

Synthesis of Semiconducting Polymers for use in Organic Electronics

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Abstract

A series of novel semiconducting co-polymers based on known, fused aromatic monomers (dibenzosilole, dithienosilole and dithienopyrrole) were synthesized for use in organic field effect transistor (OFET) devices. The fused monomers were copolymerized with triarylamine and thienothiophene units to give a series of six donor polymers. Their electronic energy levels were probed by UV-Vis and photoelectron spectroscopy, and predictions regarding their performance were drawn from this information. Two polymers were tested in OFETs and conclusions were made concerning the relationship between structure and performance.

Four donor-acceptor type polymers were synthesized using dithienopyrrole as the electron rich unit. This monomer was copolymerized with benzothiadiazole, difluorobenzothiadiazole, thienopyrrolodione and 1,1'-bithienopyrrolodione. These low band gap polymers were tested as the donor polymer in polymer:fullerene BHJ devices.

A novel monomer with long branched alkyl substituents, based on the extended fused-ring system indacenodithiophene (IDT), was synthesized. The nitrogen analogue of this monomer (NIDT) was of interest as its performance could be compared to the carbon and silicon versions of IDT. A route to NIDT was devised and then it was polymerized with four electron poor monomers. The energy levels were estimated by UV-Vis and photoelectron spectroscopy, followed by testing of the materials in OFET and OPV devices. Those with the lowest lying HOMO levels performed best in OPVs.

Another series of NIDT containing polymers were synthesized, designed specifically for use in OFET devices. The aim was to produce polymers with highly planar backbones which would form ordered domains and enhance hole transport. An NIDT monomer was synthesized with linear hexadecyl substituents in order to improve π -stacking. The linear NIDT monomer was then copolymerized with thiophene, thienothiophene, thienopyrrolodione and diketopyrrolopyrrole. It was found that the diketopyrrolopyrrole containing polymer, performed best in OFETs and the molecular weight played a large role in how a polymer performed.

Declaration

The work performed in this thesis was carried out in the Chemistry Department, Imperial College London, between October 2008 and September 2011 and is the work of the author unless otherwise stated.

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Publications

The following publications have arisen from the work described in this thesis and can be found in Appendices B and C.

1) Pyrroloindacenodithiophene containing polymers for organic field effect transistors and organic photovoltaics.

J. E. Donaghey, R. S. Ashraf, Y. Kim, Z. G. Huang, C. B. Nielsen, W. Zhang, B. Schroeder, C. R. G. Grenier, C. T. Brown, P. D'Angelo, J. Smith, S. Watkins, K. Song, T. D. Anthopoulos, J. R. Durrant, C. K. Williams and I. McCulloch, *J. Mater. Chem.*, **2011**, 18744-18752.

2) Design of Semiconducting Indacenodithiophene Polymers for High Performance Transistors and Solar Cells.

I. McCulloch, R. S. Ashraf, L. Biniek, H. Bronstein, C. Combe, J. E. Donaghey, D. I. James, C. B. Nielsen, B. C. Schroeder and W. Zhang, *Acc. Chem. Res.*, **2012**, ASAP.

Abbreviations

AFM	Atomic Force Microscopy
Ar	Aromatic
BDT	benzodithiophene
biTPD	1,1'-bithienopyrrolodione
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BG-BC	Bottom-gate, bottom-contact
BG-TC	Bottom-gate, top-contact
BHJ	Bulk Heterojunction
BT	benzothiadiazole
°C	degrees Celsius
$^{13}\text{C}\{^1\text{H}\}$	proton decoupled carbon 13
calc.	calculated
CB	chlorobenzene
C8C10	2-octyl dodecyl
C2C6	2-ethyl hexyl
C8	octyl
DA	donor-acceptor
DCB	dichlorobenzene
DCM	dichloromethane
DFT	Density Functional Theory
DMF	dimethylformamide
DP	degree of polymerization
DPP	diketopyrrolopyrrole
DSC	Differential Scanning Calorimetry
DTP	dithienopyrrole
DTS	dithienosilole
E_g	Band gap
EH	2-ethyl hexyl

EI	Electron Ionization
ESI	Electrospray Ionization
EQE	External Quantum Efficiency
equiv.	equivalents
eV	electron Volts
Exp.	experimental
F8	9,9-di- <i>n</i> -octyl-9H-fluorene
FF	Fill Factor
ffBT	difluorobenzothiadiazole
GPC	Gel Permeation Chromatography
H	hours
HDMS	hexamethyldisilazane
hex	hexanes
HOMO	Highest Occupied Molecular Orbital
I_D	drain current
I_{Dsat}	drain current at saturation
IDT	indacenodithiophene
IF	indenofluorene
$I_{on/off}$	current on/off ratio
IPA	iso-propyl alcohol
ITO	Indium tin oxide
J	coupling constant
J_{sc}	short circuit current
kDa	kilo Dalton
L	channel length
LUMO	Lowest Unoccupied Molecular Orbital
λ	wavelength
min	minutes
M_n	number averaged molecular weight

MoO ₃	molybdenum oxide
mol	moles
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
m. p.	melting point
MS	mass spectrometry
M_w	weight averaged molecular weight
m/z	mass to charge
n	neo
NBS	n-bromosuccinimide
NIDT	pyrroloindacenodithiophene
NIR	Near Infra Red
NMR	Nuclear Magnetic Resonance
OFET	Organic Field Effect Transistor
OLED	Organic Light Emitting Diode
OPV	Organic Photovoltaic
OTS	Octyltriethoxysilane
P	Power
PCBM	phenyl butyric acid methyl ester
PCE	Power Conversion Efficiency
P(Cy) ₃	tricyclohexylphosphine
Pd ₂ dba ₃	tris(dibenzylideneacetone)dipalladium(0)
PDI	Polydispersity Index
PESA	Photoelectron Spectroscopy in Air
P(o-tol) ₃	tri(o-tolyl)phosphine
PPh ₃	triphenylphosphine
ppm	parts per million
R _f	retardation factor
RMS	root mean squared

rpm	revolutions per minute
SiF	dibenzosilole
SiIDT	silaindacenodithiophene
soln.	solution
T	thiophene
<i>t</i>	tertiary
TAA	triarylamine
T _c	crystallization transition temperature
T _g	glass transition temperature
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
T _m	melting transition temperature
TOF	Time of Flight
Tol	toluene
TPD	thienopyrrolodione
TT	thienothiophene
UV-Vis	Ultra violet-Visible
V _D	drain voltage
V _G	gate voltage
V _{oc}	open circuit voltage
V _{th}	threshold voltage
W	channel width
w/v	weight by volume
w/w	weight by weight
XRD	X-ray Diffraction
μ _h	hole mobility
μ _{lin}	linear mobility
μ _{sat}	saturation mobility
μW	microwave

Chapter 1: Introduction and Aims

1.1 Background

Since the discovery that the electrical conductivity of π -conjugated polymers increases substantially upon electrochemical doping, they have attracted a lot of attention for use in electronic applications.¹ By the mid-1980s they were being investigated as low-cost alternatives to inorganic semiconducting materials. Devices such as light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs) were of particular interest. From the fabrication perspective, these materials can be processed either by vapour- or solution-phase techniques, enabling the production of cheap, large-area, lightweight electronic devices. Also, these devices possess mechanical properties akin to those of plastic substrates eg. flexibility and conformability, enabling new device functionalities which are difficult to achieve with silicon.¹ This thesis will report on the synthesis of π -conjugated polymers, for use in OFETs and/or OPVs.

Table 1.1 Semiconducting Materials Overview

Semiconductor	Average mobilities ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Carbon nanotubes	10^5
Gallium Arsenide	10^4
Monocrystalline silicon	10^3
Polycrystalline silicon	10^2
Amorphous silicon	1-10
Pentacene	5
Organic semiconducting polymers	$5\text{-}10^{-4}$

1.2 Organic Field Effect Transistors

Organic based circuits are not expected to replace silicon technology where high device density, speed and stability are vital (Table 1.1).² Initial applications for these circuits, such as identification tags, smart cards and pixel drivers, do not require exceptionally high performance transistor switching speeds, but they do have to exhibit stability under a potential bias.^{2, 3} The main logic units in these circuits are OFETs which effectively act as switches.

1.2.1 Device architecture

Figure 1.1 shows a bottom-gate, top-contact (BG-TC) OFET, comprising of a gate electrode, a gate dielectric, a semiconductor and a source/drain electrode. Note that several other device architectures can be fabricated depending on the relative position of the contacts and the dielectric/semiconductor layers.⁴

The device is in an insulating state until a bias is applied to the gate electrode. Charges can accumulate at the organic semiconductor-dielectric interface, creating a “channel” in which mobile charge carriers can flow between the source and drain electrodes, thus rendering the device “on”.^{5, 6} It is the applied voltage that controls the switching of the device between its on/off states.⁶

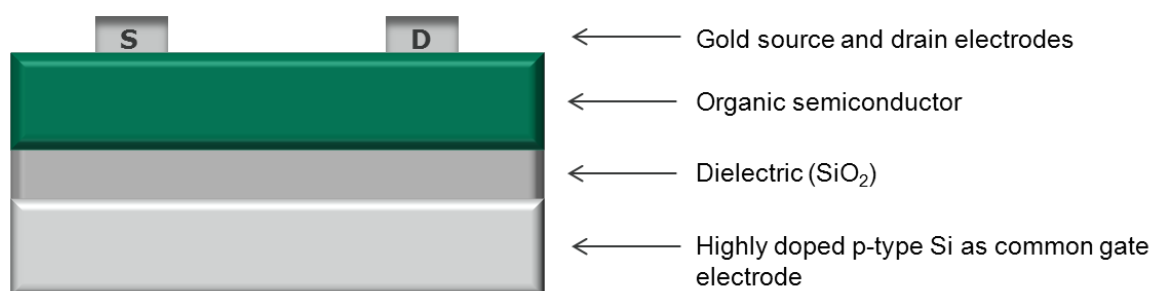


Figure 1.1 Bottom gate-top contact OFET device.

1.2.2 OFET performance

The magnitude of the current flowing between the source and drain is mainly dependent on the applied bias and the charge-carrier mobility (μ) through the semiconductor.⁶ It is possible for injected charges to get “trapped” leading to reduced mobility. Such traps may be due to oxidizable or reducible chemical impurities, grain boundaries, inhomogeneties at the dielectric interface or defects in the semiconductor structure.²

The performance of a transistor can be evaluated from the transfer and output plots (Figure 1.2). From these plots parameters such as, field-effect mobility (μ), the current on/off ratio

($I_{\text{on/off}}$) and the threshold voltage (V_T) can be measured. Mobility in the linear and saturation regimes can be calculated from the standard metal oxide semiconductor field effect transistor (MOSFET) equations (see Appendix A).^{1, 7} This thesis will be concerned with the synthesis of p-type semiconducting polymers.

In order to obtain, and maintain a high hole mobility the high occupied molecular orbital (HOMO) energy level of the semiconducting layer must be fine-tuned. The HOMO energy level must lie close to the ionization potential of the source/drain electrodes in order to minimize the barrier to charge injection.⁸ It must also be low enough to prevent photochemical oxidation of the material, which would create trap sites and lower the mobility. For a transistor with gold electrodes it is desirable to have a HOMO level between -5 and -5.5 eV.¹

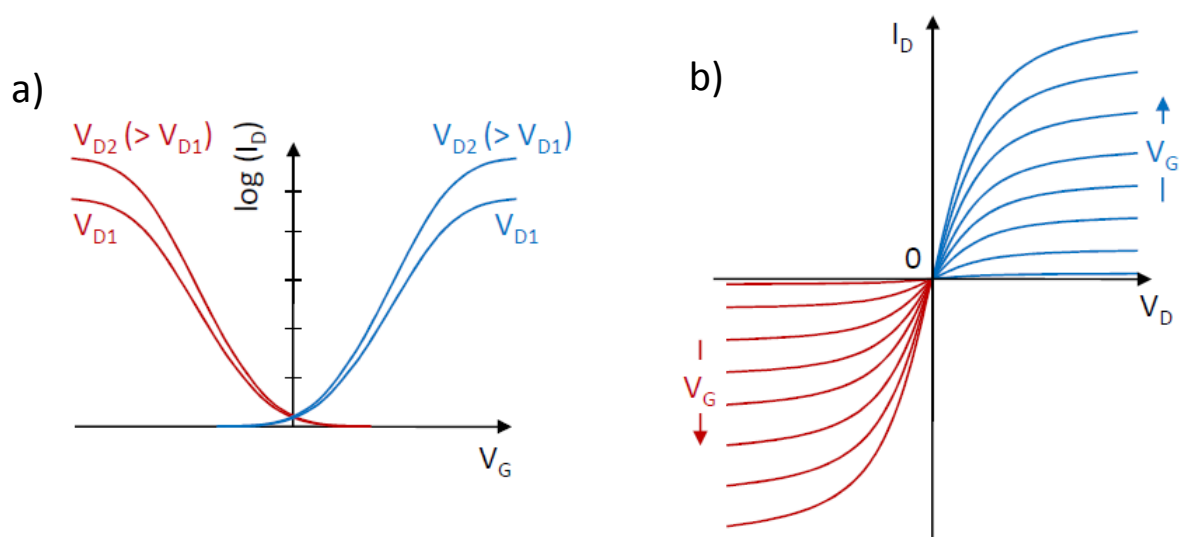


Figure 1.2 a) Typical transfer curve (blue n-type, red p-type) b) Typical output curve (blue n-type, red p-type).

1.2.3 P-type semiconducting polymers for OFETs

1.2.3.1 Donor polymers

Polythiophenes are among the most extensively investigated semiconductors for use in organic electronics (Figure 1.3). Regioregular polythiophenes such as poly(3-hexylthiophene) **1.1** (P3HT) and its derivatives are the most commonly studied due to their high charge carrier mobilities ($\sim 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), high degree of flexibility and semi-crystalline nature. The performance of P3HT has been investigated by various groups considering the effect of molecular weight,⁹⁻¹¹ film morphology^{12, 13} and fabrication process.¹⁴

One major drawback of polythiophenes is the poor air stability. Doping of polythiophenes by O_2 and H_2O can result in large off-currents, leading to low on/off current ratios. Therefore these devices require fabrication under a nitrogen atmosphere which makes them less attractive as cheap alternatives to silicon-based electronics.¹⁵ One method of improving air stability is to reduce the HOMO level of the polymer, therefore alternative polymers based on thiophene were developed. McCulloch *et al.* reported on the synthesis of PBTBT **1.2**.¹⁶ The incorporation of the thieno[3,2-*b*]thiophene (TT) unit led to a drop in the HOMO level compared to P3HT. This is a result of the increased resonance stabilization of the TT moiety which leads to reduced π -delocalization across the backbone.¹⁶ The hole mobility of this polymer is high, reaching $\sim 0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^{16, 17} This is due to the rigid backbone, interdigitated pattern of side chains and its ability to form regular crystallites.

More recently polymers containing fused units have been developed resulting in p-channel OFETs with mobilities approaching $\sim 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.¹⁸

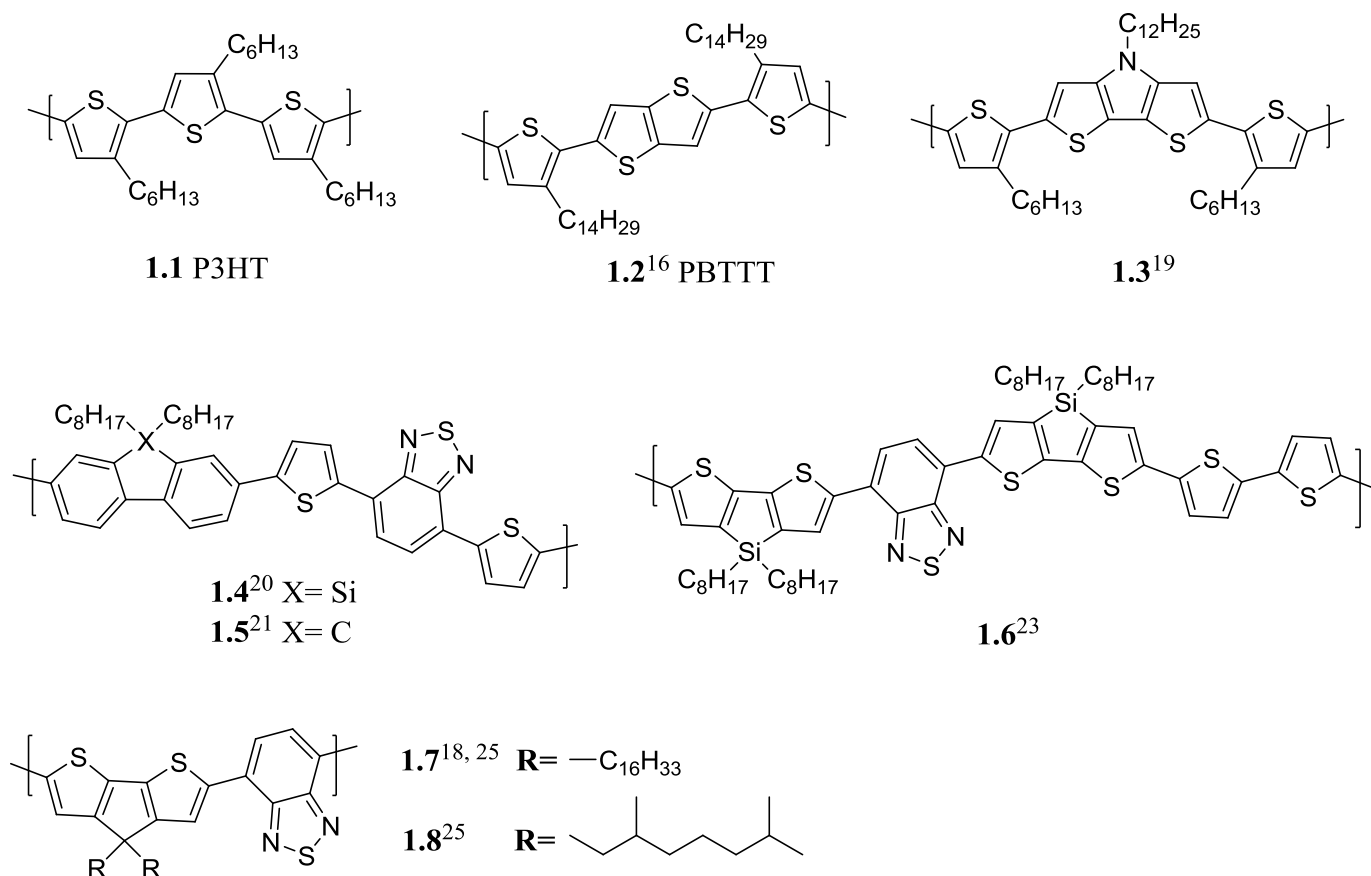


Figure 1.3 Chart of semiconducting polymers for OFETs.

In 2008 Liu *et al.* reported the synthesis and testing of a number of dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) based copolymers.¹⁹ High mobilities were observed even though there was an absence of macroscopic order. Polymer **1.3** (Figure 1.3) was designed to be amorphous with its complex repeat unit and non-regioregular side chain pattern. The rigid, planar DTP unit extended π -conjugation, whilst the alkyl-thiophenes imparted solubility allowing high molecular weights to be reached. As cast mobilities as high as $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were recorded, and due to the amorphous nature of the polymer, post deposition treatment could be avoided.¹⁹ Unfortunately the current on/off ratios were low, probably due to the high lying HOMO levels.

1.2.3.2 Donor-Acceptor polymers

Donor-Acceptor (DA) type polymers can not only be useful for obtaining broad spectral absorption in OPVs, but they can also be useful in OFETs. The enhanced molecular orbital hybridisation allows for efficient charge transport along the backbone. In 2008, Wang *et al.* synthesized a dibenzosilole containing polymer **1.4** for use in OPVs and compared its performance to that of the carbon analogue **1.5**.^{20, 21} **1.4** had already been shown to have superior electroluminescent efficiency and thermal stability when tested in OLEDs,^{22, 23} therefore it was interesting to study its photovoltaic performance. To help understand the origin of the high power conversion efficiency (PCE) (5.4 %) exhibited by this polymer, the hole transport properties were investigated and the silicon containing polymer **1.4** was found to have a mobility of $1 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, almost one magnitude larger than the carbon analogue **1.5**.²⁰ This was a promising result for the use of DA polymers in OFETs.

DA polymers typically do not possess as high a degree of crystallinity as their all donor counterparts (eg. P3HT), but X-ray diffraction techniques show that these polymers have a large degree of microstructural order. In 2009, Beaujuge *et al.* reported on a series of dithienosilole containing polymers.²⁴ Polymer **1.6** exhibited hole mobilities as high as $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which was in agreement with the close π -stacking and lamellar distances obtained from structural analysis.²⁴

Recently, the hole mobilities of these donor-acceptor type polymers have dramatically increased. Taso *et al.* synthesized a cyclopentadithiophene-co-benzothiadiazole polymer **1.7** which had a hole mobility of $1.4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.²⁵ Upon further optimization of the molecular weight, excellent hole mobilities of $\sim 3.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ were achieved.²⁶ It was apparent that the crystallinity, and in turn the hole mobility, increased with increased molecular weight. X-ray diffraction (XRD) experiments were carried out on two polymers with different alkyl side chains (**1.7** and **1.8**). The polymer with the linear hexadecyl side chains **1.7** showed a second order peak, indicating a higher order in the bulk film. When higher molecular weight fractions of **1.7** were subjected to XRD, the diffraction peak narrowed, suggesting more pronounced long range order.²⁶ Atomic force microscopy (AFM) was also carried out on the thin films of both polymers. **1.7** exhibited fibrous crystallites that elongated with increasing

M_n and **1.8** appeared to form curled nanofibres.²⁶ It was clear from this research that increasing the molecular weight was the major tool for improving OFET performance. Also, long linear side chains were preferred over the short branched side chains, leading to improved long range order and the formation of crystallites.

Upon optimization of the processing conditions for the cyclopentadithiophene-co-benzothiadiazole polymer **1.7** in OFETs, record hole mobilities as high as $5.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were reported by Wang and co-workers.¹⁸ A method known as solvent vapour enhanced drop-casting (SVED) was employed in order to grow long polymer fibres. The procedure is based on exposing a drop cast solution of the polymer, to an airtight container that is saturated with solvent vapour. The solvent vapour reduces the evaporation rate of the solution and acts as a plasticizer, giving the polymers more time to self-assemble and sufficient mobility to reach a high structural order.¹⁸ In this case chlorobenzene was chosen for the solvent and solvent vapour. The polymer fibres were clearly visible from atomic force microscopy (AFM) and scanning electron microscopy (SEM) images. Selected area electron diffraction (SAED) was carried out on a fibre, which was found to consist of polymer chains which were aligned along the fibre axis, proving that the macromolecules directionally self-assemble during SVED.¹⁸ Individual fibres were isolated and tested in OFET devices. Charge carriers travel in the same direction as the fibre axis, which means that the fibres provide an unhindered charge carrier pathway, allowing mobilities as high as $5.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to be reached.¹⁸

Upon analysis of the literature it is clear that highly crystalline polymers, such as PBTTT, will exhibit high charge carrier mobilities, but recent reports have shown that it is not a requirement, and the use of amorphous polymers can eliminate the need for post-deposition treatments.^{1, 27} The work by Taso *et al.* affirms the need for high molecular weight polymers to be synthesized in order to reach state of the art mobilities.²⁶ It also shows that careful consideration must be taken when choosing the alkyl side chains as they can have a great effect on morphology and therefore mobility. More recent work, by Wang and co-workers, has highlighted a new technique (SVED) which could be employed to many other polymers in order to improve macroscopic order and therefore mobility.¹⁸

1.3 Organic photovoltaics

In comparison to silicon based solar cells, OPVs offer high speed, low-cost solution processing on flexible substrates.²⁸ Until recently, silicon based substrates exhibited superior efficiencies (excess of 20 %) and lifetimes (over 25 years) but in the last decade OPVs have shown great improvement, producing a number of devices with efficiencies of $\sim 7\%$.²⁹⁻³²

1.3.1 Bilayer device

A bilayer device consists of a donor polymer and an acceptor semiconductor (usually a soluble fullerene such as PC₆₁BM), sandwiched between two electrodes. Figure 1.4 illustrates the photophysical processes which take place within a heterojunction solar cell when a photon of light is absorbed:^{5, 33}

1. Absorption of an incoming photon and subsequent excitation of an electron from the HOMO to the LUMO of the electron donating semiconductor, resulting in the creation of a bound electron-hole pair known as an exciton.
2. Diffusion of the exciton to the interface between the electron donor domain and the electron acceptor domain and transfer of the electron to the lower lying LUMO of the electron acceptor forming a charge separated state.
3. Dissociated charges diffuse towards the electrodes by the built in cell potential.

