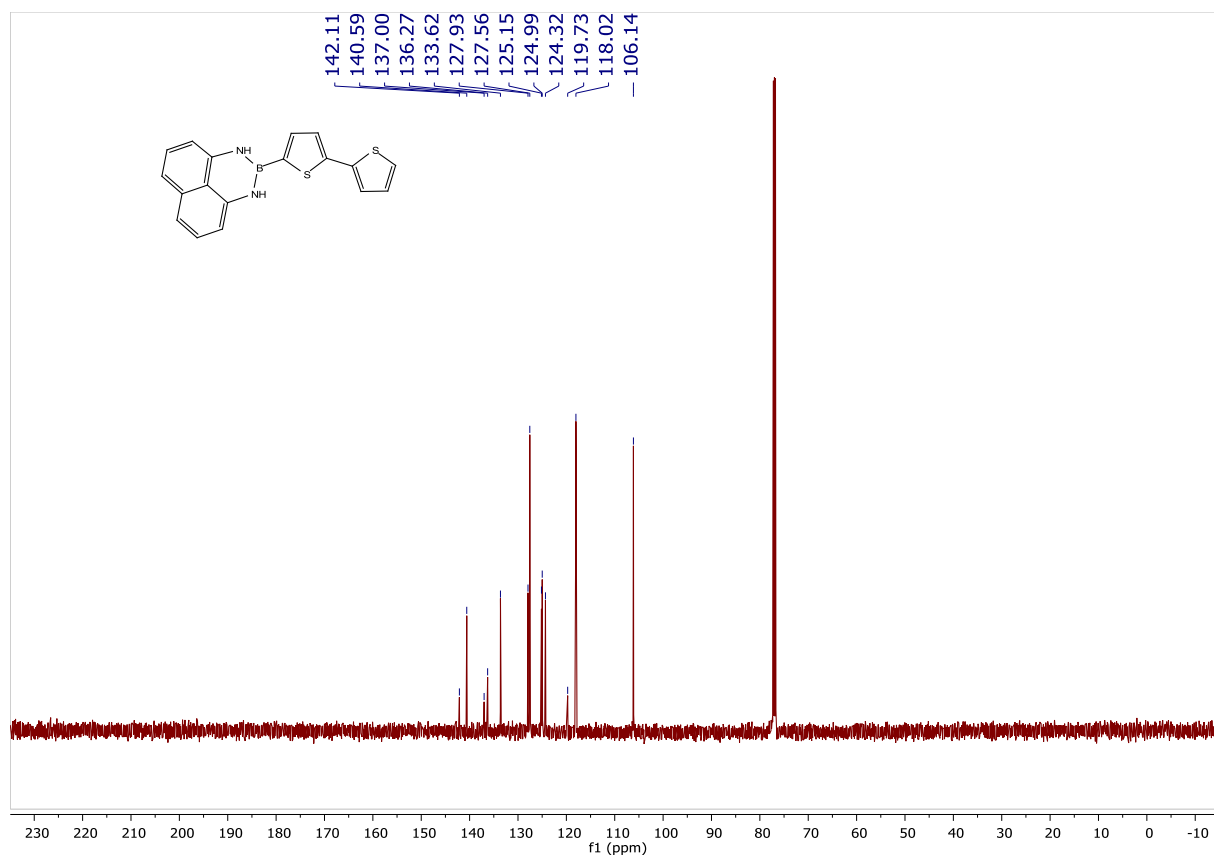
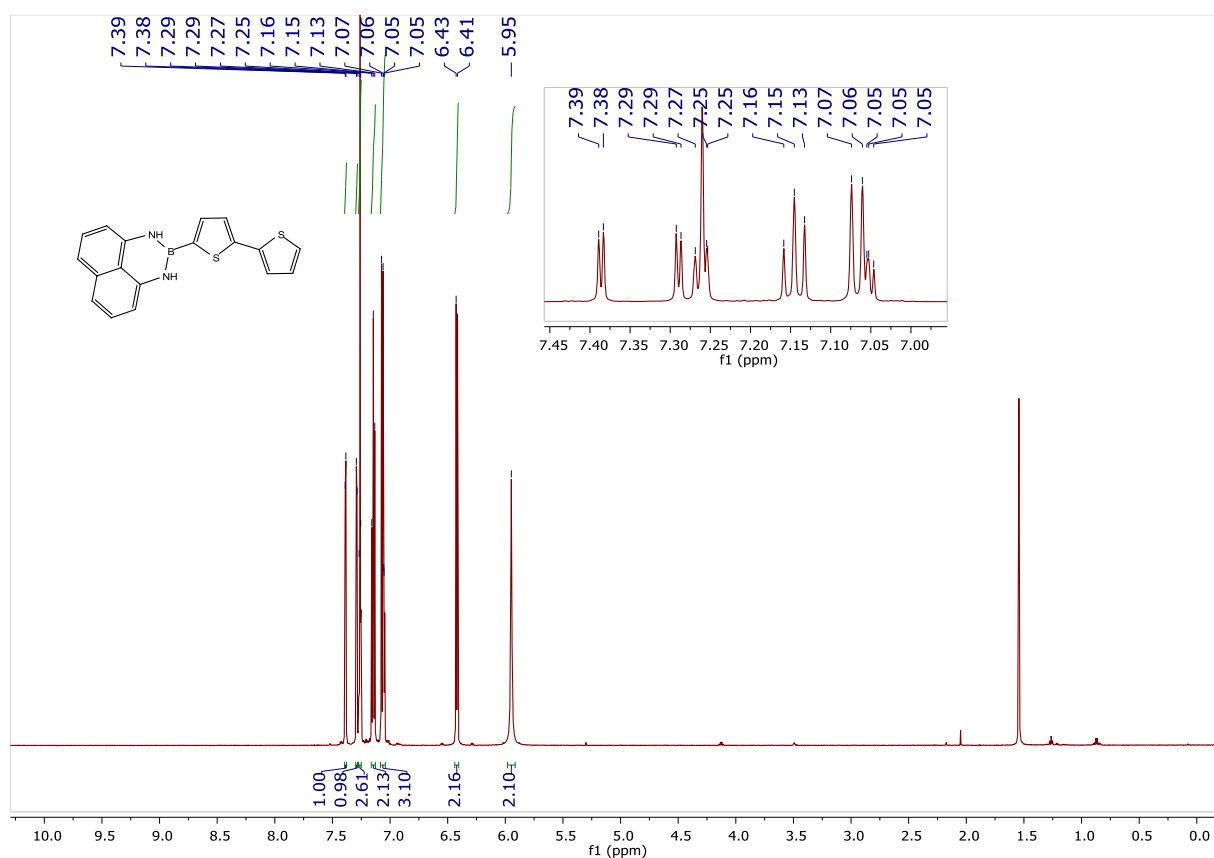