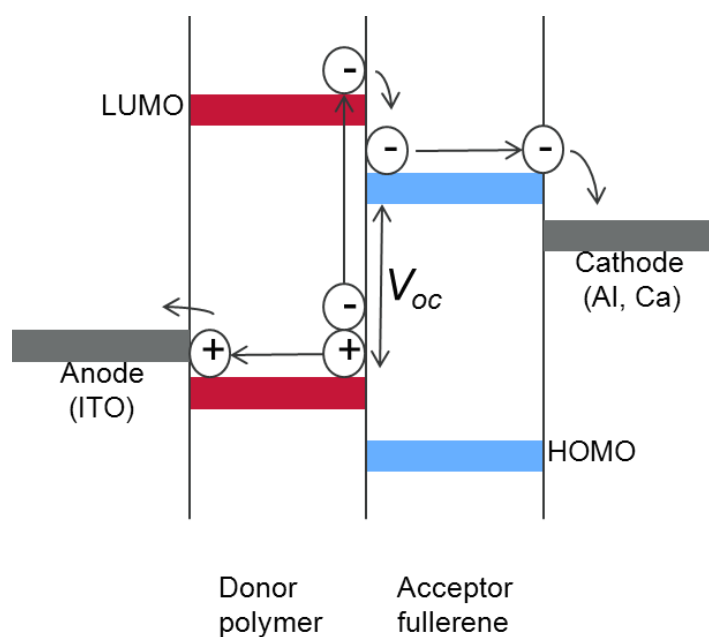


Figure 1.4 Photophysical processes within a heterojunction solar cell.⁵

1.3.2 Bulk heterojunction (BHJ) devices

The active layer in a BHJ device is made up of interpenetrating networks of donor polymer and acceptor fullerene (Figure 1.5). It is desirable for the donor and acceptor semiconductors to phase segregate on a nanometre length scale which is no more than twice the exciton diffusion length (~ 10 nm) in order to minimize charge recombination.^{34, 35} BHJ solar cells provide a much larger surface area for the dissociation of excitons compared to a simple bilayer device, therefore many more excitons will be able to reach the donor/acceptor interface before recombining, leading to much improved device efficiencies. The photoactive layer is usually sandwiched between an indium tin oxide (ITO) anode and a metal cathode (such as aluminium).³⁵

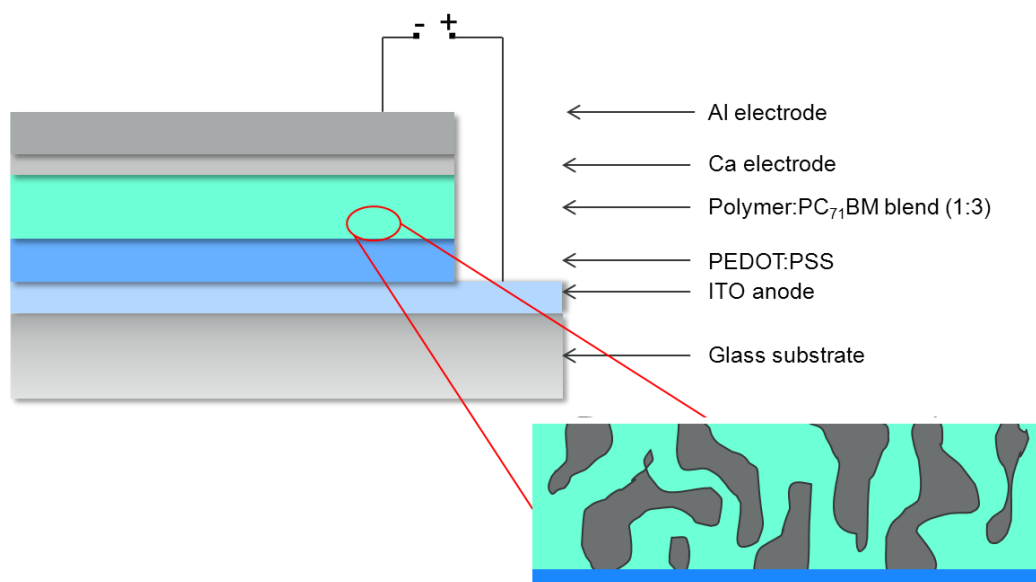


Figure 1.5 A typical BHJ solar cell device with interpenetrating network of donor and acceptor semiconductors (enlarged).

A transparent PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) interlayer can be coated on the anode in order to improve hole collection to the anode and act as an electron blocking layer (Figure 1.5 and 1.6).^{1, 33, 35}

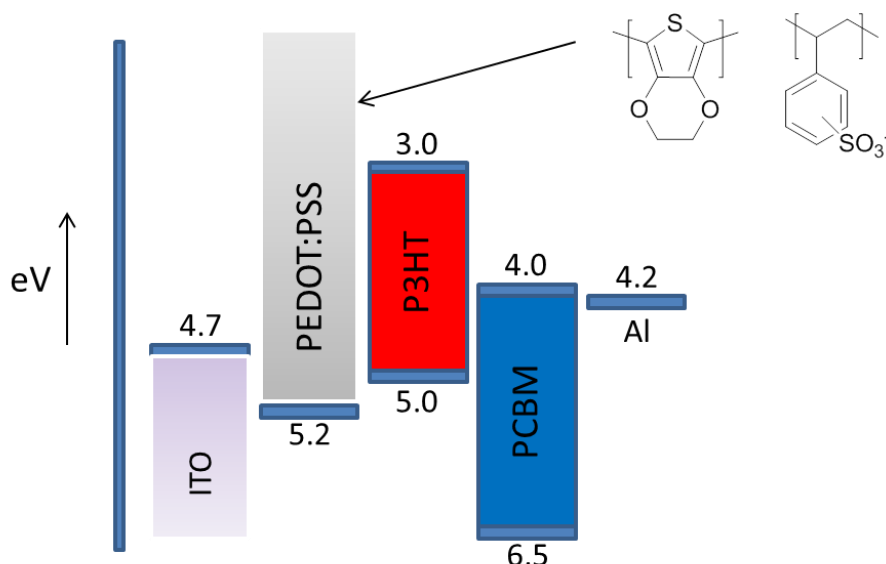


Figure 1.6 Energy levels of a P3HT (1.1):PCBM cell with a PEDOT-PSS hole injection/electron blocking layer.¹

1.3.3 Solar cell performance

The power conversion efficiency (PCE), open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (FF) can all be extracted from the J - V curve (Figure 1.7) measured under the simulated AM 1.5 solar light. The PCE may be calculated using **Equation 1**, where P_{in} is the light intensity incident on the device (Wm^{-2}) and P_{out} is the maximum output of electrical power (Wm^{-2}). The fill factor can be calculated from **Equation 2**, where J_{mp} is the current at maximum power (Am^{-2}) and V_{mp} is the voltage at maximum power (V).³⁵

$$PCE = \frac{P_{out}}{P_{in}} = \frac{FF(J_{sc}V_{oc})}{P_{in}} \quad \text{Equation 1}$$

$$FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}} \quad \text{Equation 2}$$

The fill factor measures the performance of a solar cell in terms of power generated. An ideal device would have a rectangular J - V curve and therefore a fill factor of 1. The V_{oc} can be related to the difference between the HOMO level of the donor polymer and the LUMO level of the acceptor fullerene (Figure 1.4). In order to maximize the V_{oc} a low HOMO level is required.¹ The J_{sc} can be related to the percentage of photons absorbed. A low band gap polymer would have a better spectral overlap with the solar spectrum which would increase

the proportion of photons absorbed.³⁵ It is therefore necessary to balance the requirement for a low HOMO level with the need for a low band gap, in order to maximize the PCE.³⁶

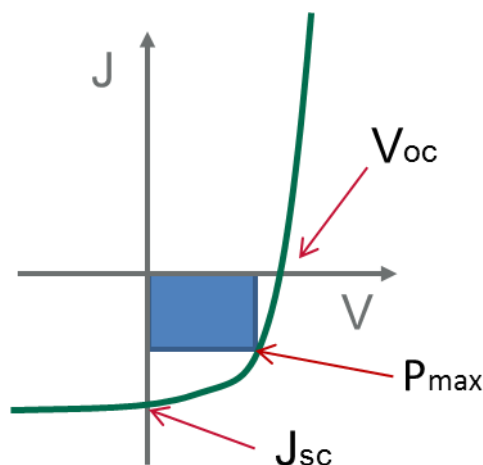


Figure 1.7 Typical J - V curve when under illuminated conditions.¹

1.3.4 Low band gap polymers

In order to increase the percentage of photons absorbed, attention has been drawn to low band gap polymers.^{1, 35, 37} A low band gap polymer is loosely defined as a polymer with a band gap below 2 eV i.e. absorbing light with wavelengths longer than 620 nm.²⁸ It is believed that the lower band gap polymers will have a better spectral overlap with the photon flux from the sun, which has a maximum at 1.8 eV (700 nm).³⁵ This will allow for more photons to be absorbed resulting in higher current and therefore greater power conversion efficiency.

One strategy employed to reduce the donor polymer band gap is to alternate a conjugated electron rich donor (D) unit with a conjugated electron poor acceptor (A) in the same polymer backbone. The introduction of these push-pull forces along the backbone facilitates electron delocalisation leading to molecular orbital hybridization between the donor and acceptor units.³⁸ Figure 1.8 shows the interaction of the D and A molecular orbitals to give a slightly raised HOMO level but a much reduced LUMO level (verses the donor energy levels), leading to a reduced band gap.³⁸

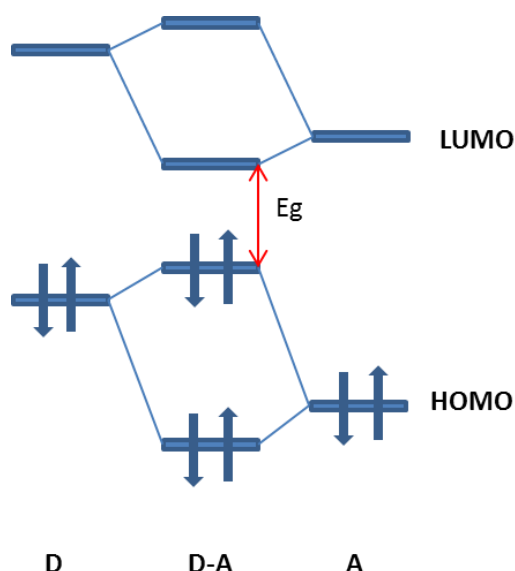


Figure 1.8 Orbital interactions of donor and acceptor units leading to a reduced band gap (E_g).³⁸

1.3.5 Semiconducting polymers for OPVs

In the field of OPVs the P3HT:PC₆₁BM active layer has been studied extensively for use in BHJ devices. Various PCEs are reported up to ~5 %.^{39, 40} As with the OFET devices, the molecular weight of P3HT, the blend morphology and fabrication process all have a significant effect on the solar cell performance.^{10, 39, 41} Unfortunately, this system is limited by the narrow absorption spectrum and the relatively low V_{oc} , due to the fixed energy level offset between the HOMO of P3HT and LUMO of PC₆₁BM. The maximum recorded V_{oc} is around 0.66 V.³⁴ Because of these limitations, research has been oriented in finding novel electron-donating polymers with reduced band gaps and lower lying HOMO levels.

Mühlbacher *et al.* were the first to report on the synthesis of the cyclopentadithiophene-co-benzothiadiazole polymer **1.9** (Figure 1.9), for use as the donor semiconductor in OPVs.⁴² The polymer exhibited good transport properties, a low band gap (E_g 1.7 eV), suitable energy level alignment (HOMO 5.3 eV) with the acceptor fullerene and excellent processing ability. A combination of these properties lead to an efficiency of 3.2 % being recorded for a **1.9**:PC₇₁BM (1:1 ratio) blend. PC₇₁BM was used as it had previously been shown to broaden the effective spectral range for photocurrent.⁴³ Further studies showed that the PCE of this

blend could be enhanced by the use of processing additives. 1,8-Octanedithiol was added to the blend solution before deposition. When the blend was spin coated onto the substrate the dithiol would take longer to evaporate allowing for the optimum morphology to be reached. PCEs of 5.1-5.5 % could be obtained after this optimization.^{44, 45}

Hou and co-workers later reported on the synthesis of a dithienosilole-co-benzothiadiazole polymer **1.10**, the silicon analogue of **1.9**.⁴⁶ The investigation was inspired by the work of Wang *et al.* on the synthesis of poly(dibenzosilole-co-benzothiadiazole) **1.4**, which showed an improvement in PCE from ~3 % to 5.2 % when the bridging carbon of **1.5** was replaced with a silicon atom.²⁰ Replacing the carbon atom of **1.9** with silicon, reduced the band gap to 1.5 eV and produced a PCE of 5.1 % when blended with PC₇₁BM in an un-optimized device.⁴⁶

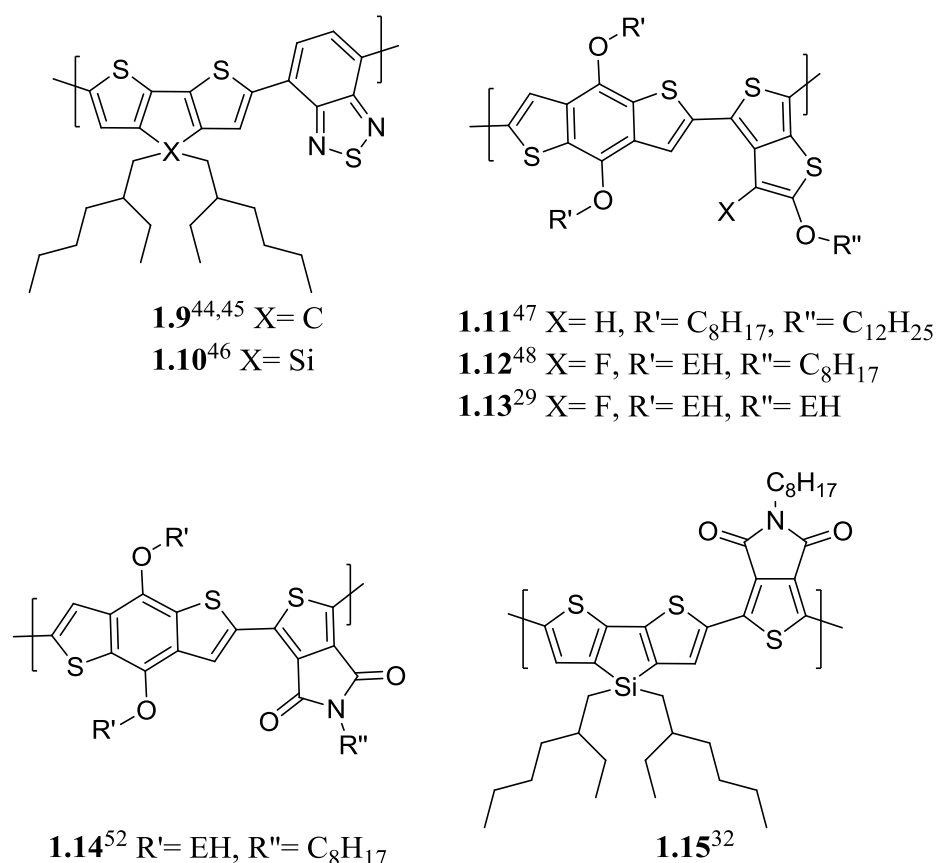


Figure 1.9 Semiconducting polymers for OPVs (EH = 2-ethylhexyl).

In 2009, Laing *et al.* reported on the synthesis of a novel benzodithiophene-co-thieno[3,4,b]thiophene polymer **1.11**.⁴⁷ The TT unit was chosen as it had previously been shown to stabilize the quinoidal structure and therefore enhance planarity along the polymer backbone. The benzodithiophene unit (BDT) was also a rigid planar molecule which would further enhance planarity and in turn increase the conjugation length. Both units also provided points from which solubilizing groups could be attached. In this case, an *n*-dodecyloxy side chain was added to the TT unit and *n*-octyloxy groups were attached to the BDT unit. The **1.11**:PC₇₁BM (1:1.2) blend was tested in an OPV device and the PCE was measured as 5.3 %.⁴⁷

In a follow up investigation by the same group, they attempted to fine tune the energy levels and morphology by using various different side chains and introducing an electron withdrawing fluorine atom.⁴⁸ Six different polymers were investigated and the reader is referred to the original paper for a detailed analysis.⁴⁸ The polymer which gave the highest PCE had a fluorine atom in the 3 position on the TT unit, an *n*-octyloxy side chain on the TT unit and 2-ethylhexyloxy groups on the BDT moiety (**1.12**). Using PC₆₁BM in a 1:1 ratio and dichlorobenzene/diiodooctane (97/3 v/v) as the processing solvent, a PCE of 6.1 % was recorded. The introduction of the fluorine atom lowered the HOMO level by 0.1 eV and promoted intermolecular packing.

Further optimization of this polymer allowed PCEs of over 7 % to be reached.²⁹ The side chain on the TT moiety was changed to 2-ethylhexyl (**1.13**). When a **1.13**:PC₇₁BM blend in 1:1.5 ratio was used along with the diiodooctane processing additive, a record PCE of 7.4 % was recorded.²⁹ This study showed the importance of substituent choice and the need to optimize the blend morphology in order to reach state of the art efficiencies.

More recently, there has been a lot of interest in the use of thienopyrrolodione (TPD) as the donor unit in DA polymers. The simple, symmetric, planar structure is beneficial for charge delocalization and the relatively strong electron withdrawing effect aids in lowering the polymer HOMO level, increasing the V_{oc} .⁴⁹⁻⁵¹ Zou and co-workers reported on the synthesis

and testing of a benzodithiophene-co-thienopyrrolodione polymer **1.14**.⁵² A low HOMO level (5.56 eV) and a band gap of 1.8 eV were measured by cyclic voltammetry (CV). A solar cell was fabricated using a **1.14**:PC₇₁BM blend in 1:2 ratio. The low HOMO level manifested itself as a high V_{oc} (0.85 V) and an un-optimized PCE of 5.5 % was reported.⁵²

In 2011, Chu and co-workers reported on the synthesis and testing of poly(dithienosilole-co-thienopyrrolodione) **1.15** in an OPV device.³² The polymer exhibited a low band gap (1.7 eV), a deep lying HOMO level (5.57 eV) and excellent solubility due to the branched 2-ethylhexyl groups on the dithienosilole unit. After optimization using a **1.15**:PC₇₁BM with a blend ratio of 1:2 and chlorobenzene/diiodooctane (97/3 v/v) as the solvent, a PCE of 7.3 % was recorded. The device exhibited a very high V_{oc} of 0.88 V, a J_{sc} of 12.2 mAcm⁻² and a FF of 0.68.³² The excellent performance of this device was attributed to the low band gap, deep HOMO level and optimal morphology.

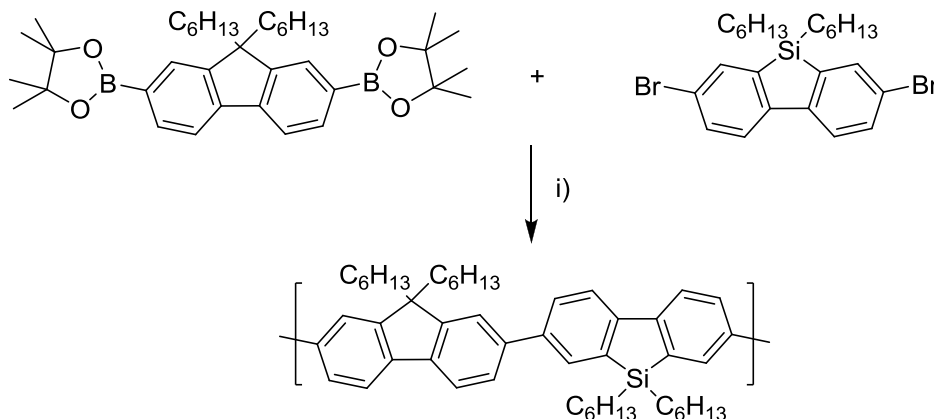
Upon reviewing the literature, it is apparent that when trying to improve OPV performance there are two areas of control: The first is achieved by modifying the structure of the donor polymer backbone in order to obtain the optimal energy level alignment. The side chains can then be substituted which will have an effect on molecular weight, processibility and self-assembly. These modifications will determine a polymers conjugation length, light absorption, carrier mobility, exciton dynamics, morphology and processibility. The second level of control is achieved by optimization of the device architecture, the choice of fullerene, processing conditions and the use of additives to control morphology.

With such a huge variety of polymers and fabrication techniques, there is much scope for continued improvement in the area of organic electronics.

1.4 Semiconducting polymer synthesis

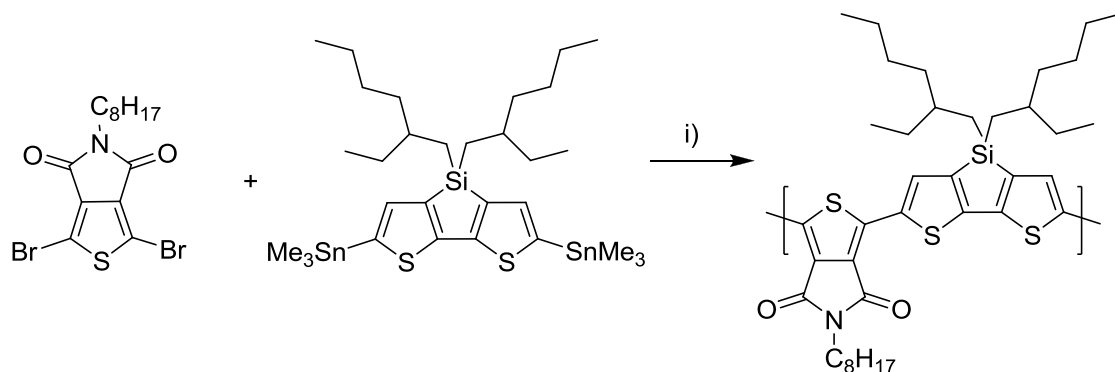
Suzuki and Stille crossing coupling reactions are widely used for the co-polymerization of two AA, BB monomers. Both reactions involve the formation of C-C bonds, via a palladium

catalysed cross coupling reaction. These are the methods that will be used throughout this thesis.



Scheme 1.1 Suzuki co-polymerization reaction. *Reagents and conditions:* i) $\text{Pd}(\text{OAc})_2$, $\text{P}(\text{Cy})_3$, aq. NEt_4OH , toluene, 90°C , 24 h.²²

A Suzuki reaction is the cross coupling between an organoboronic acid/ester and a halide, in the presence of a base (see example Scheme 1.1). The base is required to activate the boronic acid/ester, which enhances the polarization of the ligand and facilitates transmetallation.⁵³ The boronic acids are easily prepared, stable and of low toxicity, which means this reaction is generally favoured over the Stille reaction. There are however some limitations regarding what 'R' groups may be used. Initially the reaction could only be carried out on aryls, but developments in catalysts and methods now allow alkyls, alkenyls and alkynyls to be coupled. The Pd catalyst also prefers insertion in to electron poor halide bonds, so any electron donating substituents on the aryl may inhibit the reaction.⁵³



Scheme 1.2 Stille co-polymerization reaction. *Reagents and conditions:* i) $\text{Pd}(\text{PPh}_3)_4$, toluene/DMF, 120°C , 50 min, μW .⁵⁴

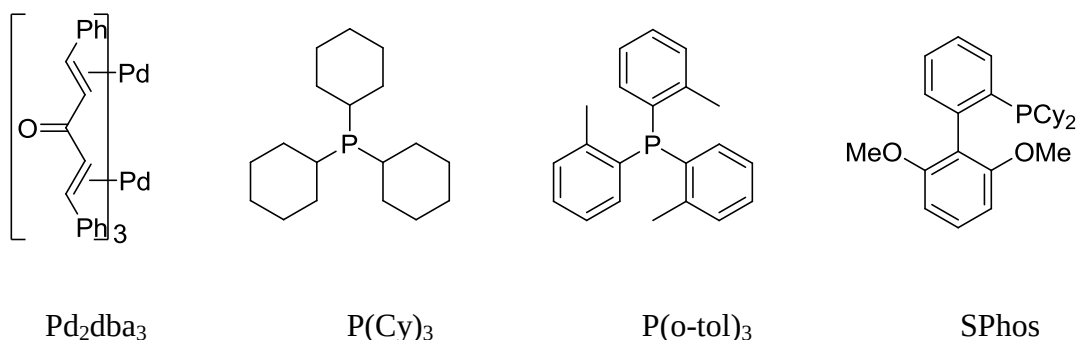


Figure 1.10 Catalyst and ligand structures.