5.9.1.9 (E)-6-([2,2'-bithiophen]-5-yl)-6'-bromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (12)

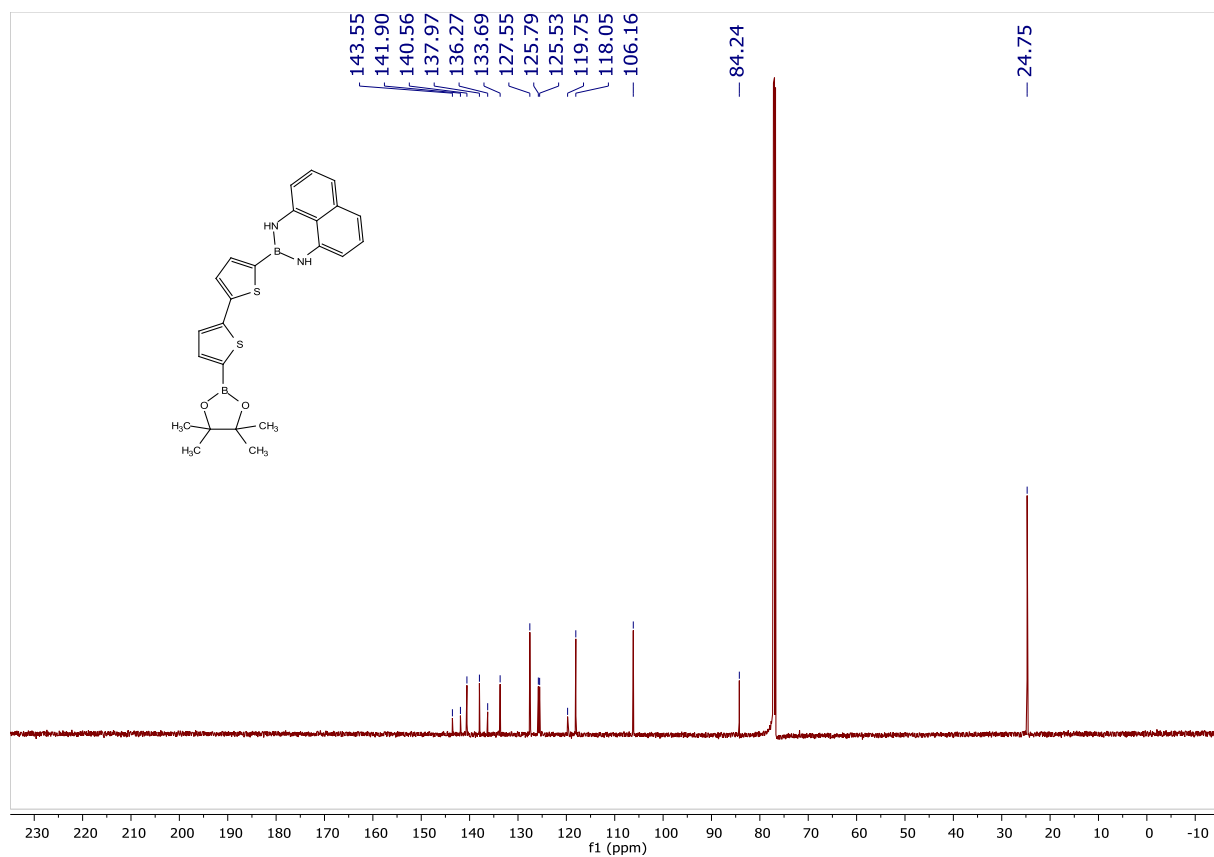
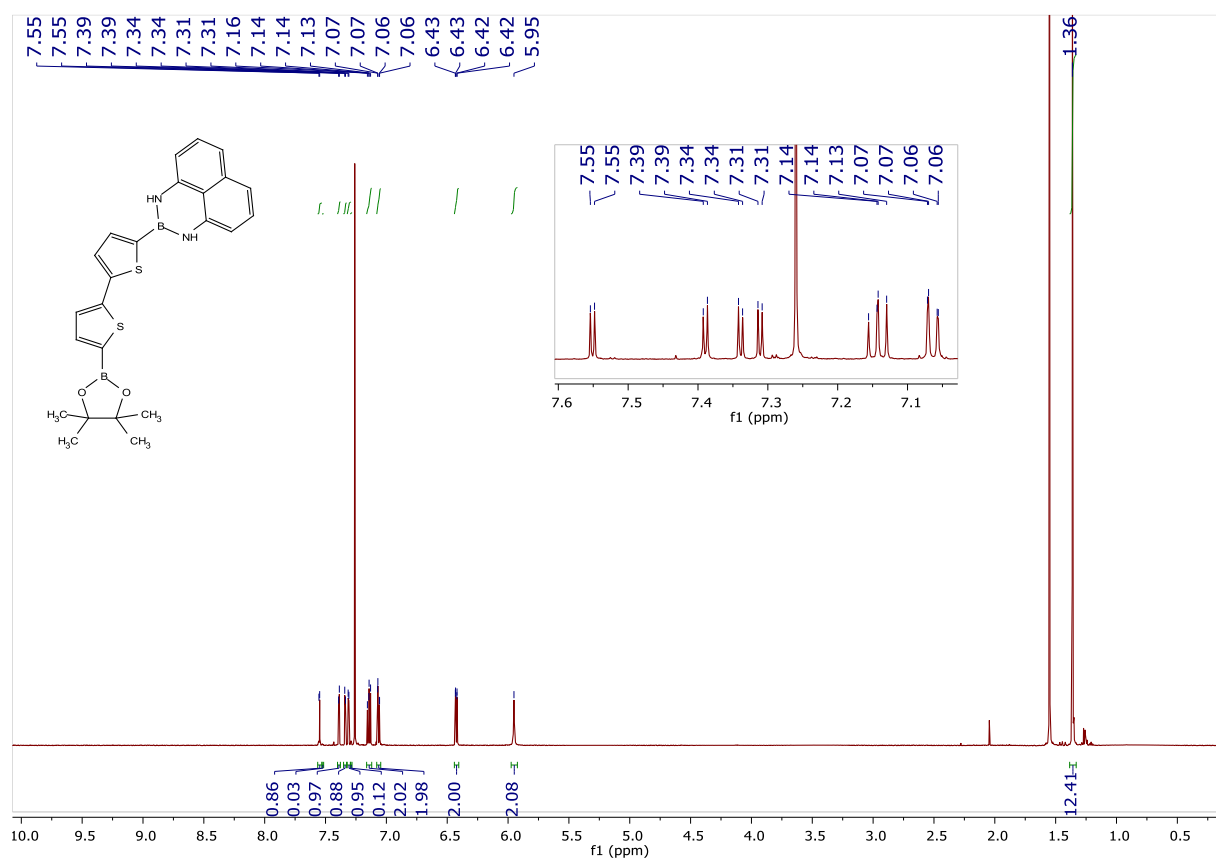