The Stille reaction involves the cross coupling of an organostannane with a halide and does not require the presence of a base (see example Scheme 1.2). This means these reactions can be carried out under anhydrous conditions. There are also few limitations regarding what molecules can be coupled as it exhibits tolerance towards most functional groups.⁵⁵ This makes the Stille reaction much more versatile than the Suzuki reaction, but the main drawback is the high toxicity of the tin reagents. Therefore in any case when the Suzuki reaction is not feasible, the Stille reaction is normally employed.

The most common catalyst used in these reactions is $\text{Pd}(\text{PPh}_3)_4$, but sometimes a Pd^{II} pre-catalysts, that are reduced to Pd^0 *in situ*, can be employed (Figure 1.10):

- $\text{Pd}(\text{OAc})_2 + \text{P}(\text{Cy})_3$
- $\text{Pd}_2\text{dba}_3 + \text{P}(\text{o-tol})_3$
- $\text{Pd}_2\text{dba}_3 + \text{SPhos}$

1.5 Aims

The aim of this thesis is to strategically design and synthesize semiconducting polymers, with the objective of achieving state of the art materials for use in OFETs and/or OPVs.

The first study will focus on a series of polymers based on previously reported fused ring systems: dibenzosilole, dithienosilole and dithienopyrrole (Figure 1.11). These monomers have all previously been incorporated into high performing materials.^{19, 20, 24, 32, 46} They will be copolymerized with carefully chosen donor or acceptor units with the aim of improving their performance in transistor and/or solar cell devices. The correlation between structure and performance will be addressed.

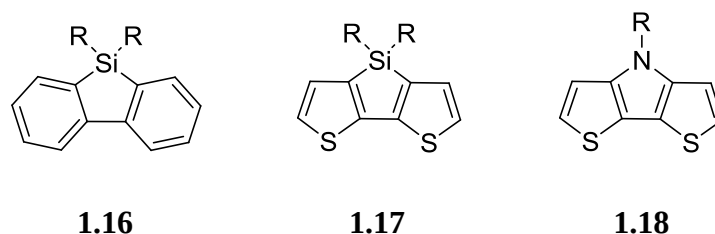
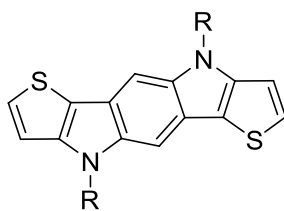


Figure 1.11 Structure of dibenzosilole **1.16**, dithienosilole **1.17** and dithienopyrrole **1.18**.

The second study will focus on the synthesis of a novel donor monomer, pyrroloindacenodithiophene (NIDT) **1.19**. The structure of this monomer is based on the carbon analogue, indacenodithiophene (IDT). IDT has previously been reported in the literature and its copolymers have exhibited high performance in both OFET and OPV devices.^{56, 57} Replacing the carbon bridging groups of IDT with the nitrogen bridging groups of NIDT is expected to enhance the planarity and π -stacking ability of the resulting polymers, as well as improve molecular orbital hybridization with acceptor units due to the electron rich nature of the nitrogens, leading to reduced band gaps. The effect of extending the conjugation of these fused ring systems, and a comparison between C, Si and N bridging groups will be discussed.

A final study will then look at improving the hole mobility of these NIDT containing polymers by varying the alkyl side chains and using more planar, electron rich co-monomers. The effect of using linear or branched side chains on the NIDT moiety will be addressed.



1.19

Figure 1.12 General structure of NIDT (R=alkyl).

Overall the thesis should help gain insight in to the structure/property relationship of organic semi-conducting polymers, so as educated decisions may be made on how to alter the structure in order to improve performance.

Chapter 2:

**Synthesis and Comparison of Semiconducting
Polymers Based on Dibenzosilole (SiF),
Dithienosilole (DTS) and Dithienopyrrole (DTP)**

2.1 Introduction

Zhang *et al.* reported on the incorporation of fluorene (F8) and indenofluorene (IF8) units into a highly stable triarylamine (TAA) polymer **2.1**.⁵⁸ The addition of these bridged monomers optimizes conjugation between adjacent units, increasing the persistence length and reducing the conformational disorder of the backbone. The hole mobility of the resulting copolymers (**2.2** and **2.3**) was around one order of magnitude greater than that recorded for the homopolymer **2.1** and they still exhibited excellent ambient photo and electrical stability.⁵⁸

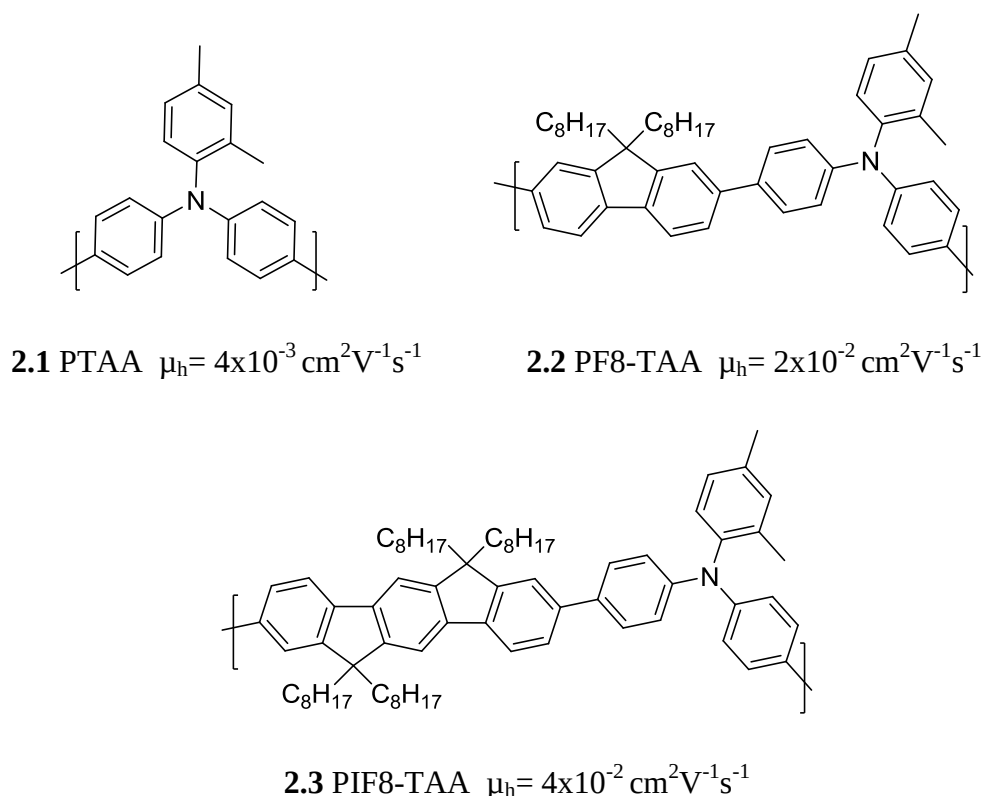


Figure 2.1 Series of TAA containing polymers reported by Zhang *et al.*⁵⁸

The same authors investigated a way of further improving the hole mobility of **2.3** without compromising on air stability.⁵⁷ Their strategy was to replace the TAA unit with planar units which had previously been shown to promote π -stacking; benzothiadiazole (BT) and thienothiophene (TT) (Figure 2.2). In order to reduce conformational disorder and increase the conjugation length the flanking phenyl groups of IF8 would be replaced with thiophenes to give the indacenodithiophene (IDT) unit. Previous studies have shown that due to steric

effects, the two alpha hydrogen atoms promote a larger out of plane twist between two coupled phenyl rings, than they would between two coupled thiophenes (Figure 2.3).^{8, 57} This design strategy lead to the synthesis of polymer **2.4** with a hole mobility as high as $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

1 57

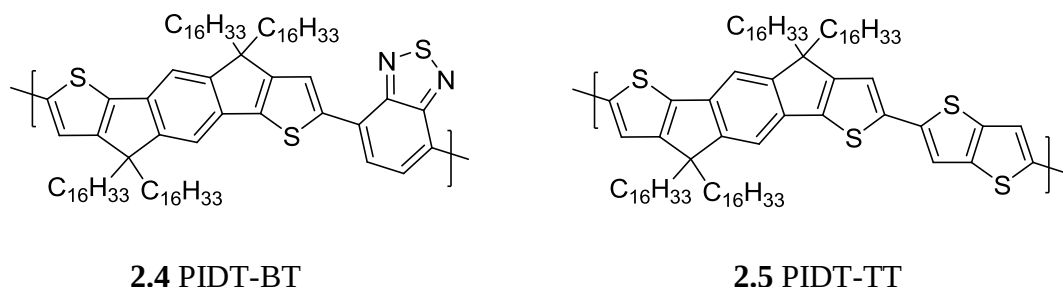


Figure 2.2 IDT copolymerized with the planar BT or TT to give the respective polymers **2.4** and **2.5**.⁵⁷

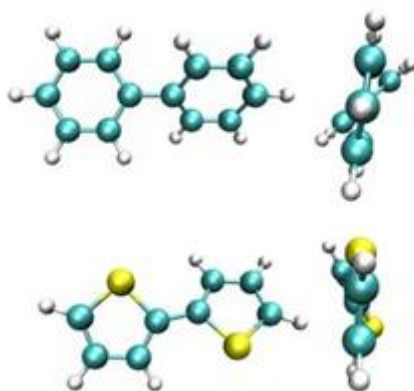


Figure 2.3 Overhead (left) and cross-section (right) view of both a phenyl-phenyl (top) and thiophene- thiophene (bottom) coupled dimer molecule.⁸

2.2 Aim

The aim of this study was to design a series of co-polymers which could be readily synthesized from well-known donor units (Figure 2.4). It was of interest to employ some of the strategic design criteria reported by Zhang and coworkers which afforded very high performing materials.⁵⁷ Zhang *et al.* reported that the steric twist between adjacent co-monomers is at its minimum when both units possess flanking thiophenes, for example PIDT-TT **2.5**. Therefore we were interested in synthesizing a series of polymers based on TAA which could be synthesized and compared to an analogous series based on TT (Figure 2.4).

The polymer energy levels would be probed by UV-Vis spectroscopy and ambient photoelectron spectroscopy (PESA). It was of interest to see whether a materials OFET performance could be predicted on the basis of its UV-Vis absorption spectrum and energy levels. It was anticipated that a TT containing polymer, copolymerized with a ‘dithieno’ monomer (dithienosilole (DTS) or dithienopyrrole (DTP)) would have the most red shifted absorption maximum and a high lying HOMO level, due to minimal steric twist between adjacent units which leads to enhanced molecular orbital hybridization.⁸

A comparison between **P1** and PF8-TAA **2.2**, was also of interest. The effect of replacing the fluorene unit of **2.2** with the dibenzosilole (SiF) unit of **P1**, on the polymers mobility, would be investigated.

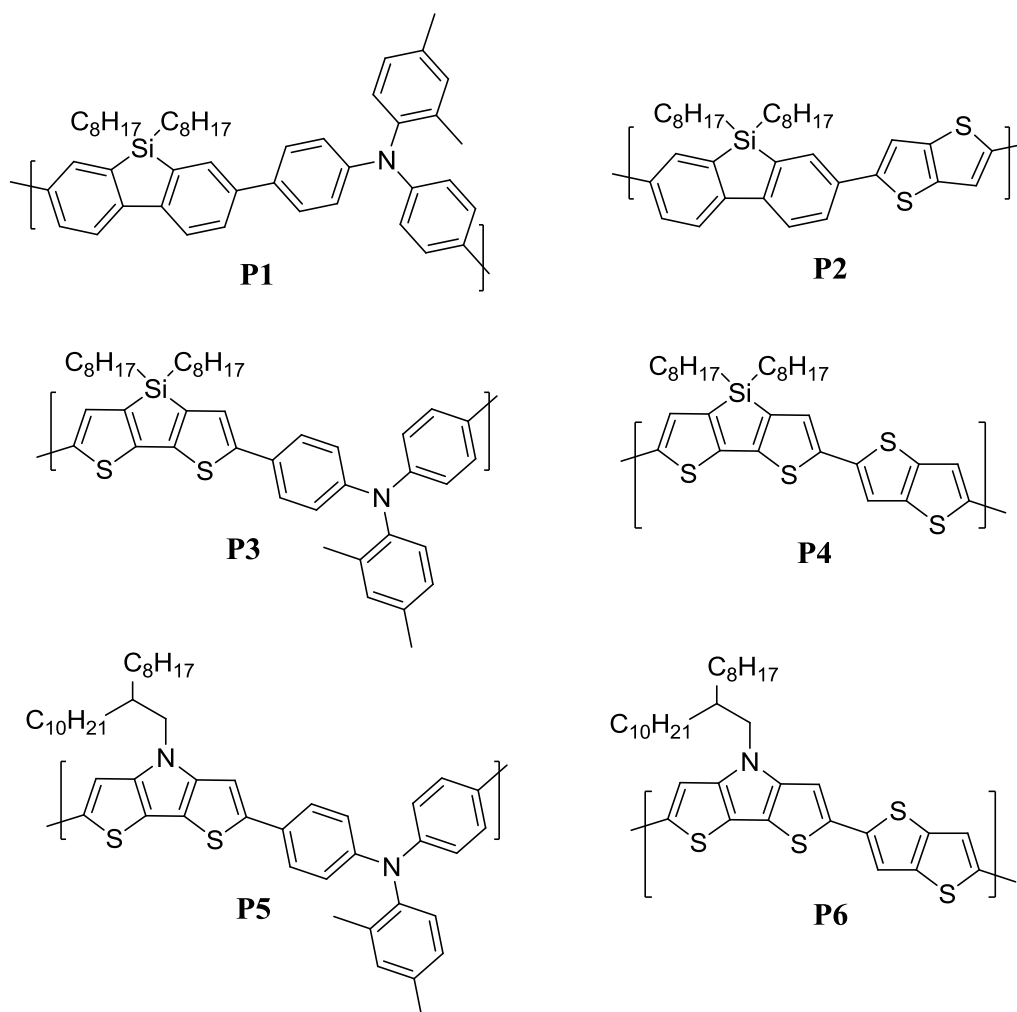


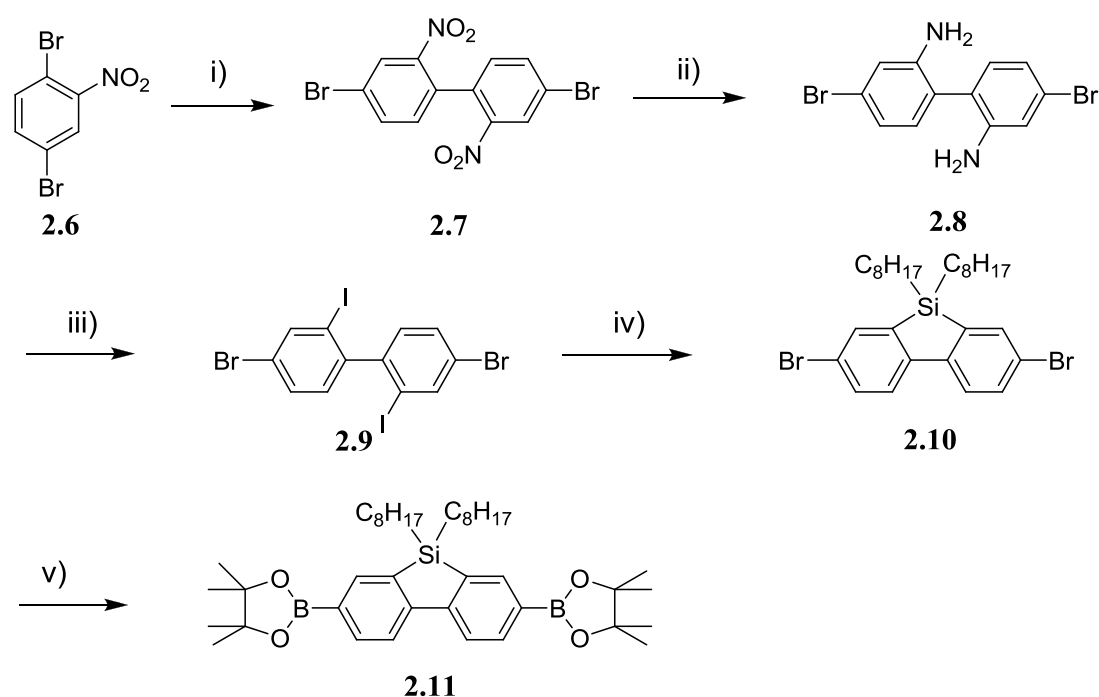
Figure 2.4 Series of polymers **P1-P6**.

2.3 Synthesis of polymers P1-P6

2.3.1 Synthesis of SiF containing polymers P1 and P2

2.3.1.1 Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralane-2-yl)-9,9-dioctyldibenzosilole 2.11

The 2,7-dibromo substituted dibenzosilole **2.10** was prepared according to the method outlined in Scheme 2.1.²²



Scheme 2.1 Reagents and conditions i) Cu, DMF, 125 °C, 82 %; ii) Sn, HCl, EtOH, 110 °C, 88 %; iii) a) aq HCl, H₂O, MeCN, NaNO₂, -5 to -10 °C b) aq. KI, -10 to 15 °C, 30 %; iv) a) 4 eq. *t*-BuLi, THF, -90 to -78 °C b) (C₈H₁₇)₂SiCl₂, -78 to 25 °C, 53 %; v) 4 eq. *t*-BuLi, THF, -78 °C b) ⁱPrO-B(pin), -78 to 25 °C, 76 %.

The Ullman coupling reaction between two units of **2.6** and subsequent reduction of **2.7** to form the diamine **2.8** was facile and proceeded in good yields in accordance with previously published procedures.²² The next step proved more difficult as the diazotization of **2.8** followed by the subsequent Sandmeyer iodination required precise low temperature control and often gave low yields. The method reported by Keyworth and coworkers was followed

but the maximum yield obtainable was only 30 % in comparison to the 58 % reported in literature.⁵⁹

An alternative method was tried utilizing a general reaction for the iodination for aromatic amines published by Krasnokustskaya *et al.* in 2007.⁶⁰ This reaction did not require the precise temperature control and they reported high yields after only 30 min of stirring at room temperature.

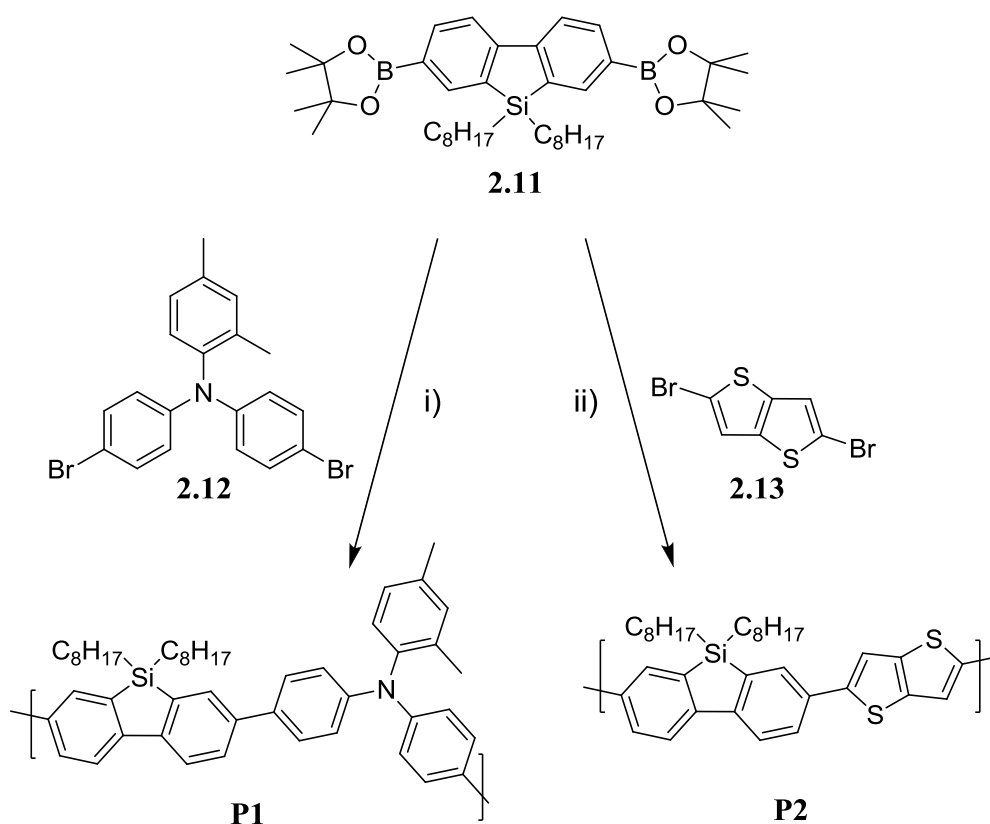
For the first attempt the aq. NaNO₂/KI was added dropwise to a solution of the diamine, in *p*-toluenesulfonic acid and acetonitrile, at 20 °C. Once addition was complete, the reaction mixture was stirred for a further 1 h before being neutralized and worked up. The product was purified by column chromatography and recrystallized as before to yield a white solid in 13 % yield. This yield was very poor so the reaction was repeated, but this time the aq. NaNO₂/KI was added at 10 °C, then allowed to warm to room temperature when addition was complete. The reaction was then heated to 80 °C, and stirred at this temperature overnight. This method gave a 26 % yield. This was still lower than the maximum yield obtained for the previous method, but it was advantageous in that the precise temperature control was not required and therefore more reproducible yields were obtained.

The ring-closure reaction of **2.9** was then carried out following the procedure developed by Chan *et al* (Scheme 2.1).²² A lithium-halogen exchange reaction using *t*BuLi at -90 °C, followed by the addition of di-*n*-octyldichlorosilane afforded **2.10** in 53 % yield which was in accordance with the literature value.²² The ¹H NMR spectrum was also in agreement with the literature.²²

The dibenzosilole monomer had previously been shown to form high molecular weight polymers under Suzuki coupling conditions.²² The diboronic ester **2.11** was synthesized via the method reported by Chan *et al.* (Scheme 2.1) and the product was obtained in high yields (76 %) with excellent purity.²² The ¹H NMR spectrum and the melting point (116-117 °C) were in agreement with the literature.²²

2.3.1.3 Synthesis of P1 and P2

The polymers **P1** and **P2** were synthesized via a Suzuki polycondensation of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralane-2-yl)-9,9-dioctyldibenzosilole **2.11** with 4,4-dibromo-2,4-dimethyltriarylamine **2.12*** or 2,5-dibromo-thieno(3,2-*b*)thiophene **2.13**, respectively. The Suzuki conditions reported by Chan *et al.* for the copolymerization of dibenzosilole with fluorene (Scheme 2.2) were employed.²² 2,5-Dibromo-thieno(3,2-*b*)thiophene **2.13** was synthesized from the bromination of commercially available thieno(3,2-*b*)thiophene with *n*-bromosuccinimide (NBS). The product was obtained as a yellow crystalline solid in 92 % yield (Lit. yield 96%).⁶¹



Scheme 2.2 Reagents and conditions: i) Pd(OAc)₂, P(Cy)₃, aq. NEt₄OH, toluene, 110 °C, 72 h; ii) Pd(OAc)₂, P(Cy)₃, aq. NEt₄OH, toluene, 110 °C, 72 h.

The starting materials were reacted in a 1:1 ratio of diboronic ester **2.11** to the appropriate dibromide. Pd(OAc)₂/P(Cy)₃ was used as the catalyst, 20 % w/v aqueous sodium

* Supplied by McCulloch group, Chemistry Dept., Imperial College London.

tetraethylammonium hydroxide as the base and toluene as the solvent. The reaction mixture was heated for 72 h at 110 °C, allowed to cool, then precipitated in to acidic methanol.

The polymers were purified by Soxhlet extraction using acetone, hexane and, finally, chloroform. Each chloroform fraction was concentrated and washed with aqueous sodium diethyldithiocarbamate tetrahydrate to remove any palladium catalyst, then the chloroform fraction was separated and the polymer reprecipitated into methanol. The molecular weights were measured using Gel Permeation Chromatography (GPC)^{*}, at 80 °C using chlorobenzene as the eluent.

After purification **P1** was isolated in 38 % yield as a yellow solid and **P2** was obtained in 42 % as a yellow/green solid. Both polymers exhibited high number average molecular weights as determined by GPC: **P1** had M_n 29, M_w 75 kDa; **P2** had M_n 38, M_w 75 kDa.

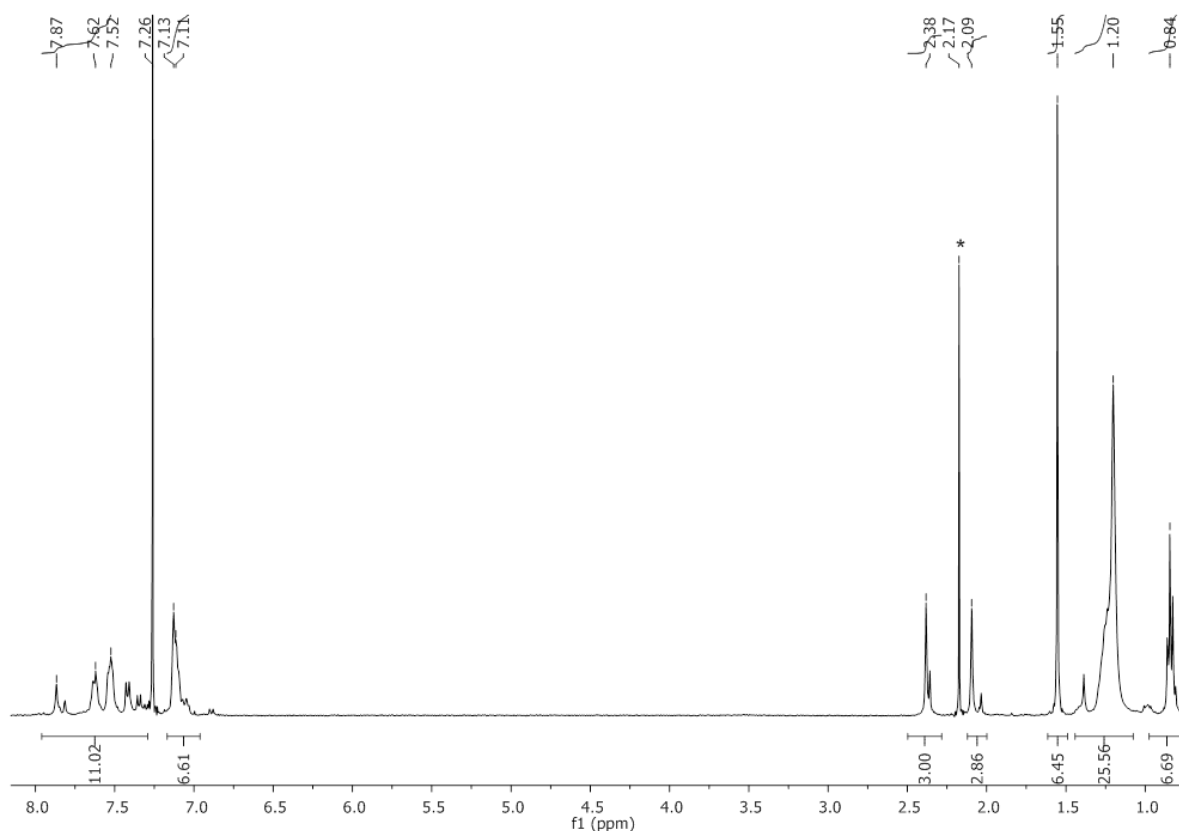


Figure 2.5 ¹H NMR spectrum of **P1** (*solvent peak).

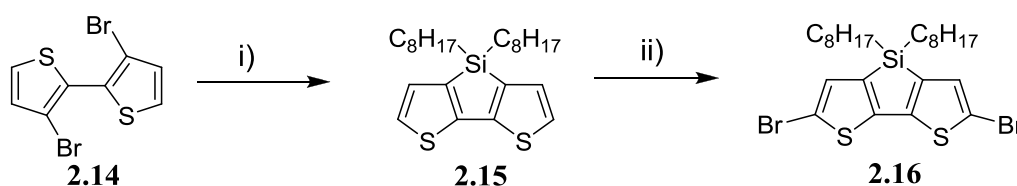
^{*} GPC traces of polymers **P1** and **P4** can be found in Figure 2.16. The remainder can be found in Appendix A.

The polymers were analysed by ^1H NMR spectroscopy. The ^1H NMR spectrum of **P1** (Figure 2.5) showed the 17 aromatic peaks, between 8-6 ppm, corresponding to the protons on the dibenzosilole and TAA units. The alkyl protons of the dibenzosilole unit were present along with the methyl protons of the TAA unit which were observed at 2.41 and 2.12 ppm. The ^1H NMR spectrum of **P2** showed 8 aromatic protons and peaks in the aliphatic region corresponding to the octyl side chains of the dibenzosilole unit.

2.3.2 Synthesis of DTS containing polymers P3 and P4

2.3.2.1 Synthesis of 2,6-dibromo-9,9-di-n-octyldithienosilole 2.16

It was proposed that 2,6-dibromo-9,9-di-n-octyldithienosilole **2.16** would be synthesized via the method reported by Utsa *et al.* (Scheme 2.3), only octyl chains would be used rather than hexyl in order to improve the solubility of the resulting polymers.⁶²

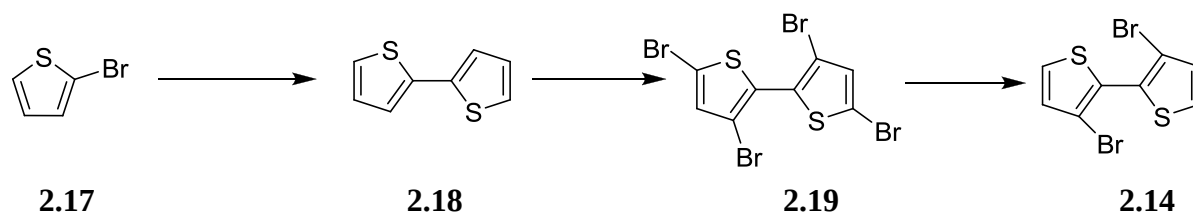


Scheme 2.3 Reagents and conditions i) a) $n\text{BuLi}$, $-78\text{ }^\circ\text{C}$, 1 h b) $(\text{C}_8\text{H}_{17})_2\text{SiCl}_2$, $-78\text{--}25\text{ }^\circ\text{C}$, 24 h;⁴ ii) NBS, DCM, $25\text{ }^\circ\text{C}$.

2.3.2.1.1 Synthesis of 3,3'-dibromo-2,2'-bithiophene 2.14

The **2.14** starting material was synthesized following the procedure reported by Utsa and coworkers.⁶² The first step involved the synthesis of 2,2'-bithiophene **2.18**. The 2-thiophenyl magnesium bromide was synthesized by reacting 2-bromothiophene with activated magnesium turnings. This was then added to more 2-bromothiophene in the presence of $[\text{NiCl}_2\text{.dppp}]$ at $5\text{--}10\text{ }^\circ\text{C}$ and the resulting mixture was stirred overnight at room temperature. Transferring the Grignard reagent via cannula into the flask containing the 2-bromothiophene was problematic due to the poor solubility of the Grignard reagent. Therefore it was not possible to transfer all of the Grignard reagent leading to a lower yield (43 %) than that recorded in literature (72 %).⁶³ In future the 2-bromothiophene should be

added to the Grignard reagent to avoid this problem. The product was purified by column chromatography and the ^1H NMR spectrum was in agreement with the literature values.⁶³



Scheme 2.4 Reagents and conditions: i) a) Mg, diethyl ether, I_2 , 60 °C, 1 h b) 2-bromothiophene, $[\text{NiCl}_2\text{.dppp}]$, 10 °C, 15 h; ii) Br_2 , AcOH, CHCl_3 , 70 °C, 20 h; iii) Zn dust, n-propanol, AcOH, H_2O , 100 °C, 2 h.

The next step involved the bromination of **2.18** to form 3,3',5,5'-tetrabromo-2,2'-bithiophene **2.19**. Five equivalents of bromine were added slowly to the bithiophene which was dissolved in a chloroform/acetic acid solvent mixture. The reaction was heated to reflux until no more HBr was evolved. A reasonable yield of 53 % was obtained in comparison to the 77 % recorded in the literature.⁶² The ^1H NMR spectrum consisted of a singlet at 7.05 ppm which was in agreement with the literature.⁶²

Synthesis of **2.14** required the reduction of 3,3',5,5'-tetrabromo-2,2'-bithiophene **2.19** with zinc. **2.19** was added in 6 portions over 30 min to a refluxing dispersion of zinc dust in a solution of ethanol, water, acetic acid and a few drops of 12M HCl. The reaction was heated under reflux for 2 h, before being cooled and subjected to an aqueous work up. A pale yellow solid was obtained in high yield (87 %). The ^1H NMR spectrum showed two doublets at 7.41 and 7.08 ppm which both had coupling constants of 5.39 Hz. This was in agreement with literature.⁶²

2.3.2.1.2 Synthesis of 2,6-dibromo-9,9-di-n-octyldithienosilole 2.16

Once the starting material **2.14** had been isolated the ring closure reaction could be carried out following the conditions reported by Utsa *et al.* which are outlined in Scheme 2.3.⁶² A lithium halogen exchange reaction with 2.2 equivalents of $n\text{BuLi}$, followed by addition of the di-n-octyldichlorosilane and subsequent purification by column chromatography (silica gel,

hexane, R_F 0.43) afforded the dithienosilole **2.15** in 64 % yield in accordance with the literature (68 %).⁶² The formation of the product was confirmed by ^1H NMR spectroscopy. The ^1H NMR spectrum showed two doublets in the aromatic region corresponding to the four protons on the thiophene moieties. Two multiplets were observed in the aliphatic region, which were attributed to the 34 protons on the alkyl chains.

For the final step, the synthetic method had to be altered to that reported in literature.⁶² Utsa *et al.* had reported that the bromination using NBS had been carried out using DMF as the solvent but the 9,9-di-*n*-octyldithienosilole **2.15** was insoluble in DMF, therefore dichloromethane was used as the solvent.⁶² NBS was added to the dithienosilole monomer **2.15**, in DCM, in one portion and left to react for 30 min at 25 °C. After work up and column chromatography (silica gel, hexane, R_F 0.60) the pure product **2.16** was obtained as a green oil, which eventually solidified, in 90 % yield [Lit. yield 91 %].⁶²

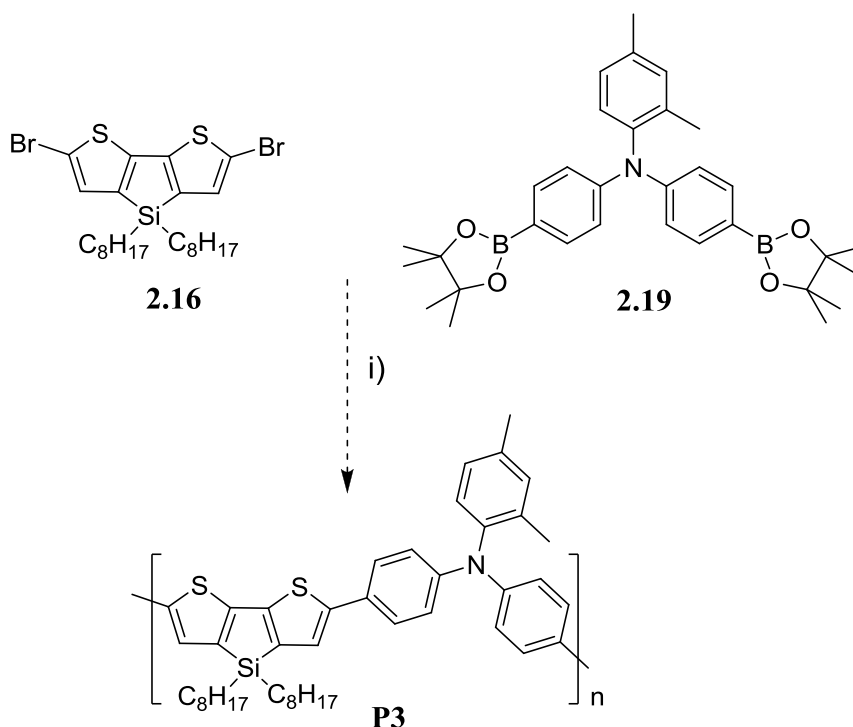
The product was characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and EI mass spectrometry. All data were in agreement with the literature.⁶²

2.3.2.2 Synthesis of P3

This polymer would be synthesized via the Suzuki polymerization of 2,6-dibromo-9,9-di-*n*-octyldithienosilole **2.16** with 2,4-dimethyl-4,4'-(4,4',5,5'-tetramethyl-1,3,2-dioxaboralane-2-yl)triarylamine **2.19**^{*} as shown in Scheme 2.5.

The dibrominated TAA **2.12** was available therefore the diboronic ester **2.19** was synthesized via addition of 2.2 equivalents of *n*BuLi to **2.12** followed by the addition of 2-isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaboralane to the reaction mixture. After several recrystallizations from hexane, **2.19** was obtained as a white crystalline solid in 27 % yield [Lit. yield 55 %].⁶⁴ The ^1H NMR spectrum was in agreement with literature.⁶⁴

^{*} Supplied by McCulloch group, Chemistry Dept., Imperial College London.



Scheme 2.5 Reagents and conditions: i) $\text{Pd}(\text{OAc})_2$, $\text{P}(\text{Cy})_3$, aq. NEt_4OH , toluene, 110 °C, 72 h.

The co-polymerization reaction shown in Scheme 2.5 was carried out three times in order to improve molecular weight (Table 2.1). The first attempt used the same Suzuki conditions that were employed for the synthesis of **P1** and **P2**. $\text{Pd}(\text{OAc})_2$ /tricyclohexylphosphine tetrafluoroborate was used as the catalyst system, aqueous tetraethylammonium hydroxide as the base and toluene as the solvent. The reaction mixture was heated for 48 h at 110 °C. The polymer was worked up and purified by the method outlined in Section 2.3.1.3. GPC analysis in chlorobenzene showed that the polymer had a M_n 3.5 and M_w 7 kDa.

The next attempt involved the use of Pd_2dba_3 with the SPhos ligand, aqueous 1M sodium carbonate as the base and toluene as the solvent. This was heated for 48 h at 110 °C, then cooled and precipitated into methanol. GPC analysis of the polymer gave a M_n 3 and M_w 5 kDa. These conditions gave even poorer molecular weights than before.

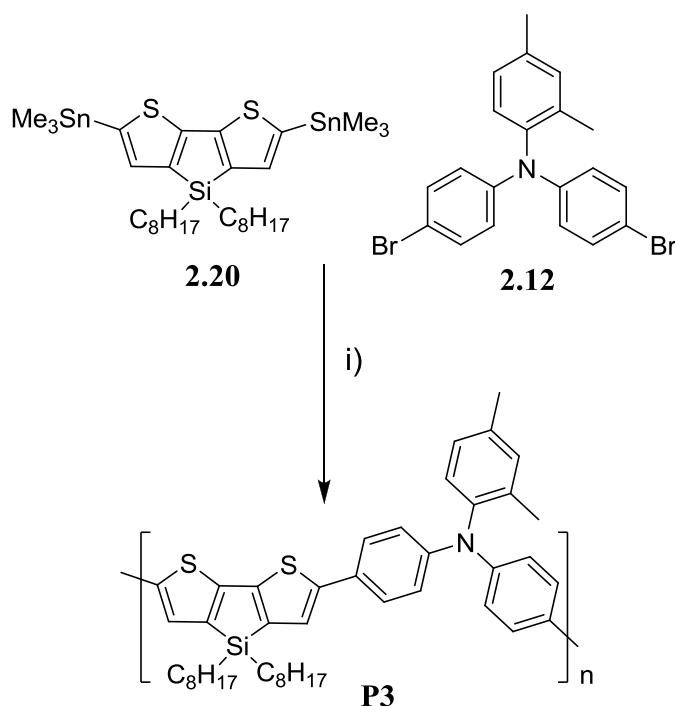
For the final attempt the same catalyst system was employed but aqueous 1M potassium carbonate was used as the base and a drop of the transfer agent, Alliquat 336, was added to the system. The reaction mixture was heated for 48 h at 110 °C but unfortunately even lower molecular weights were obtained; M_n 2.5, M_w 4.5 kDa.

Table 2.1 Conditions used for optimization of molecular weight of P3; Temp=110 °C for each attempt

Attempt	Catalyst	Solvent	Time (h)	M_n (kDa)	M_w (kDa)
1	Pd(OAc) ₂ / P(Cy) ₃	Toluene	48	3.5	7
2	Pd ₂ dba ₃ /SPhos	Toluene	72	3	5
3	Pd ₂ dba ₃ /SPhos	Tol/Alliquat 336	48	2.5	4.5

Alternative Method

As the molecular weights were so low it was thought that a Stille cross-coupling polymerization between the distannylated DTS **2.20** and dibrominated TAA **2.12** might give better results (Scheme 2.6).



Scheme 2.6 Reagents and Conditions: Pd(PPh₃)₄, toluene, 120 °C, 72 h.

The distannylated monomer **2.20** was synthesized directly from the unsubstituted DTS **2.15** following the method reported by Ashraf *et al.* for the stannylation of silaindacenodithiophene.⁶⁵ *n*BuLi was added dropwise to a solution of **2.15** in THF at -40 °C, followed by the addition of trimethyltin chloride 2 h later. The solution was stirred at 25 °C overnight, worked up and used in the following step without further purification due to the poor stability of the distannylated compounds on silica and alumina.⁵⁴ The product was obtained in high yield 89 % and characterized by ¹H NMR spectroscopy (Figure 2.6).

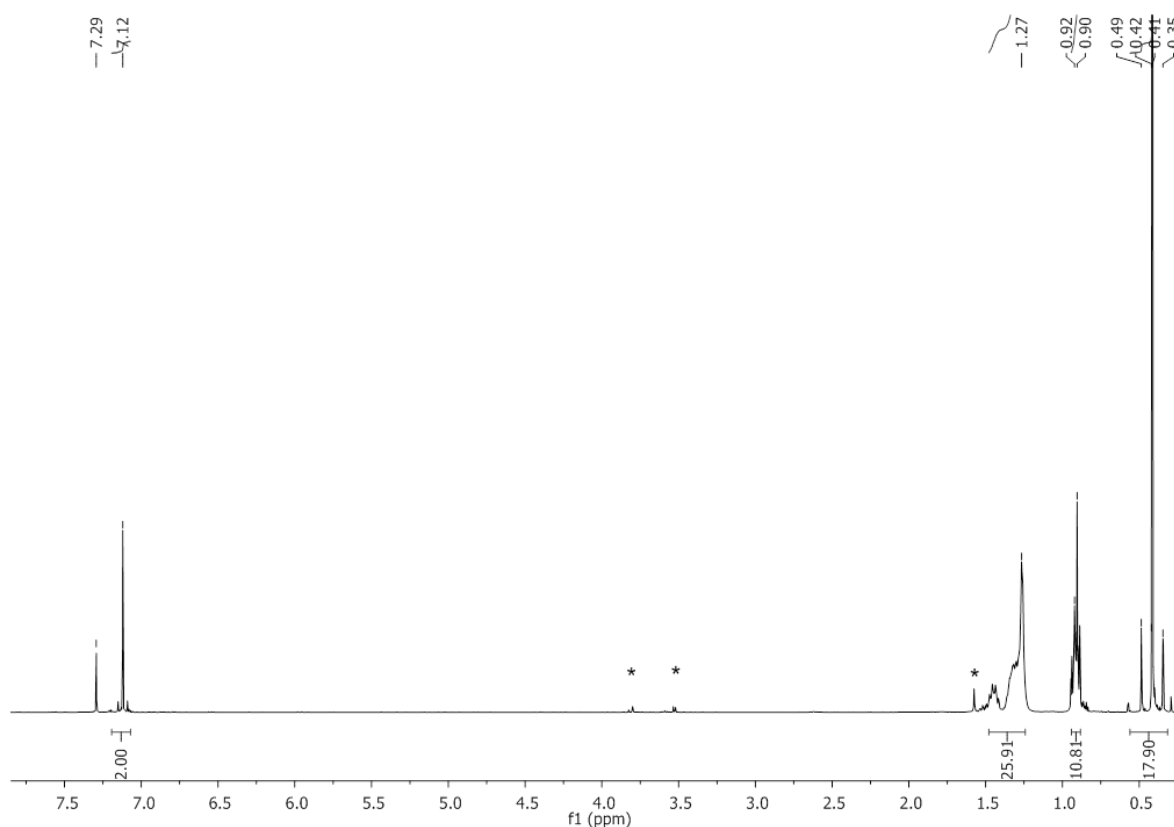


Figure 2.6 ¹H NMR spectrum of distannylated DTS **2.20** (*impurities).

Minor impurities were observed in the ¹H NMR spectrum of the distannylated DTS **2.20**, therefore it was used in slight excess. In the first polymerization attempt the ratio of DTS:TAA was 1.05:1. The reaction was heated in the microwave reactor for 40 min at 180 °C, using Pd(PPh₃)₄ as the catalyst and xylene as the solvent. Unfortunately only oligomers were formed. The second attempt used a ratio of 1.01:1 and rather than carrying out the reaction in a microwave, the reaction was heated in an oil bath for 72 h at 120 °C. Unfortunately these conditions also gave poor molecular weights (Table 2.2).

The final attempt employed $\text{Pd}(\text{PPh}_3)_4$ as the catalyst once more, toluene as the solvent and a DTS:TAA ratio of 1.03:1. The reaction mixture was heated in an oil bath for 72 h at 120 °C. The green polymer was precipitated in acidic methanol and purified using the same method as that outlined in Section 2.3.1.3. The green polymer was obtained in a low yield (21 %) and analysed by ^1H NMR spectroscopy (Figure 2.7). GPC analysis in chlorobenzene showed that there was a slight improvement in molecular weight: M_n 3.5, M_w 8 kDa, DP 5. The results are summarized in Table 2.2.