5.9.1.10 2-([2,2'-bithiophen]-5-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine

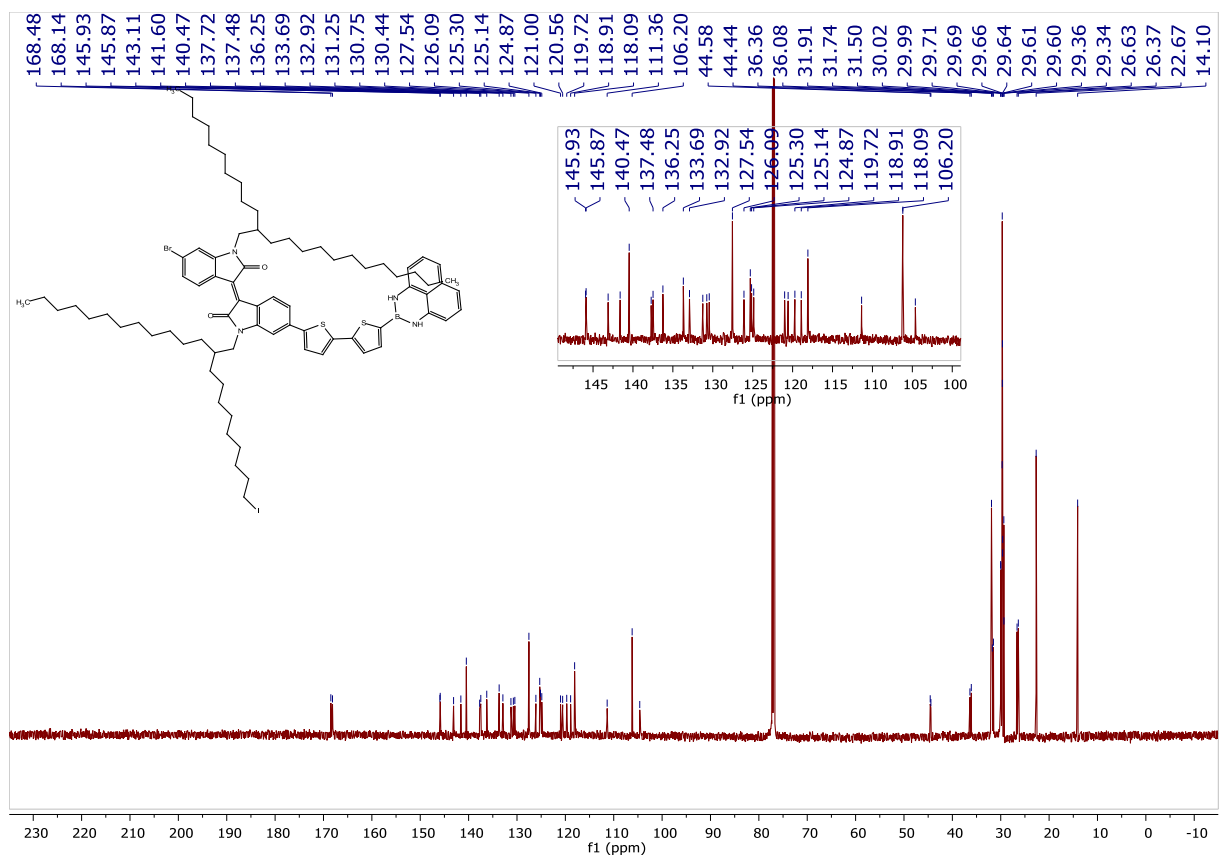
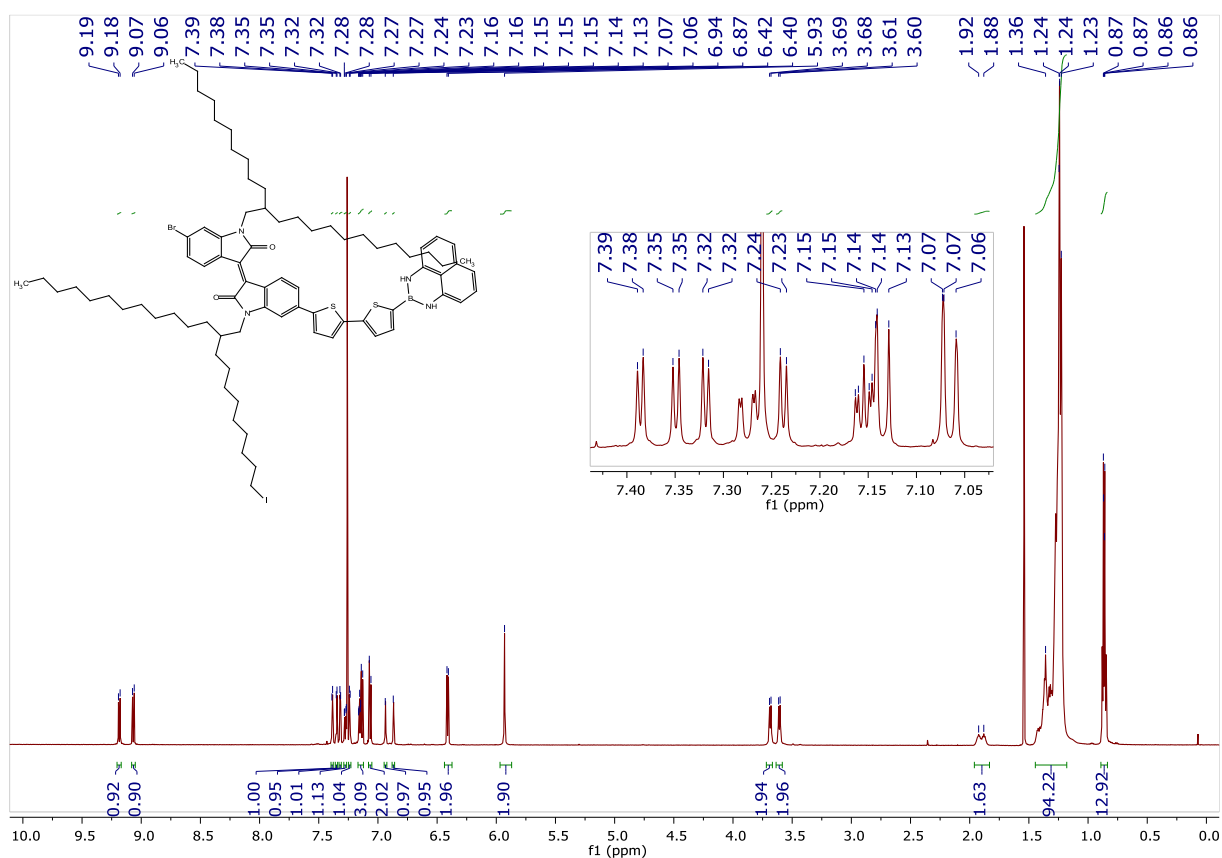
(16)