Table 2.2 Conditions used for optimization of molecular weight of P3 via Stille coupling

Attempt	Catalyst	Solvent	Ratio DTS:TAA	Temp (°C)	Time (h)	Heating method	M_n (kDa)	M_w (kDa)
1	$\text{Pd}(\text{PPh}_3)_4$	xylene	1.05:1	180	40 min	μW	2	3
2	$\text{Pd}(\text{PPh}_3)_4$	toluene	1.01:1	120	72	Oil bath	3	5
3	$\text{Pd}(\text{PPh}_3)_4$	toluene	1.03:1	120	72	Oil bath	3.5	8

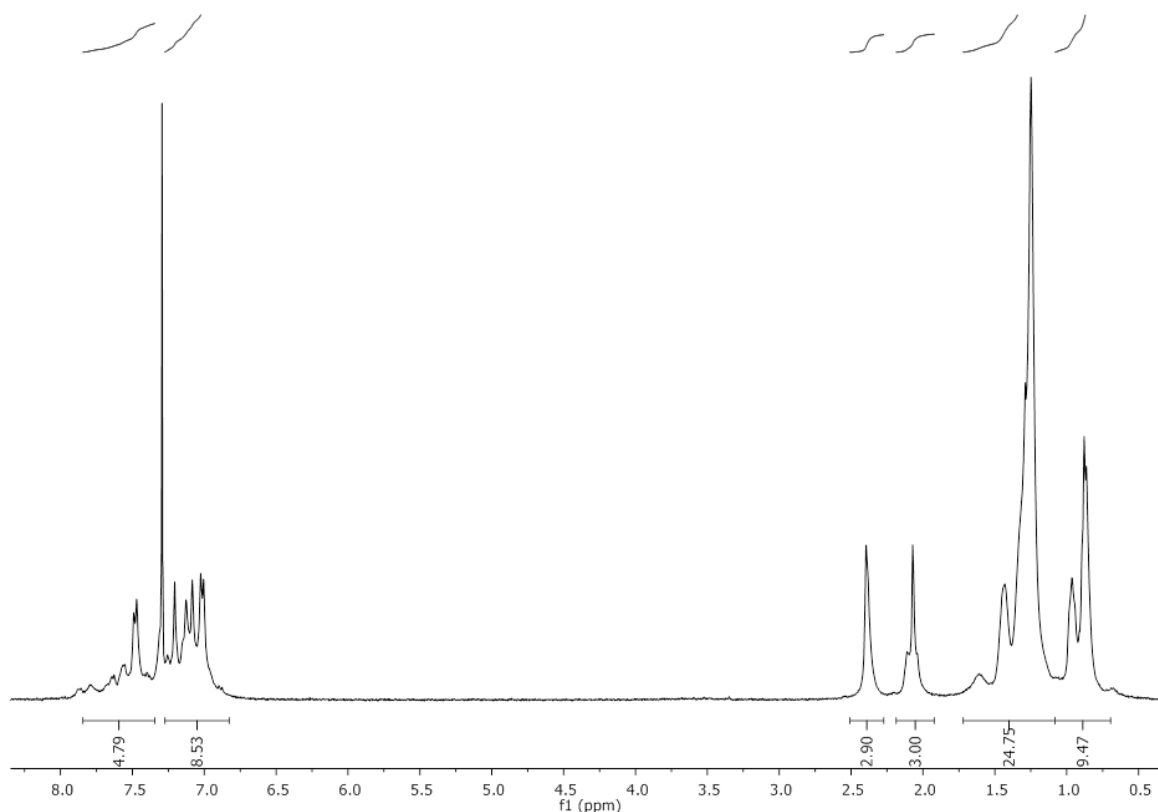
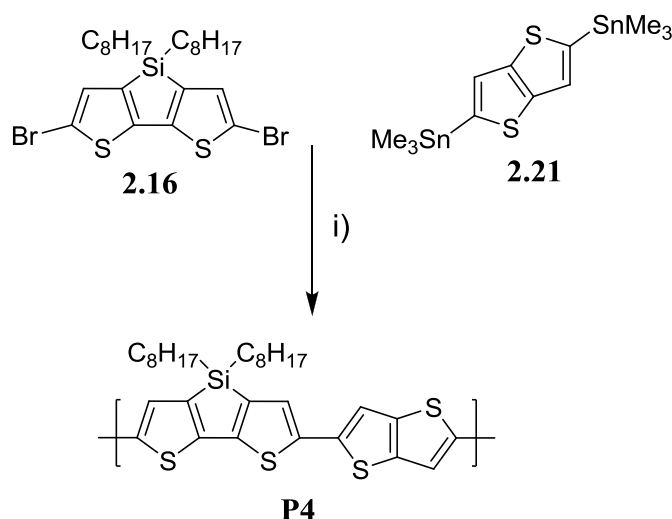


Figure 2.7 ^1H NMR spectrum of P3.

2.3.2.3 Synthesis of P4

A Stille coupling reaction between 2,6-dibromo-9,9-di-*n*-octyldithienosilole **2.16** and the distannylated thieno-(3,2-*b*)-thiophene **2.21*** was carried out using Pd(PPh₃)₄ as the catalyst and xylene as the solvent. The monomers were added in 1:1 ratio and the reaction mixture was heated in the microwave reactor for 40 min at 170 °C. The viscous, dark red solution was precipitated in to methanol and the polymer was collected by filtration and purified as mentioned previously in Section 2.3.1.3. The polymer was collected as a dark red powder in 88 % yield. GPC analysis in chlorobenzene at 80 °C showed the polymer had a *M_n* 10, *M_w* 16 kDa and PDI 1.6, corresponding to a DP of 17.



Scheme 2.7 Reagents and conditions: i) Pd(PPh₃)₄, xylene, 170 °C, 40 min, μ W.

2.3.3 Synthesis of DTP containing polymers P5 and P6

2.3.3.1 Synthesis of dithienopyrrole (DTP) 2.26

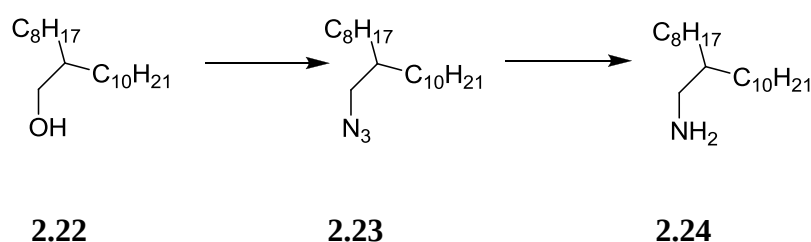
It was proposed that 2,6-di(trimethylstannyl)-9-*n*-(2-octyl-1-dodecyl)dithienopyrrole **2.26** would be synthesized via the method reported by Koeckelberghs *et al.* (Scheme 2.9) only 2-octyl-1-dodecyl chains would be used rather than octyl in order to improve the solubility of

* Supplied by McCulloch group, Chemistry Dept., Imperial College London.

the resulting polymers.⁶⁶ This DTP monomer has never previously been synthesized using the 2-octyl-1-dodecyl side chain.

2.3.3.1.1 Synthesis of 2-octyl-1-dodecylamine 2.24

The synthesis of this branched amine **2.24** was required for use in the Buchwald-Hartwig amination reaction (Scheme 2.9) during the preparation of DTP. The long alkyl chains were required in order to improve solubility of the monomer, which would in turn improve the solubility of the polymers and help enable high molecular weights to be reached.



Scheme 2.8 Reagents and Conditions: i) PPh₃, DPP, DIAD, THF, 25 °C, 24 h; ii) LiAlH₄, THF, 70 °C, 2 h.

The synthetic method used was analogous to that reported by Ashraf *et al.* for the synthesis of pentacosan-13-amine.⁶⁷ The first step was to make the azide **2.23** from the alcohol **2.22** (Scheme 2.8). A round bottomed flask was charged with 2-octyl-1-dodecanol **2.22**, triphenylphosphine and diisopropylazodicarboxylate (DIAD), followed by diphenylphosphoryl azide (DPP). The flask was placed under nitrogen and dry THF was added. The reaction mixture was stirred overnight at room temperature under nitrogen. After extraction with hexanes the yellow viscous oil was purified by column chromatography (silica gel, hexane) to give the azide as a colourless oil in 77 % yield.

The product was characterized by ¹H NMR spectroscopy. A doublet was observed at 3.26 ppm which represents the two protons on the carbon next to the azide group (-NCH₂-). The multiplet between 1.61 and 1.56 was due to the proton on the carbon attached to the two alkyl chains (-NCH₂CH-) and the triplet at 0.91 ppm corresponded the two methyl groups on the end of the alkyl chains.

The next step required the reduction of the azide to an amine using lithium aluminium hydride (LiAlH_4) in THF. The LiAlH_4 was added dropwise to a solution of the azide **2.23** in THF then the reaction was heated under reflux for 2 h before being cooled down and quenched with a 15 % NaOH aqueous solution. The organic layer was washed with water several times to remove lithium salts. The product was obtained as colourless oil (88 %) after the volatiles were removed. No further purification was required.

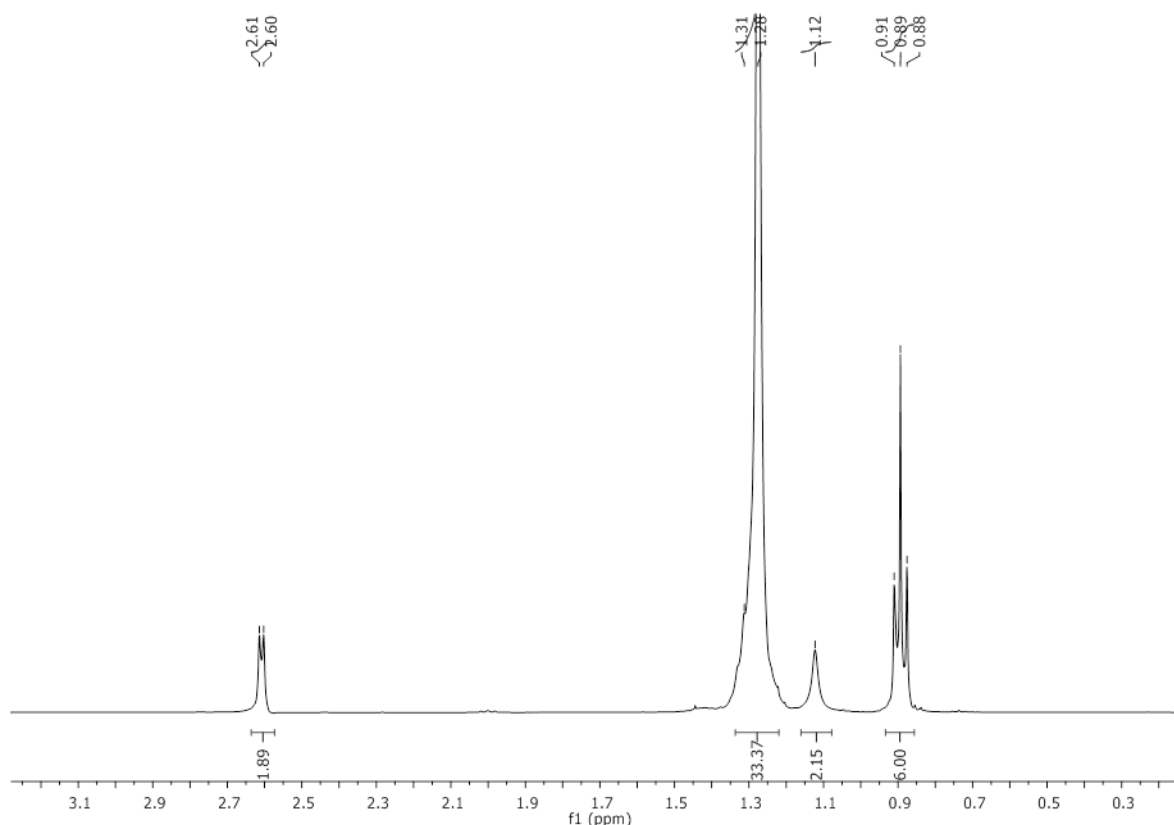
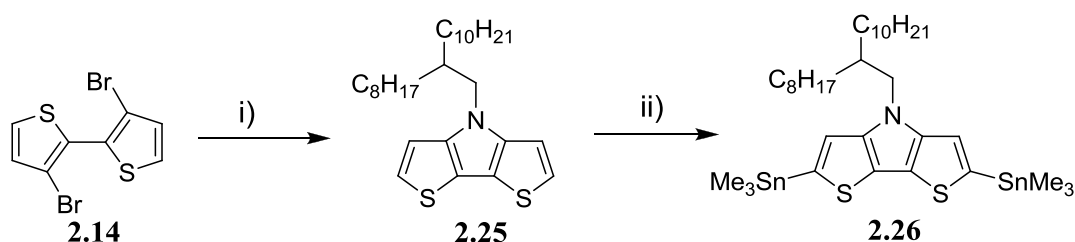


Figure 2.8 ^1H NMR spectrum of amine **2.24**.

The product **2.24** was characterized by ^1H NMR spectroscopy. The proton NMR spectrum (Figure 2.8) shows that the signal for the two protons next to the nitrogen, are shifted to 2.61 ppm compared to the azide where they are observed at 3.26 ppm. The appearance of a new signal at 1.12 ppm helps to confirm the formation of the amine, as this corresponds to the two protons on the nitrogen. The data is in agreement with the literature values.⁶⁸

2.3.3.1.2 Synthesis of 2,6-di(trimethylstannyl)-9-n-(2-octyl-1-dodecyl)dithienopyrrole 2.26

A clean dry Schlenk tube was charged with 3,3'-dibromo-2,2'-bithiophene **2.12**, Pd₂dba₃, BINAP and 3 equivalents of sodium *tert*-butoxide (NaO^tBu). This was purged with nitrogen then toluene was added, followed by the 2-octyl-1-dodecylamine **2.24**. The reaction was heated for 24 h at 120 °C before being quenched with water and extracted with ethyl acetate. The crude product was purified by column chromatography (silica gel, 0-5 % ethyl acetate in hexanes, R_F 0.36) to give a pale yellow oil in moderate yield (67 %).



Scheme 2.9 Reagents and conditions i) Pd₂dba₃, BINAP, NaO^tBu, toluene, 2-octyldodecylamine, 120°C, 24h ii) a) *n*BuLi, -40°C, 2h b) SnMe₃Cl, -40-25°C, 24 h.

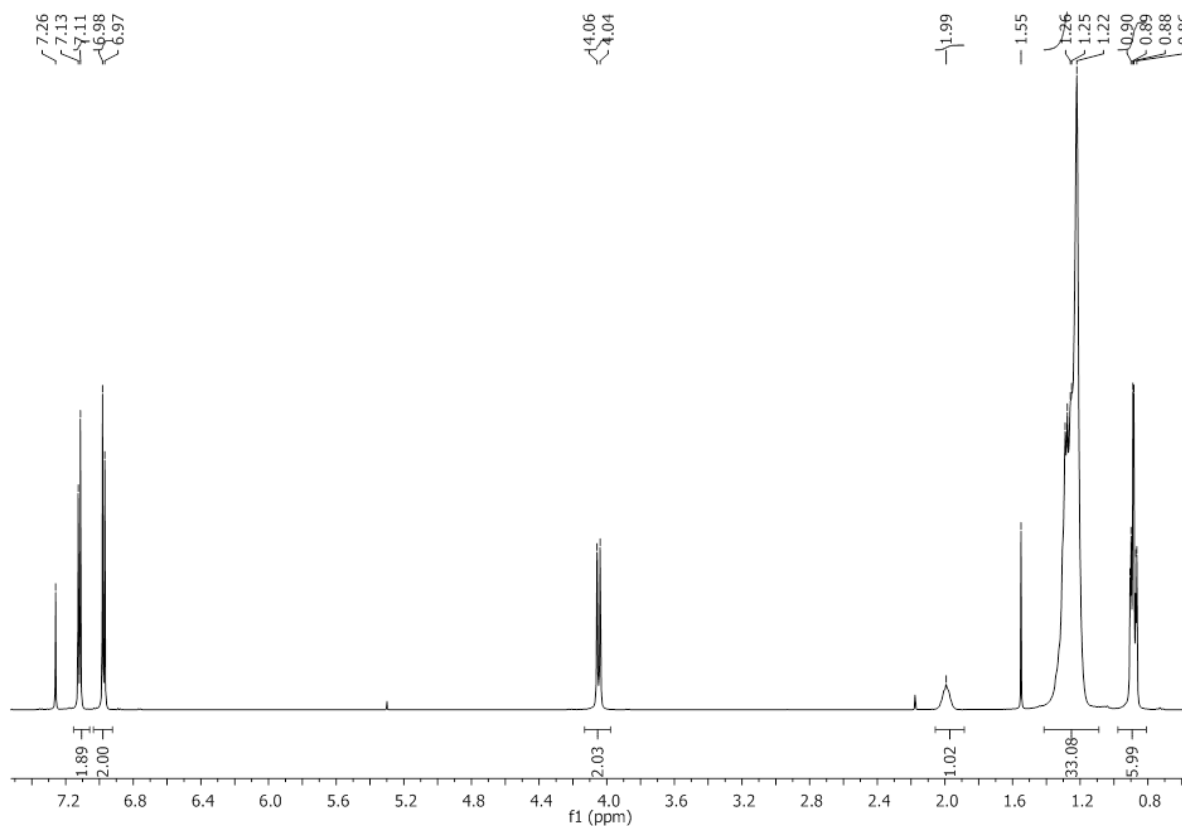


Figure 2.9 ¹H NMR spectrum of dithienopyrrole (DTP) **2.25**.

The ^1H NMR spectrum showed that the pure product had been obtained (Figure 2.9). The two doublets in the aromatic region correspond to the four protons on the thiophene rings. The doublet at 7.11 ppm is due to the protons in the 2 and 6 positions of the DTP unit. The doublet at 4.05 ppm is due to the $-\text{CH}_2\text{CH}-$ protons on the alkyl chain and the broad multiplet at 1.99 ppm represents the $-\text{CH}_2\text{CH}-$ proton on the alkyl chain. The triplet at 0.90 ppm is due to the 6 methyl protons of the alkyl chain.

The stannylation reaction of DTP **2.25** was carried out following the same method used for the stannylation of DTS. Direct lithiation of the monomer followed by addition of trimethyltin chloride yielded the product in high yield (91 %) as a yellow/brown oil which solidified in the freezer.

Product formation (**2.26**) was confirmed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and ESI mass spectrometry. The ^1H NMR spectrum (Figure 2.10) clearly shows the loss of two aromatic protons; instead of two doublets being observed there is one singlet (6.96 ppm) as the protons are no longer coupling to those in the 2 and 6-positions. The presence of the singlet at 0.40 ppm is due to the 18 methyl protons on the tin groups. The $^{13}\text{C}\{^1\text{H}\}$ NMR showed four resonances corresponding to the 8 aromatic carbons of the DTP unit and the molecular ion was observed by electrospray mass spectrometry at 786 m/z . The monomer also passed elemental analysis showing it was of very high purity.

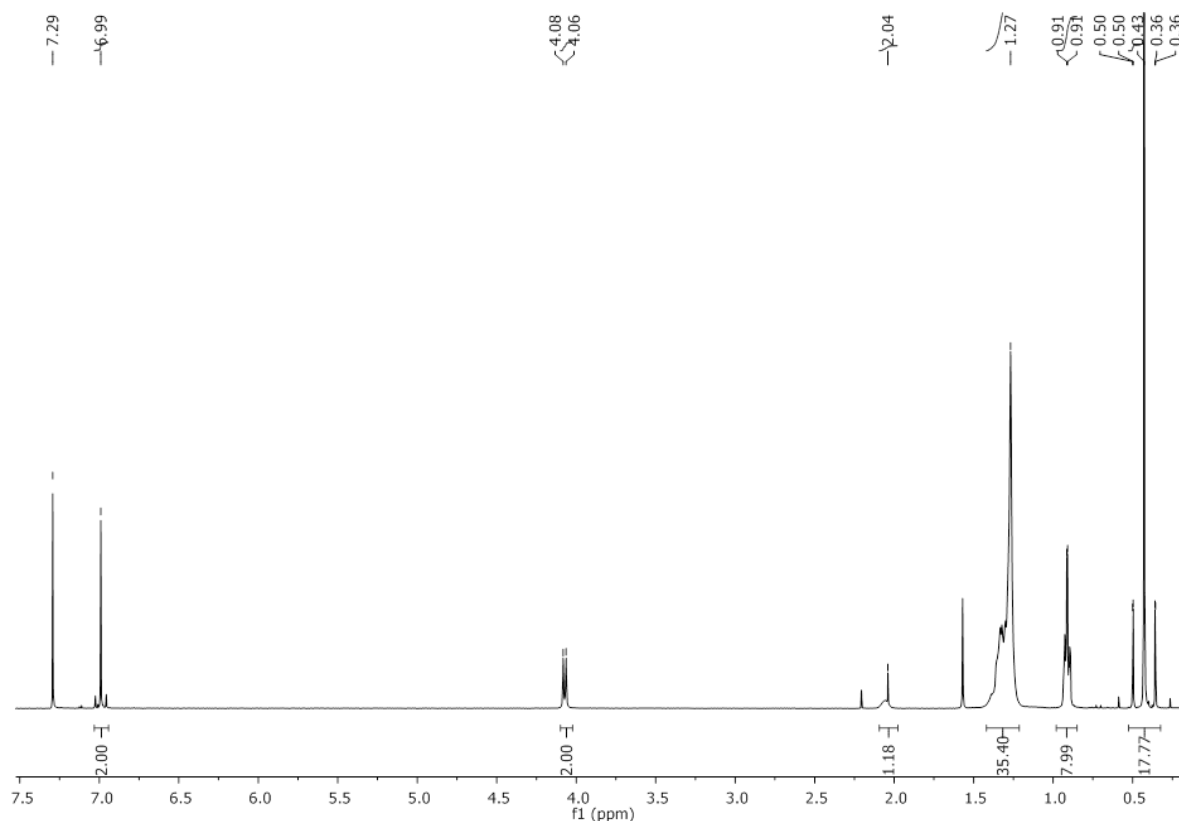


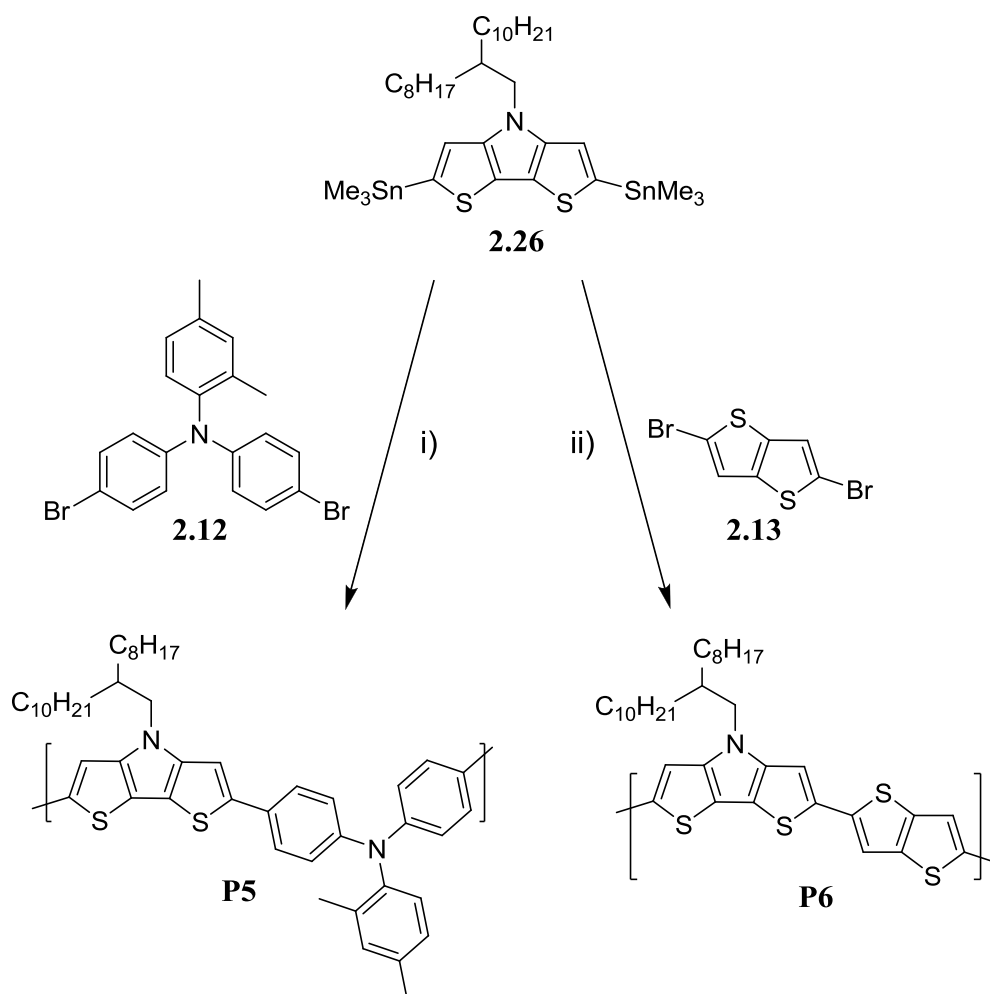
Figure 2.10 ^1H NMR spectrum of the distannylated dithienopyrrole **2.26**.

2.3.3.2 Synthesis of **P5** and **P6**

Both polymers were synthesized via the same microwave assisted Stille cross-coupling reaction conditions using the distannylated DTP **2.26** with either the dibrominated TAA in the case of **P5**, or the dibrominated TT in the case of **P6** (Scheme 2.10).

$\text{Pd}_2\text{dba}_3/\text{P}(\text{o-tol})_3$ was used as the catalyst system and chlorobenzene as the solvent. Also, an equimolar ratio of each monomer was used due to the high purity of **2.26**. After 30 min in the microwave reactor at 200 °C, the reaction mixture was cooled to room temperature and precipitated in acidic methanol. The polymers were purified and low molecular weight oligomers removed following the method reported in Section 2.3.1.3. **P5** was recovered as an orange powder in low yield (30 %) and **P6** as a very insoluble, dark purple powder in 27 % yield. The yields were poor due to the large proportion of low molecular weight oligomers present, which were removed during the Soxhlet extraction. The molecular weight was

estimated by GPC analysis of the polymers, using chlorobenzene as the eluent; **P5** M_n 7, M_w 15 kDa; **P6** M_n 3, M_w 5 kDa. The low molecular weight of **P6** was a result of its poor solubility which caused the polymer to precipitate from solution before high molecular weights could be reached.



Scheme 2.10 Reagents and conditions: i) Pd_2dba_3 , $P(o-tol)_3$, chlorobenzene, 200 °C, 30 min; ii) Pd_2dba_3 , $P(o-tol)_3$, chlorobenzene, 200 °C, 30 min.

Both polymers were characterized by ^1H NMR spectroscopy. Figure 2.11 shows the ^1H NMR spectrum of **P5**. The 13 aromatic protons are observed as two multiplets between 8-7 ppm. The peak at 4.07 ppm is due to the $-NCH_2-$ protons on the DTS unit. The two peaks at 2.40 and 2.09 ppm are due to the methyl groups on the TAA moiety. This confirms that the two monomers have coupled together.

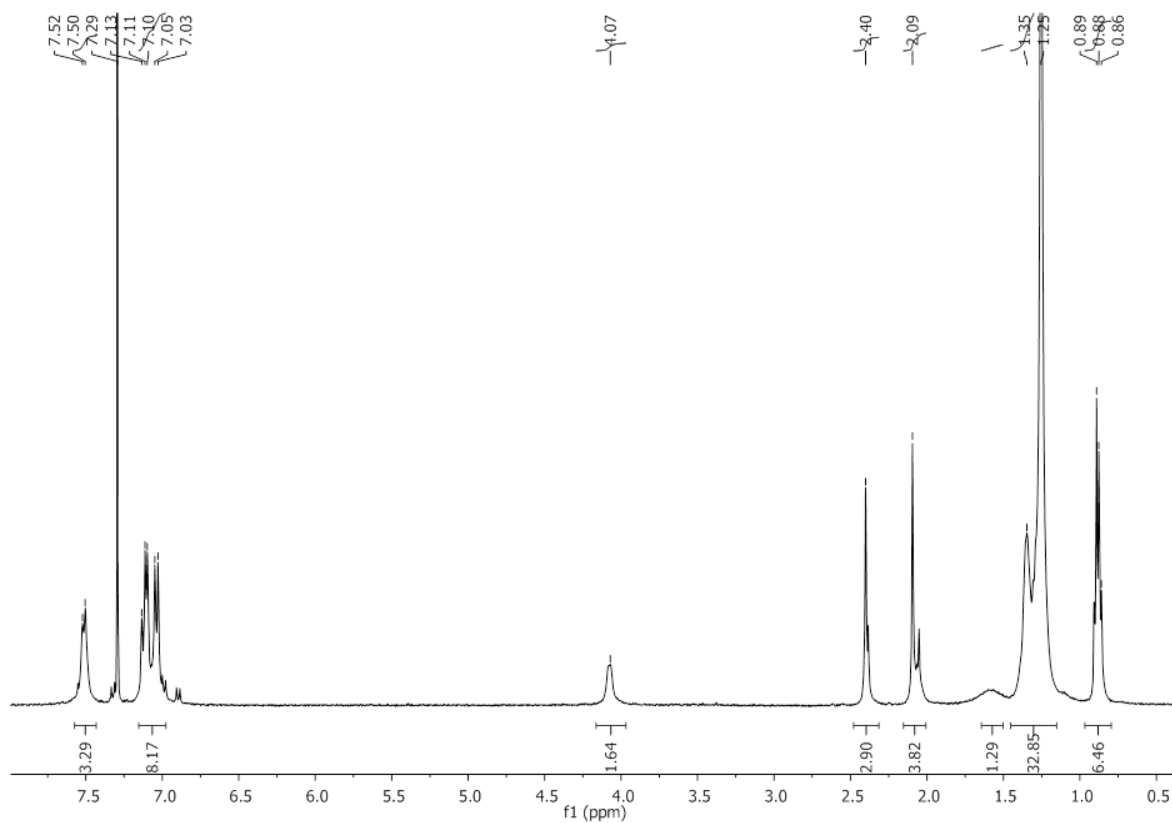


Figure 2.11 ^1H NMR spectrum of **P5**.

Both reactions were repeated under different Stille conditions, using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst, toluene as the solvent and an oil bath for heating (120 °C for 72 h). Unfortunately these conditions gave even poorer molecular weights.

2.3.4 Summary

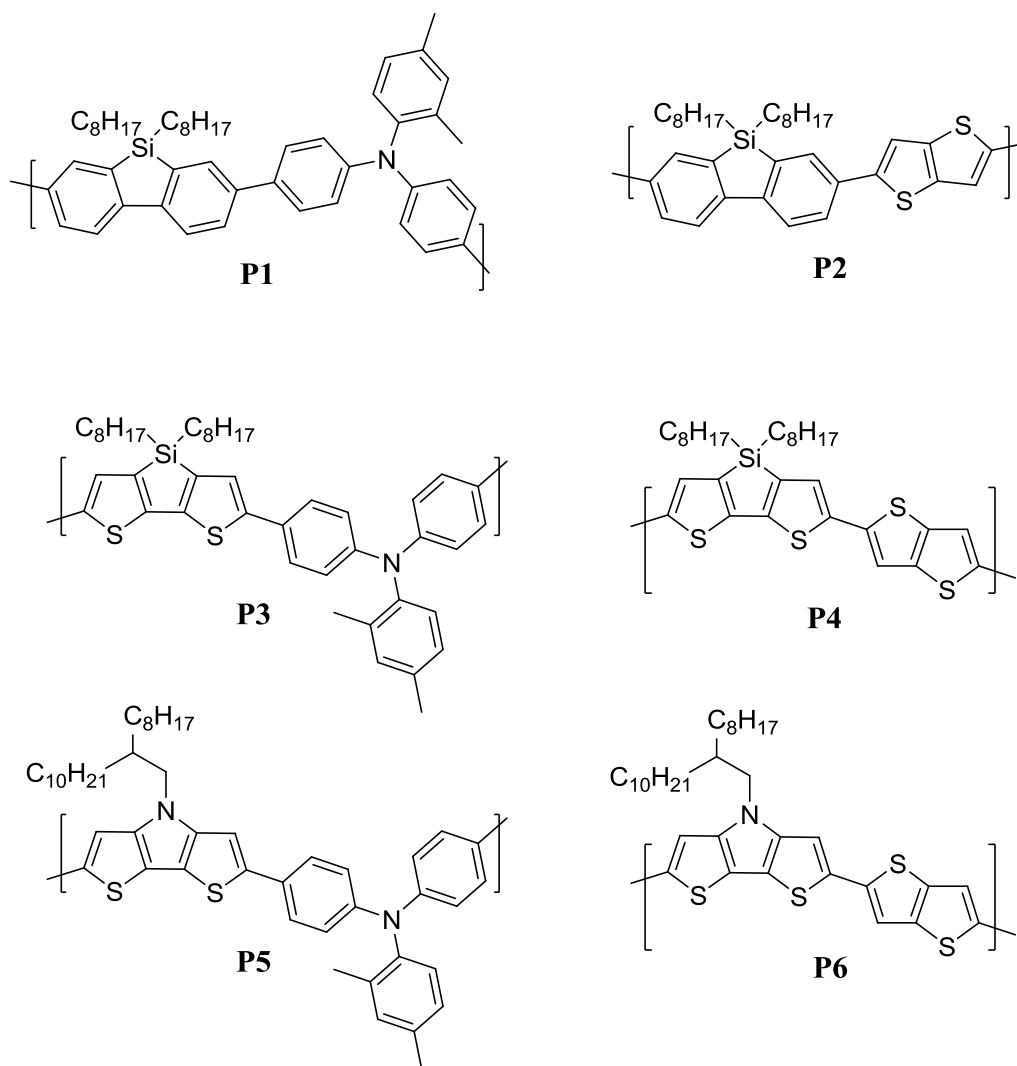
**Figure 2.12** Series of polymers **P1-P6**.

Table 2.3 summarizes the yields and molecular weights obtained for each polymer. It is clear that the Suzuki coupling reactions gave higher molecular weights than the Stille. It has been reported in literature that the boronic ester/acid groups on thiophenes are unstable under Suzuki conditions resulting in low molecular weight polymers, therefore Stille coupling was the preferred route for the DTS and DTP polymerization reactions.⁶⁹ Unfortunately it is not possible to purify the distannylated monomers by column chromatography (unlike the diboronic esters) as they will decompose on silica or alumina to give back the unsubstituted monomer.⁵⁴ Therefore the molecular weights obtainable from the Stille reactions could be limited by the impurities present in the distannylated monomer.

Table 2.3 Summary P1-P6

Polymer	Reaction	Colour	Yield %	M_n/kDa	M_w/kDa	DP
P1	Suzuki	Yellow	38	29	75	42
P2	Suzuki	Yellow/green	42	38	75	68
P3	Stille	Green	21	3.5	8	5
P4	Stille	Red	88	10	16	17
P5	Stille	Orange	30	7	15	9
P6	Stille	Purple	27	3	5	5

2.4 Optical properties and energy levels of P1-P6

The UV-Vis absorption spectra of **P1-P6**, in both solution and thin film, are shown in Figure 2.13 and summarized in Table 2.4. Chloroform was used for the solution spectra as it is a common laboratory solvent. The thin films were spin coated from a solution of the polymer in chlorobenzene as this is the solvent used during device fabrication. The SiF containing polymers, **P1** and **P2**, have a blue shifted absorption, relative to the other materials. It is likely that this is due to the larger steric twist between adjacent co-monomers. As mentioned in Section 2.1, due to steric effects, two alpha hydrogen atoms promote a larger out of plane twist between two coupled phenyl rings, than they would between two coupled thiophenes (Figure 2.3). As predicted, **P2** is red shifted in comparison to **P1**, as the phenyl-thiophene link between adjacent co-monomers, reduces the steric twist, leading to a more planar conformation, improved π -overlap and therefore a reduced band gap. When going from solution to thin film there is no red shift observed for **P1** and **P2**, suggesting there is little order gained in the solid state.

The DTS containing polymers, **P3** and **P4**, have a much lower band gaps which is evident from the red shifted absorption onset with respect to **P1** and **P2**. Due to the flanking thiophenes of DTS, there is a reduced steric twist between the co-monomers, leading to improved π -overlap, which raises the HOMO level (as calculated by photoelectron spectroscopy in air PESA). The absorption maximum of **P4** is red shifted by ~125 nm in comparison to **P3**. This is due to the replacement of TAA with the rigid, planar TT co-

monomer. The LUMO is also lowered leading to a low band gap polymer (1.8 eV). Going from solution to the solid state has little effect on the absorption characteristics of **P3** or **P4**, suggesting negligible solid state packing effects. However, **P4** does exhibit a shoulder on the long wavelength side of the absorption maximum in both solution and the solid state, indicative of solution and solid state aggregation. When studying the GPC curve of **P4** (Figure 2.14b), a shoulder can be seen on the high molecular weight side (low retention time). This could just be due to the distribution of molecular weights, or it could be another indication of solution state aggregation.

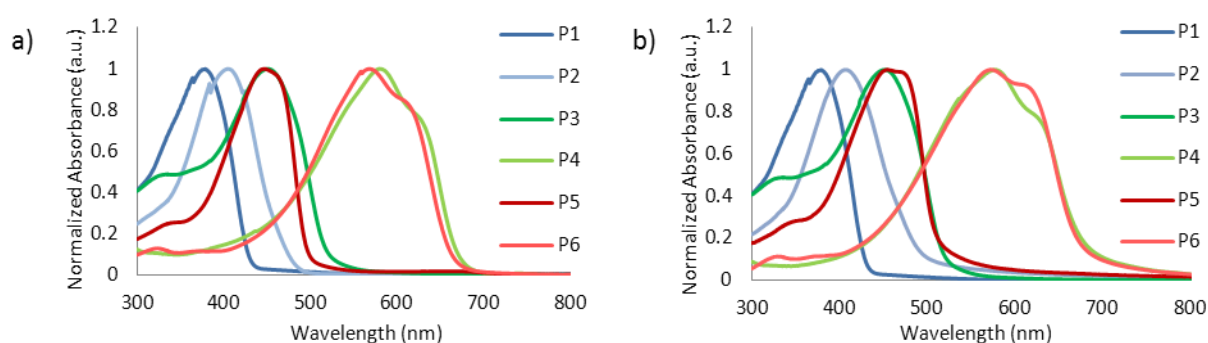


Figure 2.13 a) Solution (in chloroform) UV-Vis spectra of polymers **P1-P6**; b) Thin film (from chlorobenzene) UV-Vis spectra of polymers **P1-P6**.

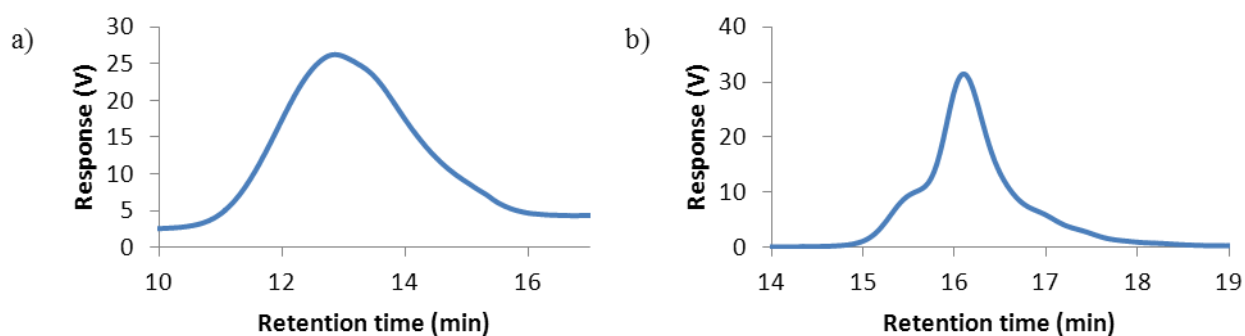


Figure 2.14 GPC curve of a) **P1**; b) **P4** at 80 °C using chlorobenzene as the eluent.

When comparing polymers **P3** and **P5**, the substitution of the DTS unit with a DTP unit results in the HOMO level being raised due to the electron rich nature of DTP. This was not observed when comparing **P4** and **P6**. In this case the band gap and energy levels are not affected by the introduction of the electron rich DTP. This could be due to the low molecular

weight of **P6**, which in turn leads to a lower HOMO level; as at low molecular weights the energy levels can be molecular weight dependent.⁷⁰

In conclusion, it is evident that the TT containing polymers had red shifted absorption maxima and lower band gaps than the TAA containing polymers. This is attributed to the reduced steric twist between adjacent monomers, leading to improved π -orbital overlap. Eliminating the conjugation blocking nitrogen of TAA from the backbone also extends the π -orbital delocalisation. The shoulder on the long wavelength side of the absorption spectra of **P4** and **P6** can be attributed to solid state packing effects, indicating improved π -stacking when TT is incorporated. The use of monomers with flanking thiophenes (DTS or DTP) rather than phenyls (SiF) also leads to reduced conformational disorder, higher HOMO levels and lower band gaps.

Table 2.4 Optical properties and energy levels P1-P6

Polymer	λ_{max} (nm)		E_g (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^e
	soln. ^a	film ^b			
P1	378	379	2.9	-5.7	-2.8
P2	405	406	2.8	-5.7	-2.9
P3	451	451	2.4	-5.3	-2.9
P4	580	576	1.8	-4.9	-3.1
P5	448	454	2.4	-5.0	-2.6
P6	569	568	1.8	-4.9	-3.1

^a Measured in chloroform solution. ^b Spin cast from 5 mg/mL chlorobenzene solution. ^c Estimated from the absorption onset of thin film UV-vis spectra. ^d Measured by ambient photoelectron spectroscopy (PESA). ^e Estimated by addition of E_g to the HOMO.

2.5 OFET studies*

2.5.1 P1 versus P4

Upon analysis of the UV-Vis and energy level data it was predicted that **P4** would be the highest performing OFET material. It possesses the preferred thiophene-thiophene link between adjacent co-monomers and it has a HOMO level that lies close to the work function of a gold electrode (approx. -5 eV): This should reduce the barrier to charge injection. Also, its UV-Vis spectrum suggests the presence of some structural order. **P6** possesses similar characteristics, but due to its low molecular weight, it was not expected to outperform **P4**.

A prediction was also made on which would be the poorest performing material. Due to the phenyl-phenyl links long the backbone in **P1** and its low lying HOMO level (well below that of gold), we expected to observe reduced hole mobilities and high threshold voltages for this polymer.

In order to confirm our hypotheses, OFET devices were fabricated using **P1** and **P4** as the semiconducting layer.

To measure the p-type charge carrier mobility of **P1** a bottom gate-bottom contact (BG-BC) architecture device was fabricated. Si/SiO₂ substrates with lithographically patterned gold electrodes were cleaned by sonication in acetone and IPA. Electrodes were treated with a self-assembled monolayer by immersion in a pentafluorobenzene thiol (PFBT) solution in IPA (1:1000) and then rinsed with neat IPA. Polymer solutions (10 mg/mL in chlorobenzene) were spin coated on the pre-printed substrate at 1500 rpm for 0.5 min and annealed at 100 °C for 2 min. DSC analysis showed no crystallization, melting transitions or decomposition between 40-300 °C.[†]

* All OFET device fabrication in Section 2.5 was carried out by Jeremy Smith, Physics Dept., Imperial College.

[†] DSC analysis carried out by the Stingelin Group, Materials Dept., Imperial College London.

The charge carrier mobility was calculated from the transfer characteristics of the device, in the saturation regime, using previously reported procedures.⁷¹ The results are summarized in Table 2.5 and Figure 2.15a displays the transfer curve obtained from the OFET device (channel length (L)/width (W) of 15/1000 μm) at a drain voltage (V_D) of -10 V and -60 V. The reader is referred to the Appendix A for device output characteristics.

By analysis of the transfer curve it can be seen that a large gate bias was required in order to achieve a small current flowing between the source and drain electrodes. This is evident from the large threshold voltage (-39 V). As predicted, due to the low lying HOMO level, the barrier to injection was too low to achieve efficient charge transfer when a gold electrode was employed. The use of an electrode with a lower work function, such as platinum or molybdenum oxide (MoO_3), may be the answer to obtaining higher drain currents at a lower gate bias. The hole mobility was also very poor, at only $3 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

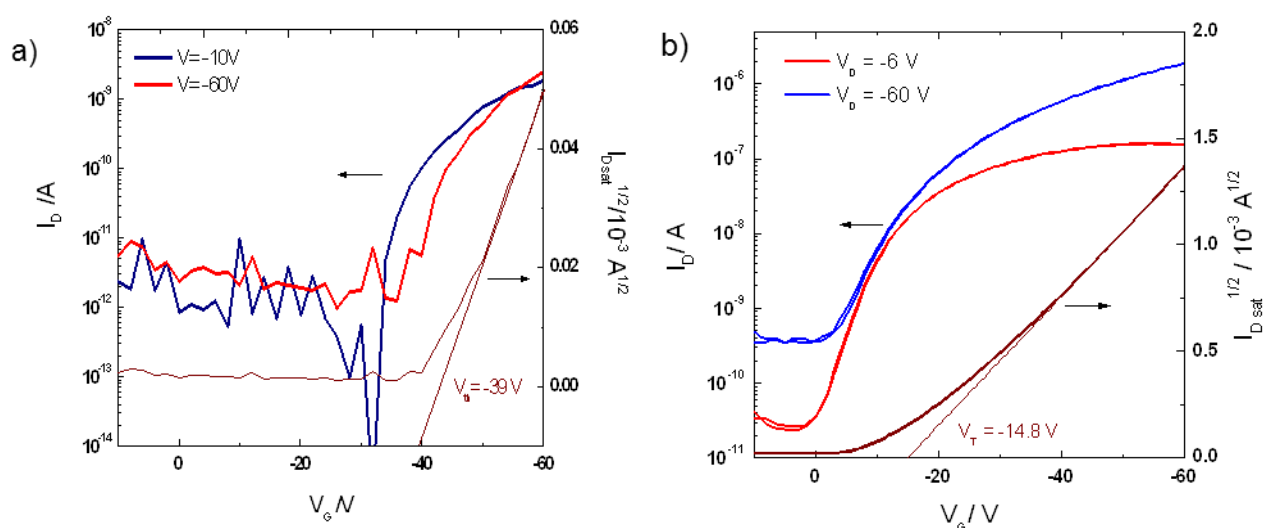


Figure 2.15 Transfer curves of polymers a) **P1**; b) **P4** when used as the semiconducting layer in OFET devices.

To measure the p-type charge carrier mobility of **P4** a top gate-bottom contact (TG-BC) architecture device was fabricated using Au/PFBT electrodes on glass and CYTOP as the dielectric. The polymer was spin coated at 2000 rpm for 0.5 min from a 10 mg/ml solution in

chlorobenzene. The devices were then annealed at 140 °C for 10 min prior to CYTOP deposition.

As for **P1**, the charge carrier mobility of **P4** was calculated from the transfer characteristics of the device, in the saturation regime and found to be $0.05 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Figure 2.15b displays the transfer curve obtained from the OFET device (channel length (*L*)/width (*W*) of 50/1000 μm) at a drain voltage (V_D) of -6 V and -60 V. The reader is referred to the Appendix A for device output characteristics.

In comparison to **P1** the threshold voltage of **P4** is much lower (-15 V). This is attributed to the higher lying HOMO level which reduces the barrier to charge injection. The mobility of the device is also two orders of magnitude higher than that recorded for **P1**. This could be due to the presence of the thiophene-thiophene links, which reduce conformational disorder and increase the conjugation length.⁸ The TT co-monomer has also been shown to promote π -stacking, improving local structural organization which should improve inter-chain charge transport.¹⁶

TG-BC devices were also fabricated using **P1** as the semi-conducting layer but they showed poorer results than those obtained from the BG-BC devices mentioned previously. From these results it can be confirmed that polymer **P4** has superior hole transport mobilities than **P1**. This study has shown that by following a few design criteria, a high performance polymer can be synthesized. The UV-Vis and estimated energy levels can also aid in deducing which polymers will perform the best.

OFET studies are also being carried out on the remaining four polymers, which will provide further information to aid the study.

Table 2.5 Summary of OFET device results

Polymer	Electrodes	Architecture	μ_h (cm ² V ⁻¹ s ⁻¹)	V _{th} (V)	I _{on/off} /A
P1	Au	BG-BC	0.0003	-39	10 ³
P4	Au	TG-BC	0.05	-15	10 ³
PF8-TAA ⁵⁸	Au	TG-BC	0.02	-6	10 ⁶
P1	Au-MoO ₃	TG-BC	0.009	-22	10 ⁴
PF8-TAA	Au-MoO ₃	TG-BC	0.04	-18	10 ⁴

2.5.2 P1 verses PF8-TAA (2.2)

Polymer PF8-TAA **2.2** had previously been shown to perform well in OFET devices.⁵⁸ In the past the replacement of a fluorene unit with a dibenzosilole unit has had a positive effect on transistor mobilities,²⁰ therefore it was of interest to see whether **P1** would exhibit superior mobilities to PF8-TAA **2.2**.