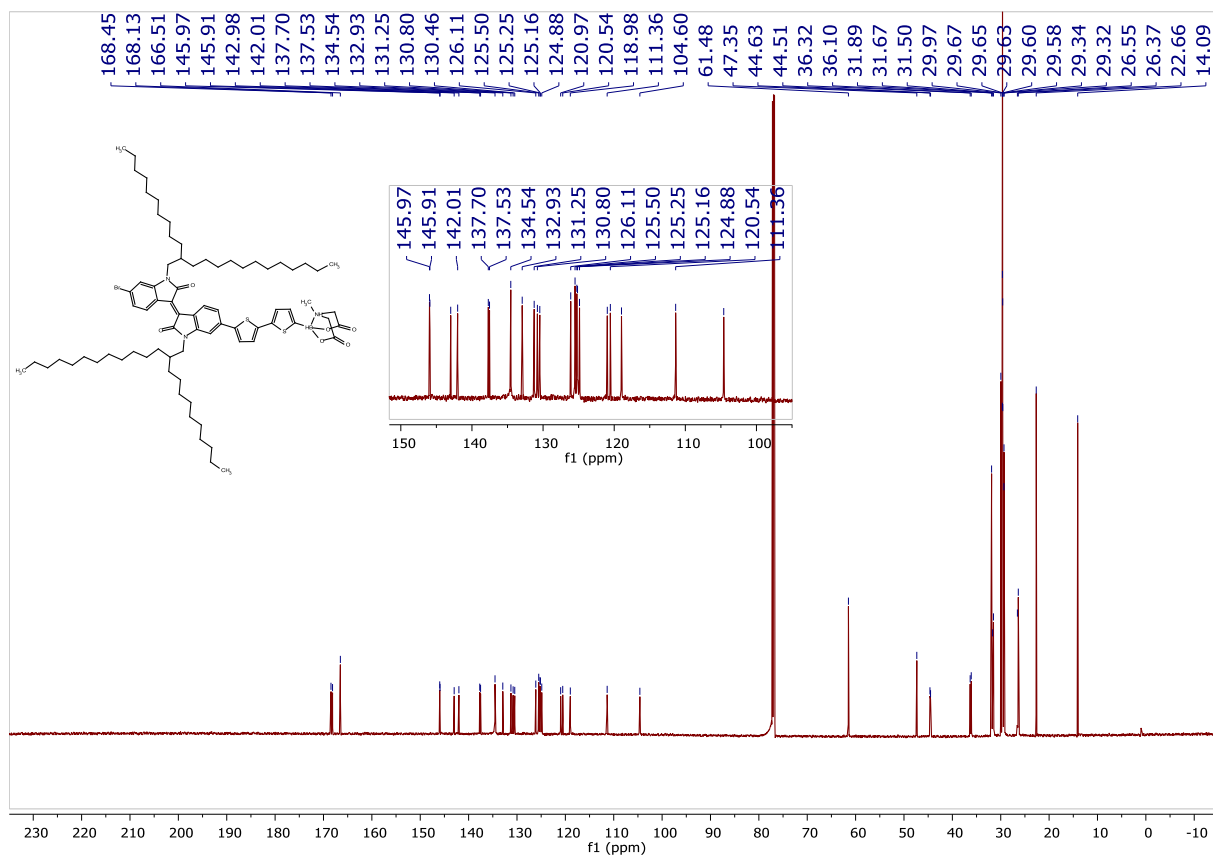
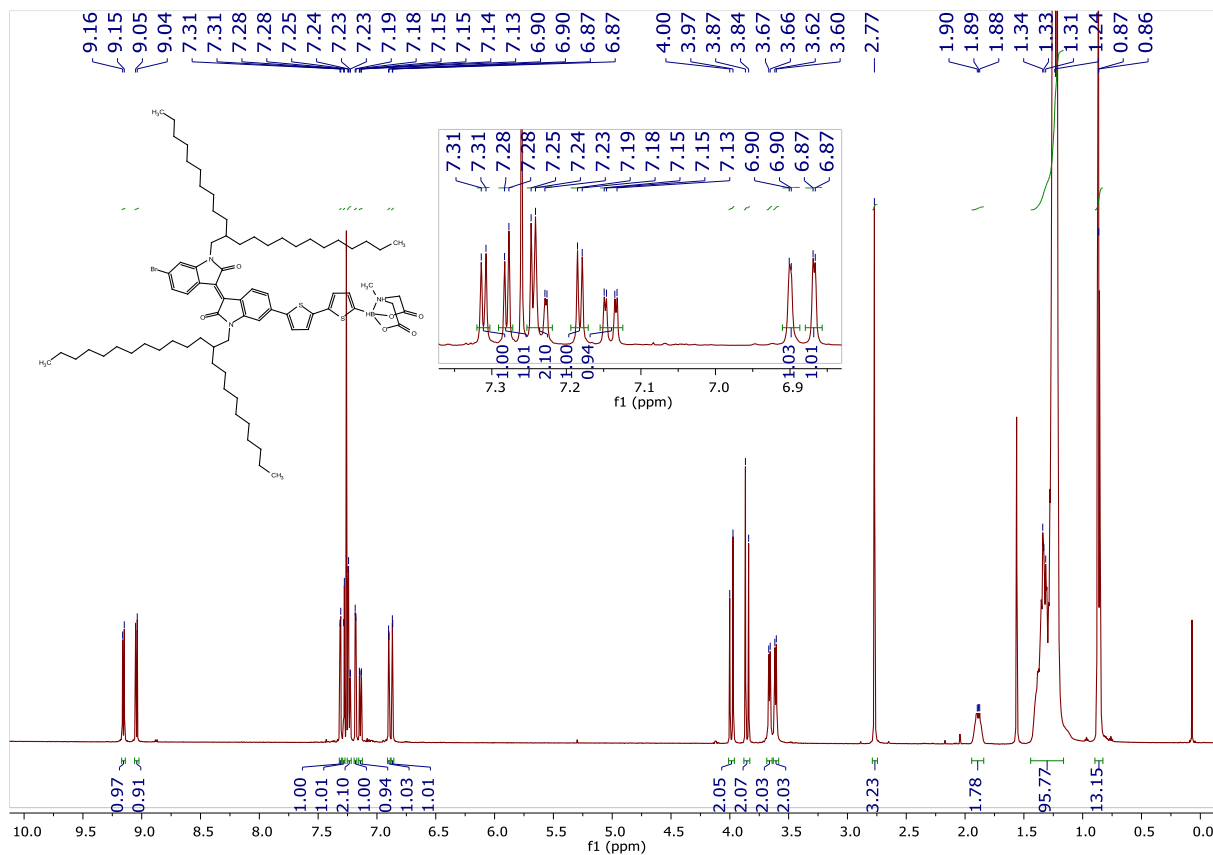
5.9.1.11 2-(5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2'-bithiophen]-5-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (17)



5.9.1.12 (E)-6-(5'-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-[2,2'-bithiophen]-5-yl)-6'-bromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolylidene]-2,2'-dione (18)

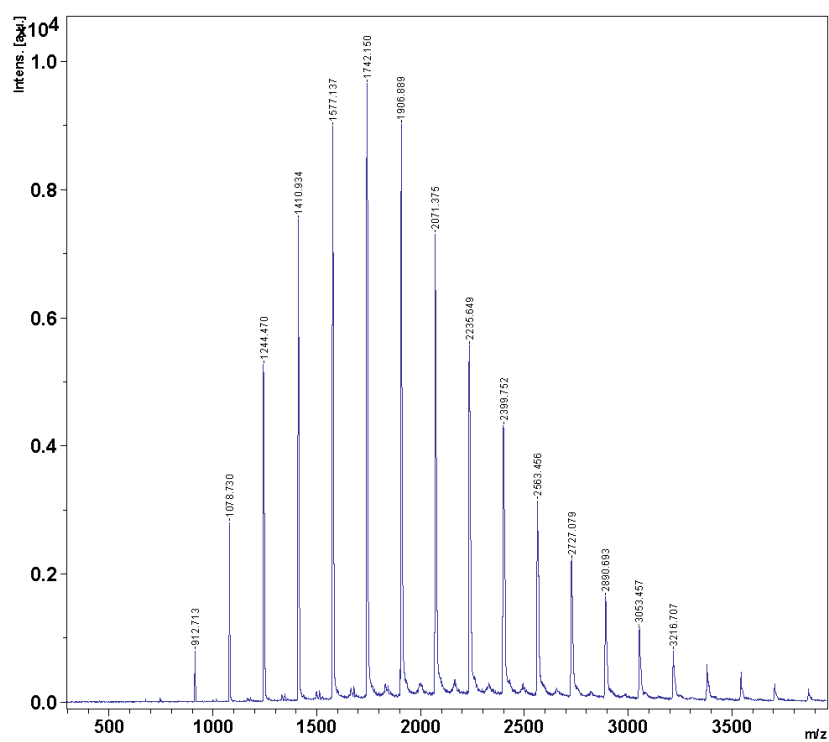


5.9.1.13 i(E)-8-(5'-(6'-bromo-1,1'-bis(2-decyltetradecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)-[2,2'-bithiophen]-5-yl)-4-methyl-2,6-dioxohexahydro-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-ium-8-uide (iT2-B)