The device mobility of **P1** was compared to that of PF8-TAA **2.2** which had been reported by Zhang *et al.* (Table 2.5).⁵⁸ Unfortunately, the replacement of fluorene with dibenzosilole had led to a decrease in hole mobility by a magnitude of 2. It was believed that due to the low lying HOMO level of **P1**, the mobility was greatly reduced as a result of poor charge injection. In order to address this poor hole injection, it was decided that devices would be fabricated using gold electrodes that had been treated with a layer of molybdenum oxide (MoO₃), effectively lowering the work function of the electrodes.

TG-BC devices were fabricated on glass using Au/MoO₃ electrodes, CYTOP as the dielectric and an Al gate electrode. The polymers were spin coated at 2000 rpm for 0.5 min from a 10 mg/ml solution in chlorobenzene. The devices were then annealed at 100 °C for 5 min prior to CYTOP deposition.

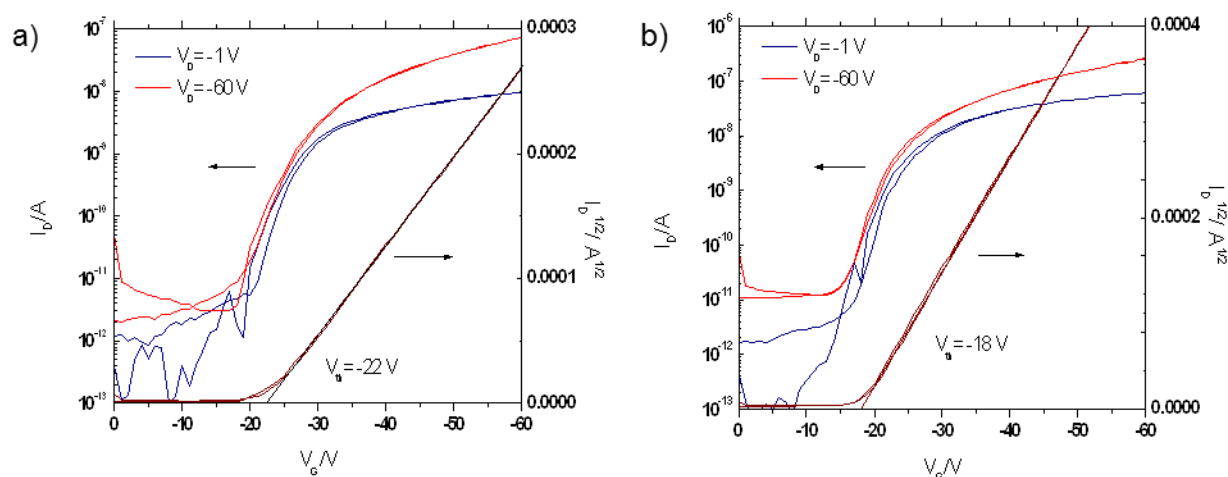


Figure 2.16 Transfer curves of polymers a) **P1**; b) PF8-TAA **2.2** when used as the semiconducting layer in OFET devices employing Au/MoO₃ electrodes.

In contrast to the previous devices, the mobilities were calculated from the transfer characteristics of the device in the linear regime, as the saturation mobilities were found to vary with channel length. Figure 2.16 displays the transfer curves obtained from OFET devices (channel length (L)/width (W) of 50/1000 μm) at a drain voltage (V_D) of -1 V and -60 V. The reader is referred to the Appendix A for device output characteristics. The linear mobilities were averaged over three devices (Table 2.5).

The transfer curves show that the use of the Au/MoO₃ electrodes eliminates any injection problems. Injection is also very good at low drain voltages, which is not observed for the simple Au electrodes. The hole mobility of **P1** has improved by almost 2 orders of magnitude, but it still does not perform as well as PF8-TAA **2.2**. In fact, the mobility of PF8-TAA **2.2** has also improved with the use of the lower work-function electrodes (Table 2.5). The poorer performance of **P1** could be attributed to a change in morphology with the introduction of the silicon atom, which may be detrimental to hole transport. The molecular weights of the polymers are comparable, so this is unlikely to be the cause of the reduced mobility.

Time of flight (TOF) experiments are underway on both polymers. This eliminates the problems associated with charge injection from the electrodes and provides more information on bulk mobility through the materials. Morphological studies (AFM, XRD) will also be carried out to provide insight in to the effect the silicon bridge has on morphology.

2.6 Conclusion

Six novel semi-conducting polymers were synthesized and their energy levels probed by UV-Vis spectroscopy and PESA. It was found that those with thiophene-thiophene links (**P4** and **P6**) had the most red shifted absorption and higher lying HOMO levels.

OFET devices were fabricated using gold source and drain electrodes, with polymers **P1** and **P4**. This study showed that the hole mobility of a device could be increased by two orders of magnitude by following two simple design rules:

- 1) The use of co-monomers with flanking thiophenes
- 2) The use of planar, conjugated co-monomers, such as TT

A comparison of OFET performance between **P1** and PF8-TAA **2.2** was also carried out in order to investigate the replacement of a C bridge with a Si bridge. With the use of Au electrodes, PF8-TAA **2.2** had a far superior hole mobility. This was attributed to the low lying HOMO level of **P1** which led to hole injection problems. Therefore devices were fabricated using Au/MoO₃ electrodes, which had a lower work function. The result was an increase in the hole mobility of **P1**, but it was still inferior to that of PF8-TAA **2.2**. Further investigations are underway to assess the differences in performance of the two materials.

2.7 Expansion of DTP series

The next series of polymers to be investigated were based on donor-acceptor type materials, where DTP acts as the donor. This would lead to low band gap materials which could be used in OPV devices.

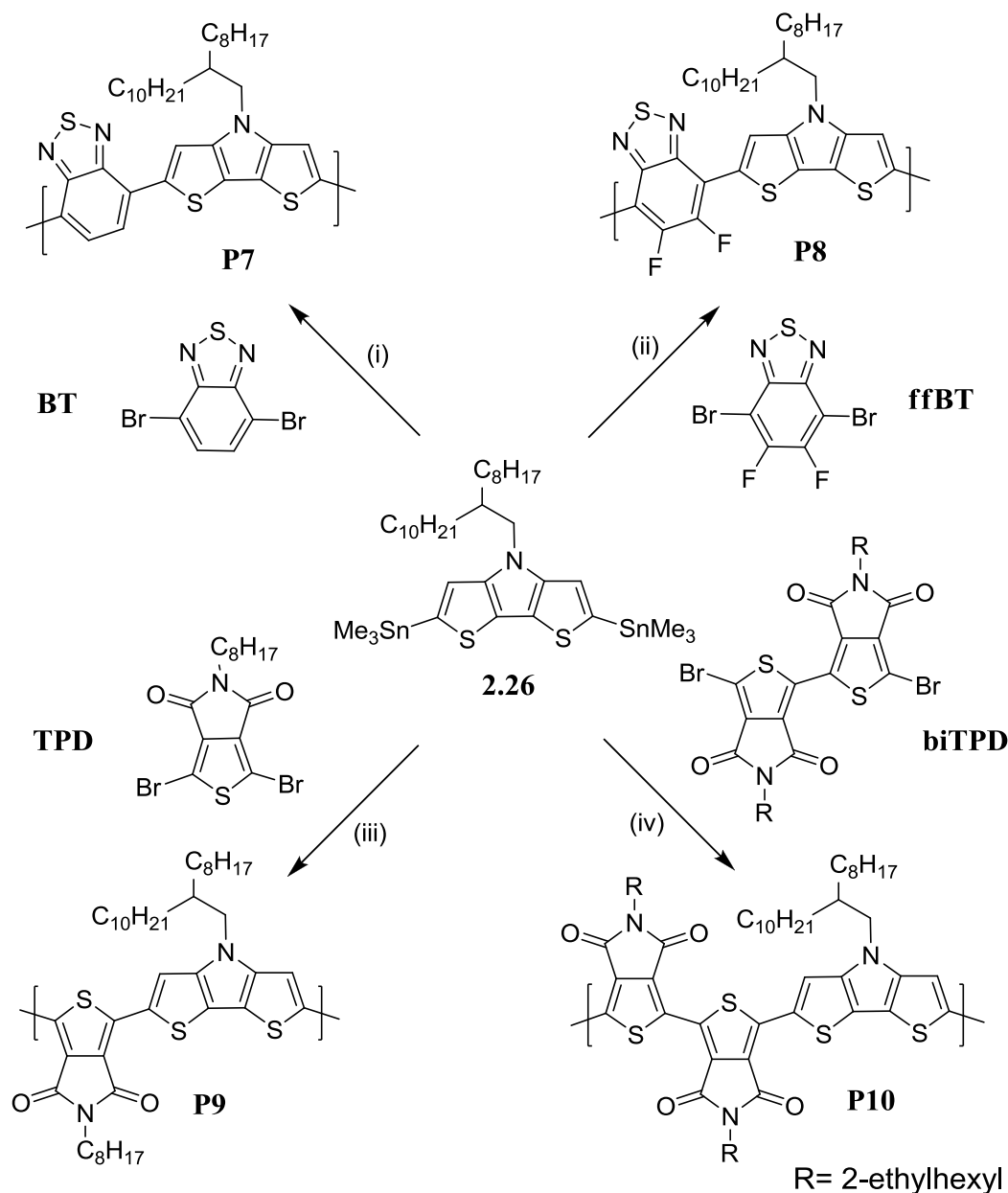
A lot of work has been reported on low band gap DTP containing polymers. For example, it has been copolymerized with the ubiquitous benzothiadiazole (BT)⁷²⁻⁷⁵ and more recently with the thienopyrrolodione unit (TPD)^{54, 76, 77} and tested in both OFET and OPV devices. Unfortunately the BT unit cannot sufficiently lower the HOMO level of the polymers, which results in a low V_{oc} when tested in OPV devices.^{73, 75} With the introduction of the thienopyrrolodione unit, it acts to lower the HOMO, increasing the V_{oc} from around 0.4 eV to 0.7 eV, which should improve device performance.^{75, 77} However, there has never been a comparative study between BT and TPD copolymers of DTP. In every study different alkyl chains have been used on the DTP unit which greatly affects morphology and consequently device performance. It was therefore interesting to study the effect of changing the comonomer from BT to TPD, whilst maintaining the same alkyl chain length throughout.

In order to improve device performance further the difluorobenzothiadiazole (ffBT) and 1,1'-bithienopyrrolodione (biTPD) units were considered. The ffBT unit has previously been shown to lower the HOMO level in relation to BT containing polymers,³¹ however there is also expected to be S-F short contact interactions between neighbouring monomers, which should enhance planarity and therefore raise the HOMO level.⁷⁸ Therefore we expect to see a small stabilization of the HOMO. The biTPD unit has been reported to lower the LUMO level significantly in relation to TPD containing polymers, and to a lesser extent lower the HOMO level.⁷⁹ Overall this should lead to an improved V_{oc} and a reduced band gap which should improve the J_{sc} .

2.7.1 Aim

The aim of this study is to synthesize a series of DTP containing polymers with the 1-octyl-2-dodecyl side chain used in the previous study. The distannylated DTP unit will be

copolymerized via Stille cross coupling reactions, with the dibrominated BT, ffBT, TPD and biTPD units to form the polymers **P7-P10** shown in Scheme 2.11. The effect of changing the co-monomer from BT to TPD (**P7** to **P9**) on OPV performance, will be investigated. It was also of interest to see how the addition of the two fluorine groups to BT (**P7** to **P8**) or the addition of an extra TPD unit (**P9** to **P10**) could change the materials performance.



Scheme 2.11 Reagents and conditions: i) $Pd(PPh_3)_4$, xylene, 180 °C, 40 min; ii) $Pd(PPh_3)_4$, toluene, 120 °C, 72 h; iii) Pd_2dba_3 , $P(o-tol)_3$, chlorobenzene, 200 °C, 30 min; iv) $Pd(PPh_3)_4$, toluene, 120 °C, 72 h.

2.7.2 Synthesis of P7 and P9*

The catalyst used most often in literature for the polymerization of distannylated DTP **2.26** is $\text{Pd}(\text{PPh}_3)_4$, therefore this catalyst was used, along with xylene as the solvent, for the polymerization of **P7** and **P9**. As **2.26** was of high purity, an equimolar ratio of monomers was used. The reactions were then heated in a microwave reactor at 180 °C for 40 min. Analysis of the purified polymers by GPC, using chlorobenzene as the eluent, showed **P7** had a M_n 10, M_w 18 kDa; **P9** had a M_n 6, M_w 9 kDa. **P7** was isolated as a dark green powder in 51 % yield.

The molecular weight of **P9** was quite low so the reaction was repeated, this time using a catalyst system which is very reactive under Stille conditions; $\text{Pd}_2\text{dba}_3/\text{P}(\text{o-tol})_3$. Chlorobenzene was used as the solvent and the reaction was heated for 30 min at 200 °C. After work up and purification the dark blue polymer was recovered in 42 % yield. The GPC analysis showed the resulting polymer had a M_n 7 and M_w 12 kDa, which was an improvement on the previous attempt. The results are summarized in Table 2.6.

2.7.3 Synthesis of P8 and P10†

Polymers **P8** and **P10** were made from a batch of **2.26** which was slightly impure. Therefore these polymerizations were carried out using a DTP:ffBT (or biTPD) ratio of 1.1:1. For **P8** a catalyst system of $\text{Pd}_2\text{dba}_3/\text{P}(\text{o-tol})_3$ was used, with chlorobenzene as the solvent and the reaction was heated for 30 min at 120 °C. Unfortunately due to the poor solubility of this polymer only 10 mg of higher molecular weight polymer (M_n 6, M_w 16 kDa) was obtained from the chlorobenzene fraction after Soxhlet extraction.

The reaction was repeated using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst, toluene as the solvent and it was heated for 72 h at 120 °C. This time 19 % yield was obtained from the chloroform fraction, but it was of low molecular weight (M_n 6, M_w 10 kDa) and 9% yield was obtained from the

* BT and TPD supplied by McCulloch group, Chemistry Dept., Imperial College London.

† ffBT and biTPD supplied by Christophe Grenier, Plextronics Inc., Pittsburgh, USA.

chlorobenzene fraction which was of acceptable molecular weight (M_n 9, M_w 17 kDa). The higher molecular weight fraction was used for characterization of the polymer.

For **P10** Pd(PPh₃)₄ was used as the catalyst, toluene as the solvent and it was heated for 72 h at 120 °C. The resulting purified polymer was isolated from the chloroform fraction in 30 % yield with M_n 7, M_w 9 kDa. The yield was low due to the high percentage of low molecular weight oligomers which were removed during Soxhlet extraction.

Table 2.6 Summary P7-P10

Polymer	Colour	Yield %	M_n /kDa	M_w /kDa	DP
P7	Dark green	51	10	18	17
P8	Dark green	9	9	17	14
P9	Dark blue	42	7	12	10
P10	Dark blue	30	7	9	7

The polymers were characterized by ¹H NMR spectroscopy. The resonances in the polymer spectra are much more broadened than that observed for the monomers. In every case we see the presence of DTP peaks in the aromatic and alkyl regions, as well as the peaks corresponding to the co-monomer. This confirmed that the monomers had coupled to form the polymers shown in Scheme 2.11.

2.7.4 Optical properties and energy levels of P7-P10

The UV-Vis solution and thin film spectra of all four polymers are shown in Figure 2.17. When going from solution to thin film, **P7** and **P8** experience a significant red shift in their absorption maxima, a result of what appears to be the longer-wavelength shoulder increasing in intensity and becoming the dominant feature. In the case of **P8** this longer-wavelength shoulder is prominent in the solution phase, which can be attributed to solution state aggregation. This shoulder increases in intensity in the solid state due to a large proportion of

solid state aggregation.⁸⁰ This indicates that the introduction of the ffBT unit, over BT, has contributed to the planarization of the conjugated backbone, and lead to an enhanced π -stacked microstructure. **P9** and **P10** do not exhibit large red shifts in their absorption maxima, on going from solution to thin film. This suggests that the TPD units do not promote π -stacking, leading to highly amorphous polymers.

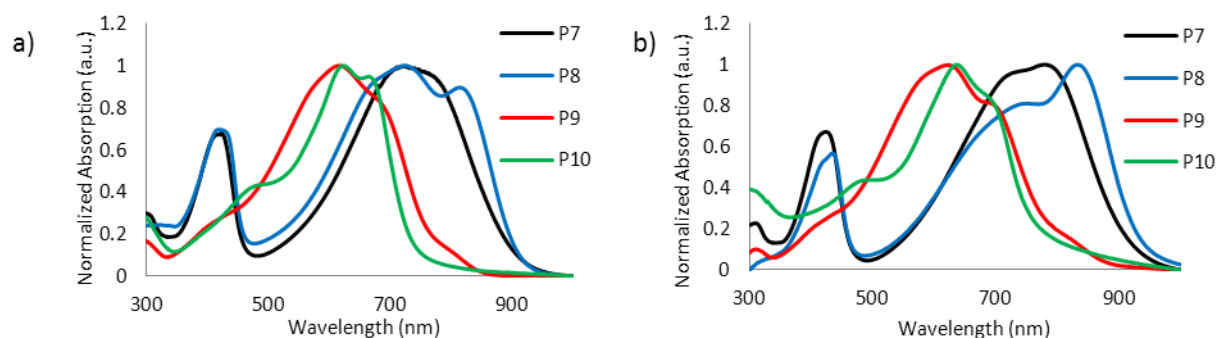


Figure 2.17 a) Solution (in chloroform) UV-Vis spectra of polymers **P7-P10**; b) Thin film (from chlorobenzene) UV-Vis spectra of polymers **P7-P10**.

The band gaps were estimated from the absorption onset of the polymers UV-Vis absorption spectra in the solid state and the HOMO levels were estimated by PESA (Table 2.6). When the BT unit of **P7** is replaced by ffBT (**P8**) a reduction in the band gap of 0.1 eV, is observed. This is a result of the addition of the fluorine groups, which decreases the electron density of the benzene ring. The results are in agreement with the literature.³¹

When comparing the energy levels of the BT containing polymer **P7**, with the TPD containing polymer **P9**, a reduction in the HOMO level is observed with little effect on the LUMO level. This results in an increase in the optical band gap. This was expected as the electron rich imide groups of the TPD unit contribute to the stabilization of the HOMO level, while having little effect on the LUMO level.⁸¹

The biTPD containing polymer **P10**, exhibited a stabilization of both HOMO and LUMO levels to the same extent, in comparison to **P9**. This was unexpected as the literature reports a

larger stabilization of the LUMO level and therefore a reduction in the band gap. It was possible that the low molecular weight of **P10** compared to **P9**, leads to a lower than expected HOMO level and a higher than expected LUMO level. This could help explain why we don't see the predicted reduction in the band gap. However, the reduction in the HOMO level should aid in improving the V_{oc} when tested in OPV devices.

Table 2.7 Optical properties and energy levels of P7-P10

Polymer	λ_{max} (nm)		E_g (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^e
	soln. ^a	film ^b			
P7	726	780	1.4	-4.7	-3.3
P8	726	823	1.3	-4.9	-3.6
P9	617	623	1.6	-4.9	-3.3
P10	624	636	1.6	-5.2	-3.6

^a Measured in chloroform solution. ^b Spin cast from 5 mg/mL chlorobenzene solution. ^c Estimated from the absorption onset of thin film UV-vis spectra. ^d Measured by ambient photoelectron spectroscopy (PESA). ^e Estimated by addition of E_g to the HOMO.

2.7.5 OPV properties of P7-P10

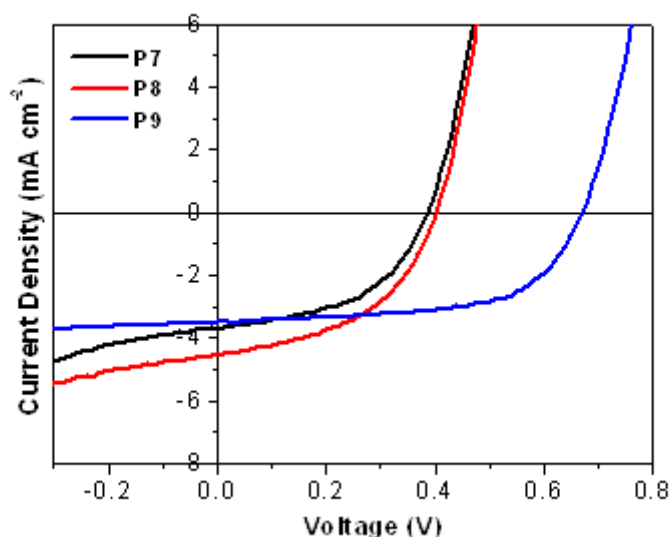
Solar cells were fabricated with all four polymers using the device structure ITO/PEDOT:PSS/Polymer:PC₇₁BM/Ca/Al.* The J - V characteristics are illustrated in Figure 2.18 and the properties are summarized in Table 2.8. The active layers were spin-coated from 1,2-dichlorobenzene (DCB), with a blend ratio of Polymer:PC₇₁BM of 1:3 (w/w). Having such high fullerene weight requirements also necessitates the use of PC₇₁BM, rather than PC₆₁BM, as an electron acceptor, in order to increase the optical absorption of the blend film. Unfortunately, due to the poor solubility of **P10**, smooth films could not be obtained and reliable device performance measurements could not be made.

* OPV fabrication and testing carried out by S. Ashraf, McCulloch group, Imperial College London, SW7 2AZ.

Table 2.8 Photovoltaic properties of polymer solar cells incorporating P7-P9:PC₇₁BM blends

Polymer	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	FF	PCE (%)
P7	3.68	0.38	0.49	0.68
P8	4.55	0.40	0.47	0.85
P9	3.46	0.67	0.61	1.41

When comparing the BT containing polymer **P7**, with the TPD containing polymer **P9**, it is clear that the addition of the TPD monomer results in a significant improvement in PCE from 0.68 % to 1.41 %. The J_{sc} values are comparable, with the **P7** blend being slightly higher as a result of the lower band gap, but the difference in V_{oc} is large. As predicted, the lower HOMO level of **P9** manifests itself as an increase in V_{oc} . The fill factor of the **P9** blend is also much higher, possibly due to the extra solubilizing group on the nitrogen of the TPD moiety. This could allow for better mixing of the polymer with the fullerene, creating a morphology which was more favourable for charge separation and transport. AFM studies will be carried out on the blends in the future.

**Figure 2.18** J - V characteristics of polymer(**P7-P9**):PC₇₁BM blends prepared at a blend ratio of 1:3 (w/w).

As predicted, the addition of two fluorine groups to the benzothiadiazole unit, on-going from **P7** to **P8**, led to an overall increase in PCE of the blend. Due to the reduced band gap of **P8** compared to **P7**, the J_{sc} has increased. However, the lowering of the HOMO level by 0.2 eV was predicted to increase the V_{oc} , but it has actually made little difference. This could be a result of experimental error associated with the measurement of the HOMO level and in reality the HOMO levels of **P7** and **P8** may be very similar. The fill factors are comparable for both blends, suggesting a similar morphology.

2.8 Conclusions

Four low band gap polymers **P7-P10** were synthesized, all employing dithienopyrrole as the electron rich unit. They were characterized by ^1H NMR spectroscopy, UV-Vis spectroscopy and PESA.

They were then tested as the donor polymer in polymer:fullerene BHJ solar cells. Unfortunately smooth films could not be obtained for **P10**, so the PCE could not be measured. The polymer which exhibited the highest PCE was **P9**. It has the largest V_{oc} due to its low lying HOMO and a high fill factor of 0.61, possibly due to a blend morphology which is more conducive to charge separation and charge extraction.