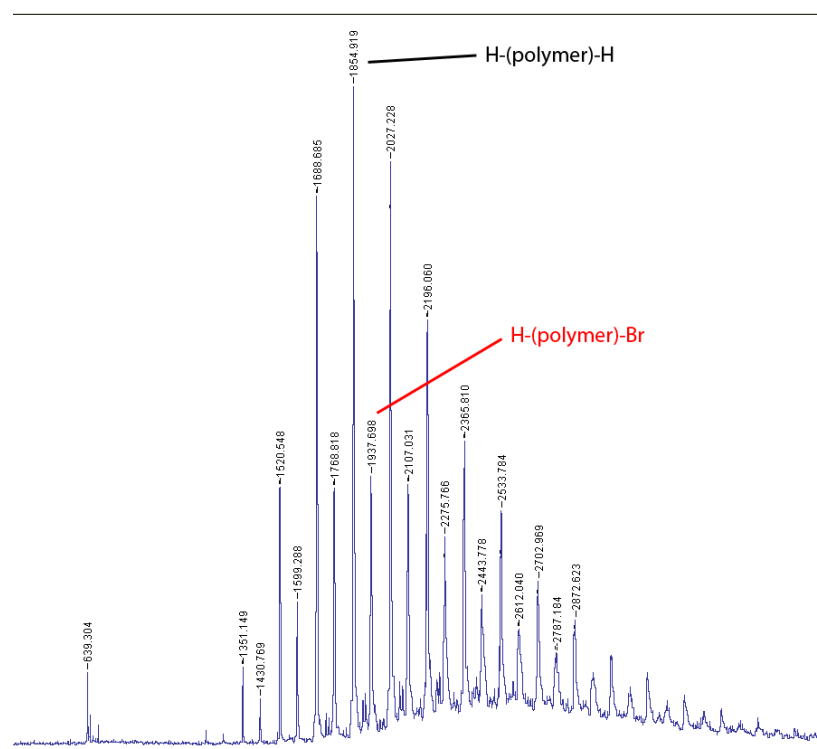


5.9.2 MALDI mass spectra of polymers

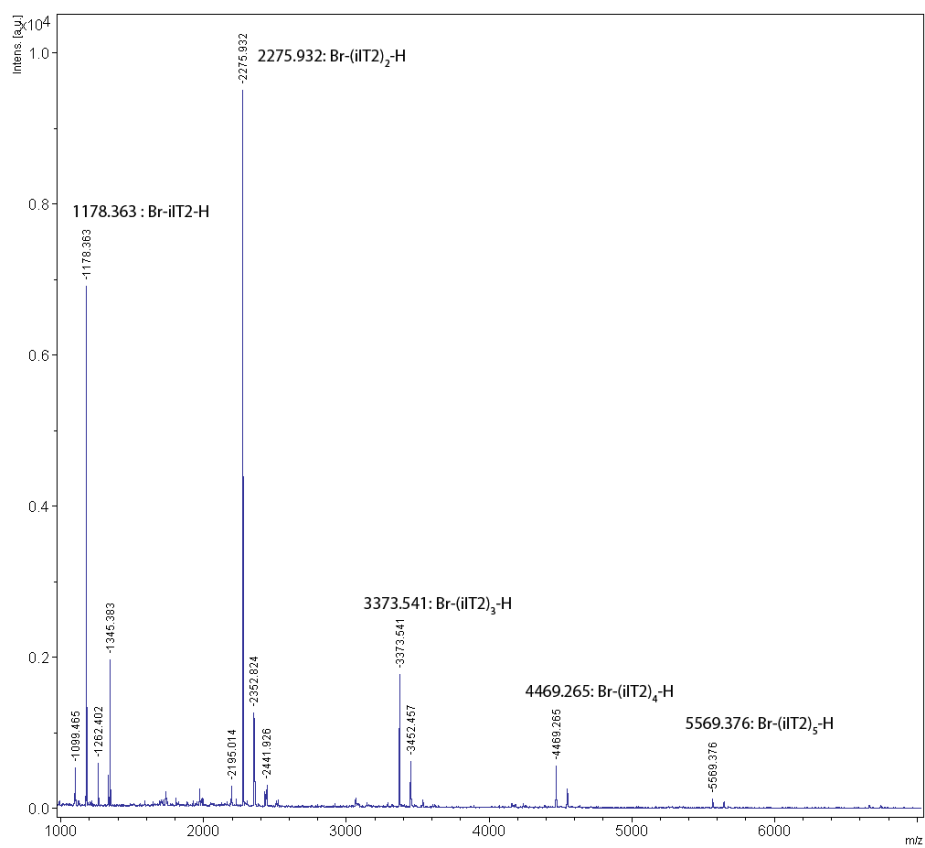
5.9.2.1 Mono-oxygenated P3HT analogue



5.9.2.2 Di-oxygenated P3HT analogue



5.9.2.3 P(il-T2)



Conclusion

All-encompassing design rules towards an active-layer morphology optimized for high efficiencies in organic photovoltaic devices is a long sought-after prize, yet is one that remains out of reach even after two decades of significant research efforts. Rapid progress in this field is complicated by a) the constantly-increasing variety of chromophores being designed for photovoltaic light-harvesting purposes, b) the large number of co-dependant, non-intuitive variables involved in chromophore deposition and film formation and c) the complex interplay between morphological features and the charge generation/harvesting processes that govern photovoltaic efficiencies. Advancement is instead primarily carried out through structure-property studies on high-performing chromophores, where a particular aspect of the chemical structure of active-layer molecular chromophores is systematically altered and then rigorously probed in order to gain insight into the impacts on thin-film morphology.

The overall objective for this thesis was to gain a greater morphological understanding of several molecular chromophores of great interest to the field, and does so through several structure-property studies revolving around alkyl sidechain engineering. Sidechains do not directly contribute to the electronic properties of these chromophores, however as their influence on molecular thin-film crystallinity -and hence photovoltaic performance- has been repeatedly demonstrated in the literature, these structural elements represent a promising route for morphological control. Here two main classes of p-type chromophores were synthesized and examined, with studies on the π -bridge sidechain substituents and benzodithiophene core substituents of benzodithiophene terthiophene rhodamine (**BTR**)-derivative chromophores detailed in Chapters 2 and 3 respectively, and studies on alkyl sidechain positioning and length performed on oligothiophene chromophores detailed in Chapter 4. The impacts of the sidechain engineering efforts on film morphology were interrogated primarily through Grazing-incidence wide angle X-ray scattering (GIWAXS) studies, and supplemented by photovoltaic device fabrication/characterization, spectroscopic studies and single-crystal structures. Chapter 5 details an alternative route investigated to achieve morphological control in OPV active layers, which proceeds through the use of amphiphilic block copolymer materials comprised of p- and n-type homopolymers. Here the use of hydrophilic sidechains on a p-type homopolymer was investigated, as well as a novel synthetic route to achieve fine end-group control for a hydrophobic n-type isoindigo polymer through the use of desymmetrized intermediates.

6.1 Chapter 2 - BTR π -bridge sidechain modifications

The work in this chapter describes the design and synthesis of two analogues of the high-performing p-type molecular material **BTR**, where the terthiophene π -bridge alkyl sidechain lengths were modified to four and eight methylene units (**BT₄R** and **BT₈R**, respectively) to investigate their impact on thin-film morphology and

photovoltaic efficiencies (PCEs). A modular synthetic protocol was developed for the catenation of 3-alkylthiophene building blocks and the subsequent assembly of **BTR** analogues, with this being shown to facilitate the synthesis of the final chromophore on a multigram scale. Integration of these two novel materials into OPV devices revealed a stark difference in performance -with **BT₄R** possessing a comparable efficiency to that of **BTR** (9%) while **BT₈R** exhibited significantly decreased PCEs of 5%- suggesting that the solubilizing alkyl chains did indeed play a significant role in solar cell efficiencies.

Further investigation of this relationship was carried out through X-ray scattering studies of the active layer morphologies of **BT₄R**, **BTR** and **BT₈R** intermixed with PC₇₁BM fullerenes, where it quickly became clear that **BT₄R** and **BTR** possessed a) significantly lower degrees of lamellar crystallization and b) smaller π - π stacking distances relative to **BT₈R**. These observations suggest that the longer sidechains of **BT₈R** result in both larger crystalline domains within the thin-film bulk through enhanced van der Waal interactions and interdigitation, as well as reduced π - π interactions, with this ultimately reducing exciton harvesting efficiencies. An overall analysis of this series suggests that hexyl-length sidechains for **BTR**-type chromophores are ideal and offer an optimal degree of crystallinity to balance exciton separation and charge transport.

6.2 Chapter 3 - BTR core substituents

Following on from the insights gained into the structure-property relationships of the **BTR** chromophore in the previous chapter, this chapter details the investigations into alteration of the benzodithiophene core substituent and its impact on morphology and photovoltaic performance. Here different core substituents of varying steric bulk and solubilities were designed, resulting in four novel analogues, namely **BTR-TIPS** (triisopropylsilylethynyl substituent), **BTR-TE** (2-ethylhexylthio substituent), **BTR-H** (2-hexyl substituent) and **BTR-EH** (2-(2-ethylhexyl)-thienyl substituent). Integration of these four materials into photovoltaic devices resulted in efficiencies ranging from 4-9%. Initial GIWAXS studies of p-type/n-type blend films suggested an intriguing relationship linking the molecular structure of our chromophores to their bulk properties and device performance. The higher-performing materials (those with <9% efficiencies, i.e. **BTR** and **BTR-TE**) were found to possess more face-on π -stacking behaviours relative to the lower-performing materials (those with <9% efficiencies), which were found to possess edge-on π -stacking.

Further analysis of these chromophores with depth-dependant GIWAXS studies -a relatively facile but underutilized technique- to probe the vertical structures of the films revealed that **BTR** and **BTR-TE** were comprised of a spectrum of crystallite orientations, with the primarily edge-on crystallites located at the air/active layer interface transitioning into face-on crystallites deeper into the film bulk. The edge-on nature of the poorer-performing analogues were found to remain constant regardless of film depth. Consideration of these observations in conjunction with the solubilities of the **BTR** analogues -as conferred by the core substituents- ultimately suggested the origin of this particular morphological behaviour, namely, that the higher-performing analogues were those that also possessed high solubilities in the deposition solvent, which

in turn lead to slower crystallization during the spin-coating deposition process allowing face-on crystallites to form. These findings illustrate the importance of chromophore solubility during thin-film deposition towards achieving optimal OPV active-layer morphologies.

6.3 Chapter 4 - Oligothiophene sidechain orientation

Considering the proven success in reorienting π -bridge alkyl sidechains for enhanced intermolecular interactions on the **BTR** substrate, it was theorized that this sidechain engineering technique could also benefit other high-performing molecular substrates. This theory forms the basis of the work in this chapter, where a series of acceptor-donor-acceptor penta- (**5T**) and hexathiophenes (**6T**) with inwards-facing sidechains known to the literature were modified to feature regioregular, outwards-facing sidechains instead. This sidechain reorientation was performed on oligothiophene substrates featuring a) different endgroup acceptors (malononitrile, **MN**; hexyl rhodanine, **HR**; and dicyanonitrile hexyl rhodanine, **CHR**) to increase the scope of this study and b) different sidechain lengths (hexyl, **T⁶**; octyl, **T⁸**) in order to optimally sensitise these chromophores to thin-film annealing processes, ultimately resulting in twelve oligothiophene analogues.

Photovoltaic efficiencies reveal a curious end-group dependence for the optimal oligothiophene conjugation length, with the relatively similar **HR** and **CHR** acceptor moieties exhibiting the highest PCEs of 7% and 8% when coupled to **5T** and **6T** substrates respectively. Generally speaking however, these chromophores possess efficiencies below that of their counterparts from the literature, with the highly structured p-type domains observed from GIWAXS studies suggesting that the outwards-oriented sidechains have instead conferred a high degree of crystallinity that is unfavourable for efficient OPV processes. These X-ray scattering studies do reveal several key structure-property relationships, namely an increased crystallinities for the octyl-functionalized analogues relative to the hexyl-functionalized analogues, more complex crystalline structures for the centrosymmetric **6T** analogues relative to the axisymmetric **5T** analogues, and a predisposition for the dicyanovinylene moiety (**MN** and **CHR** analogues) to form thermally stable structures strongly aligned along the conjugated backbone.

6.4 Chapter 5 - Amphiphilic block copolymers

Though keeping with the overall goal of achieving fine control over OPV active-layer morphologies, the work in Chapter 5 instead presents an alternative route towards this by setting the foundation for an amphiphilic diblock copolymer, where the amphiphilic nature of covalently-bound p-type and n-type homopolymers were to drive phase-separation into self-assembled active-layer domains. Here sidechain engineering techniques were used to successfully install hydrophilic glycol sidechains onto a polythiophene p-type substrate. This was followed by the synthesis of a hydrophobic n-type isoindigo polymer, with a particular focus on establishing polymer end-group control to minimize polymeric contaminants being carried forward to the target block copolymer. This culminated the establishment of an asymmetrization protocol utilizing

orthogonal boron protecting groups to yield a push-pull heterobifunctional isoindigo monomer, and which was subsequently shown to facilitate Suzuki polymerization to a target molecular weight of 20,000 Da and the desired end-group control. While the synthesis of the block copolymer itself was not achieved, this work provides a strong foundation on which further efforts may be built on.

6.5 Outlook

In conclusion this thesis reports the synthesis of a wide variety of p-type molecular semiconductors based on two chromophores of great significance to the OPV field, leading to three detailed structure-property studies that establish key relationships between molecular structure, bulk properties and photovoltaic performance through the heavy integration of X-ray scattering techniques. This work highlights how the often-overlooked sidechain elements on a chromophore strongly influences molecular packing and crystallinity, and how this in turn possess significant trickle-down impacts on film formation and the complex charge generation and harvesting processes that influence photovoltaic efficiencies. An alternative route towards fine morphological control is also presented in the form of block copolymer materials, a growing subset of OPV research with significant potential. This work presents in-depth design guidelines and synthetic protocols for the studied chromophore classes, and as they prove to remain highly relevant to the field, it is likely that these guidelines will prove to be crucial in the development of next-generation OPV materials and the ultimate realization of commercially viable, large-area OPV devices.

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It's a magical world, Hobbes, ol' buddy... let's go exploring!

Bill Watterson, *Calvin and Hobbes*