Chapter 3:

Pyrroloindacenodithiophene (NIDT) Containing Polymers for OFET and OPV Devices

3.1 Introduction

As mentioned previously in Section 2.1, the mobility of a methyl substituted triarylamine polymer (**2.1**) is enhanced by the incorporation of bridged phenyl units, namely fluorene and indenofluorene.⁵⁸ The mobility is improved two fold on going from the fluorene containing polymer (**2.2**) to the indenofluorene containing polymer (**2.3**). Zhang *et al.* state that an increase in polymer backbone planarity, and therefore persistence length, leads to an improvement in intramolecular π -orbital overlap, as well as improving local structural organization.⁵⁸ This, in turn, leads to improved charge transport in the devices. It was, therefore, interesting to study the effect of increasing the conjugation length of the DTP containing polymers (**P7-P10**) to see if this would improve their OPV performance. It was also likely that this new series would exhibit good hole transport mobilities in OFETs.

Indacenodithiophene (IDT) is a versatile conjugated unit when copolymerized with appropriate monomers, enabling high performing field effect transistors and solar cells (Figure 3.1).^{57, 65} With its rigid, planar, conjugated structure, conformational disorder is minimized, which contributes to high charge carrier mobility. Whereas the electron rich nature of the peripheral thiophene units facilitates molecular orbital hybridization with electron poor co-monomers, leading to low band gap polymers. The thiophene links along the backbone promote coplanarity by reducing the steric twist between adjacent aromatic units (Section 2.1), enhancing π -conjugation and intermolecular π -stacking.⁸¹ The bridging heteroatoms offer both a centre for solubilizing functionality, and a versatile position to fine-tune the molecular orbital energy levels.

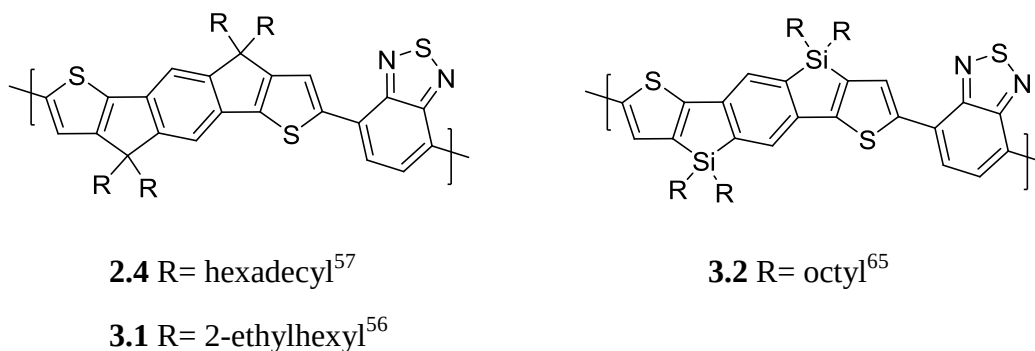


Figure 3.1: Series of IDT polymers with different side chains and bridging groups.

Table 3.1 Table summarizing the electronic properties and performance of three IDT containing polymers

Polymer	HOMO/eV ^a	E _g /eV ^b	μ _h /cm ² V ⁻¹ s ⁻¹	PCE
2.4 ⁵⁷	-5.4	1.7	1.2	0.7
3.1 ⁵⁶	-5.3	1.7	0.57	5.5
3.2 ⁶⁵	-5.5	1.8	0.008	4.3

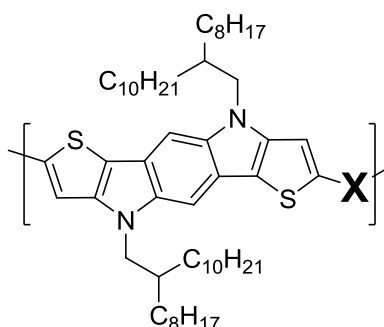
^a Measured by ambient photoelectron spectroscopy (PESA). ^b Band gap estimated from the absorption onset of thin film UV-vis spectra.

For example, polymers employing the carbon bridged unit poly(indacenodithiophene-co-benzothiadiazole) (PIDT-BT) exhibited very high hole mobilities ($\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) when tested in OFET devices, particularly when the solubilizing side chains were hexadecyl (**2.4**).⁵⁷ More recently, variation of the alkyl chains on the bridging carbons has led to excellent performance of PIDT-BT in solar cells.⁵⁶ When 2-ethylhexyl side chains are employed as the solubilizing groups (**3.1**), then a PCE as high as 5 % can be reached.⁵⁶ The silicon bridging analogue poly(silaindacenodithiophene-co-benzothiadiazole) (PSiIDT-BT) **3.2** showed reduced mobility in OFETs, but a high power conversion efficiency (PCE) of ~ 4 % in solar cell devices, with a larger open circuit voltage (V_{oc}) than the carbon bridged polymer, due to the contribution of the silicon to lower the HOMO energy level.⁶⁵ Unfortunately the reduction in HOMO level could be a reason why a drop in mobility is observed, as it can create a barrier to charge injection. These results are summarized in Table 3.1.

3.2 Aims

The aim of this study was to synthesize the pyrroloindacenodithiophene (NIDT) unit and copolymerize it with BT, ffBT, TPD and biTPD (Figure 3.2). Replacing the bridging heteroatom of the indacenodithiophene unit with the more electron donating nitrogen atom should further promote molecular orbital hybridization, leading to lower bandgaps, whereas the electron rich nature of the backbone should promote good hole transport. High charge carrier mobility is important not only in organic transistors, but can be beneficial in OPVs as this should increase both the fill factor, and also the J_{sc} . Unfortunately, the V_{oc} would be expected to be slightly reduced as the introduction of a more electron rich donor unit would

be likely to raise the HOMO level of the donor polymer, though this may be beneficial for reducing the injection barrier in OFETs.⁵⁴



3.3

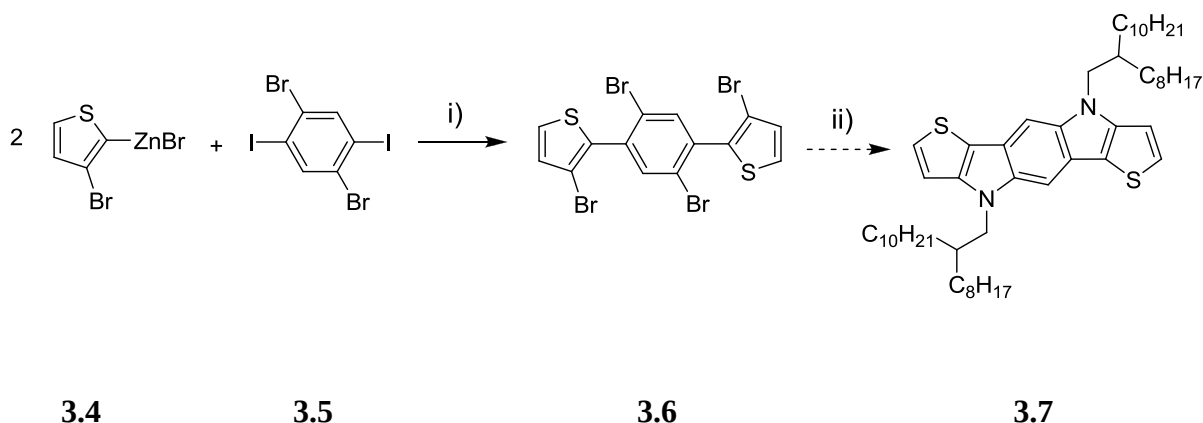
Figure 3.2 NIDT unit copolymerized with an acceptor unit; X= BT, ffBT, TPD, biTPD.

We not only want to compare the NIDT containing polymers with their carbon and silicon analogues, but we also want to make a comparison with the DTP series from the previous chapter, to see how using a more rigid, highly conjugated unit will effect polymer OPV performance.

3.3 Synthesis of Pyrroloindacenodithiophene (NIDT)

3.3.1 Buchwald-Hartwig amination

The first proposed synthetic route was analogous to the method used by Koeckelberghs *et al.* in the synthesis of dithienopyrroles,⁸² which applied a palladium catalysed Buchwald-Hartwig amination reaction, detailed in Section 2.3.3.1. The same amine (2-octyldodecylamine) was also used to allow for easy comparison between DTP and NIDT containing polymers. The route is shown in Scheme 3.1.



Scheme 3.1 *Reagents and Conditions:* i) $\text{Pd}(\text{PPh}_3)_4$, THF, 65 °C, 8 h; ii) Pd_2dba_3 , BINAP, NaO^tBu , 2-octyldodecylamine, xylene, 200 °C, 2 h.

3.3.1.1 Synthesis of 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) 3.6

The starting material **3.6** was synthesized via the method reported by Ashraf *et al.* which involves the Negishi cross-coupling reaction of 1,4-dibromo-2,5-diiodobenzene **3.5** and the organozinc reagent **3.4**.⁶⁵ The reaction was carried out under nitrogen, using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst and THF as the solvent. The resulting mixture was heated at 65 °C for 8 h, then cooled and worked up. The product was used in the next step without further purification. The ^1H NMR spectrum was in agreement with the literature values.⁶⁵

3.3.1.2 Buchwald-Hartwig Amination reaction

In the synthesis of NIDT **3.7** two rings are formed concurrently, so it was envisaged that more forcing conditions would be required. Instead of refluxing in toluene overnight under nitrogen, as had been done in the synthesis of DTP, xylene was used as the solvent and the reaction was heated to 170 °C in the microwave for 2 h (Scheme 3.1).

An aqueous work up was carried out on the reaction mixture and the crude red oil was purified by column chromatography (silica gel, hexane). Some starting material was recovered ($R_F = 0.14$) and another unknown fraction was collected ($R_F = 0.10$). The ^1H NMR spectrum (Figure 3.3) of the unknown compound indicated it could be the mono-aminated product **3.8**. Palladium catalysis favours insertion into Ar-Br bonds when the aromatic group

is electron poor, therefore it was likely that the amine group would be attached to the phenyl and not the thiophene.⁸³ The ^1H NMR spectrum also confirmed this; the now inequivalent phenyl protons were shifted from a singlet at 7.74 ppm in the starting material, to two singlets at 7.44 and 6.71 ppm due to the electron donating nature of the amine group. The four thiophene protons had also become inequivalent and appeared as four doublets. Mass spectrometry confirmed that this species had been isolated with the molecular ion peak observed at m/z 733.

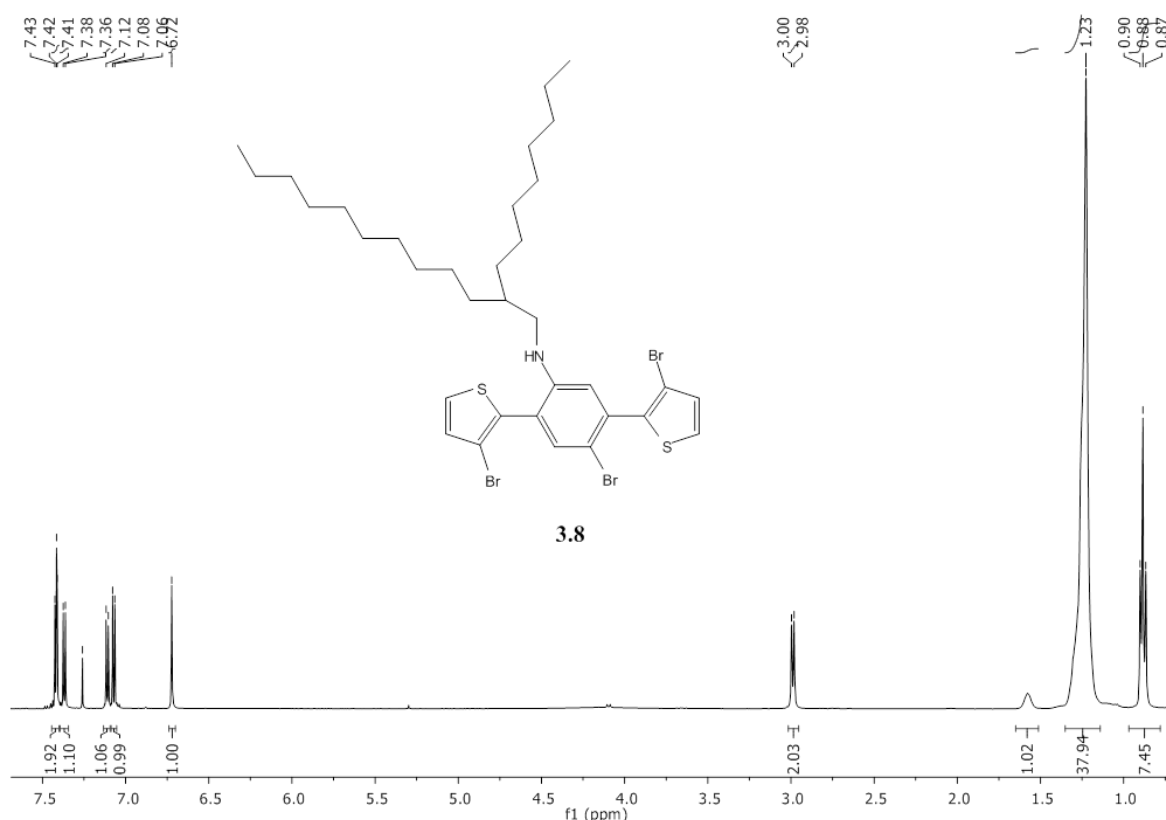
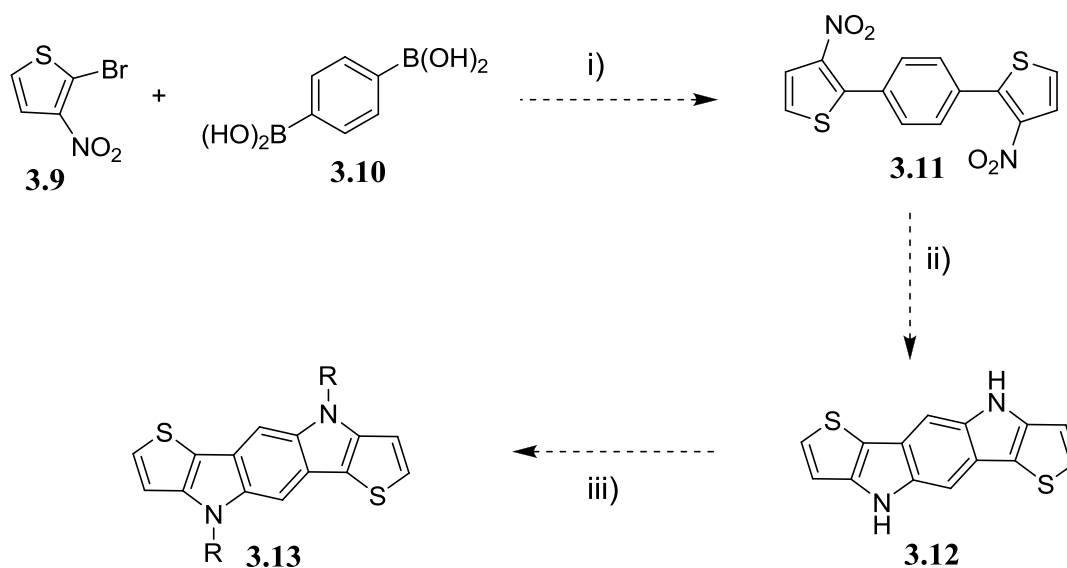


Figure 3.3 ^1H NMR of mono-aminated product **3.8**.

This reaction was repeated a second time using the same conditions, only this time oxygen was more rigorously excluded from the system. Unfortunately the same mono-coupled product **3.8** was isolated once more.

3.3.2 Cadogan Cyclization

It was decided that a new route to the monomer would have to be proposed. Research in to the different methods for carbazole synthesis found that Cadogan cyclization, which involves the ring closure of a NO₂ group, could be an effective route to the product.⁸⁴ This method would also allow the synthesis of the fully ring closed product before adding on the alkyl side chains to the N-bridge, giving us the opportunity to synthesize a series of different monomers by varying the alkyl side chains. Unfortunately this method was likely to have solubility issues as the intermediates would have no solubilizing side chains.



Scheme 3.2 Proposed alternative route to monomer; *Reagents and conditions:* i) Pd(PPh₃)₄, aq. K₂CO₃, toluene, 20 h, 110 °C; ii) PPh₃, *o*-dichlorobenzene 17h, 150 °C; iii) RBr, aq. NaOH, DMSO.

3.3.2.1 Synthesis of 2-bromo-3-nitrothiophene 3.9

This synthesis followed the method reported by Sánchez-Sixto *et al.* where nitric acid was added dropwise to a solution of 2-bromothiophene at -5 °C.⁸⁵ The reaction mixture was left in the freezer overnight and the next day an aqueous work up was carried out and the yellow solid was purified by column chromatography (silica gel, hexane: diethyl ether, 9:1, R_F= 0.57) to give a yellow/orange solid. This was recrystallized from hexane to give yellow needle like crystals in a moderate yield (57 %). The ¹H NMR spectrum was in agreement with literature.⁸⁵

3.3.2.2 Suzuki coupling reaction

The first attempt used a $\text{Pd}(\text{PPh}_3)_4$ catalyst, with potassium carbonate base and toluene as the solvent. This was heated for 20 h at 110 °C. TLC analysis showed the presence of a new compound which was believed to be the product. Unfortunately once the crude product was purified by column chromatography (silica gel, hexane:DCM, 3:1, $R_F = 0.21$) the ^1H NMR spectrum showed that this was in fact the mono-coupled product and deborylation of the benzene ring had occurred. We expected to see three aromatic peaks each corresponding to 2 protons, but instead we observed two doublets corresponding to the thiophene protons and two multiplets corresponding to the 5 protons on the deborylated benzene ring (Figure 3.4).

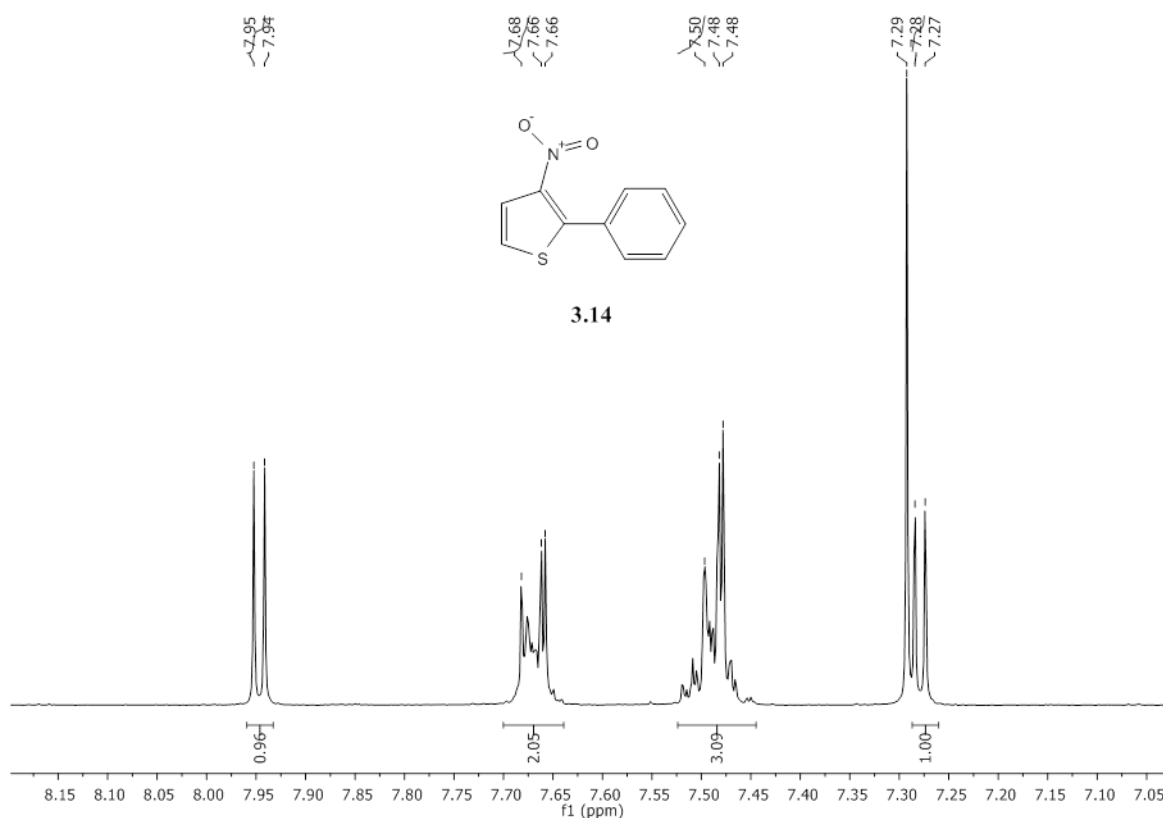


Figure 3.4 ^1H NMR spectrum of mono-coupled product **3.14**.

The second attempt used a $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ catalyst system, with aqueous potassium carbonate as the base once more. This time the solvent system was a 1:1 mixture of toluene and ethanol. The ethanol was used to provide a phase transfer medium as the boronic acid would be more soluble in the aqueous layer and the thiophene would be soluble in the organic layer. Upon purification of the crude product, by column chromatography (silica gel, hexane:DCM, 3:1),

the main fraction isolated had a highly complex aromatic region in the ^1H NMR spectrum and could not be identified.

The third attempt employed a more active catalyst system of $\text{Pd}_2\text{dba}_3/\text{SPhos}$, in THF, with sodium carbonate as the base.⁸⁶ This was refluxed for 16 h at 80 °C, but unfortunately the product could not be isolated and a similar result as the previous experiment was observed.

The final experiment used $\text{Pd}(\text{PPh}_3)_4$ once more as it had previously given the best result. In this case a toluene/ethanol solvent system was used to ensure phase transfer. The reaction was heated at 100 °C for 28 h. A lower temperature was used in order to minimize deborylation. Purification by column chromatography (silica gel, hexane:DCM, 3:1) gave the mono-coupled product **3.14** once more.

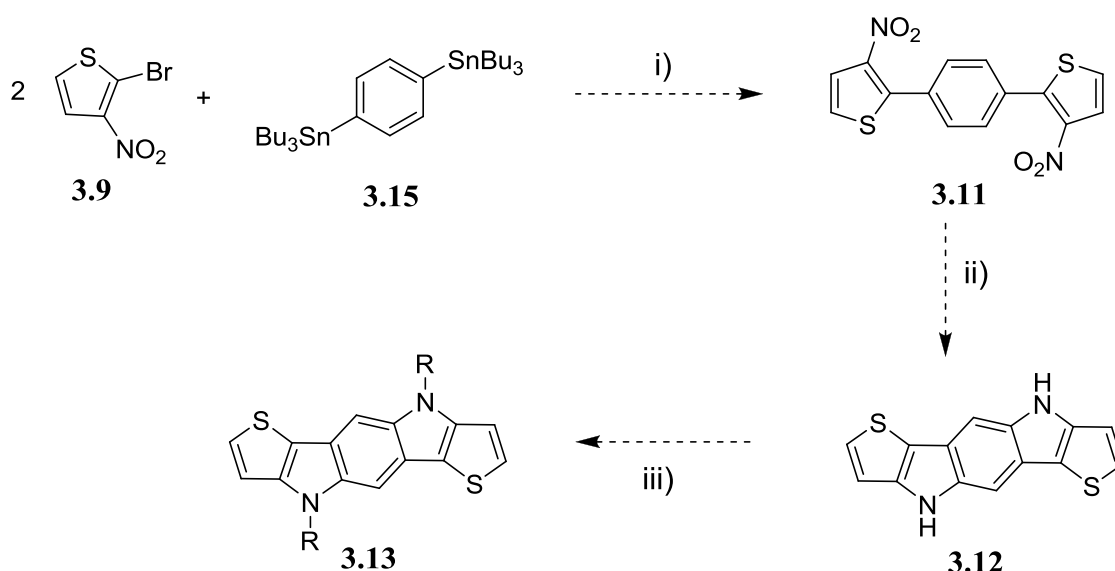
The results are summarized in **Table 3.2**. It was apparent that there was an inherent problem with this reaction: Due to the poor stability of thienylboronic acids, which results in deborylation after an aqueous work up, the boronic acid had to be located on the benzene ring.⁶⁹ This meant that the palladium had to insert in to the sterically hindered thiophene-bromine bond, which is electron rich. It has been well documented that palladium insertion occurs more readily into electron poor bonds.⁵³ Therefore, harsher conditions had to be used in order to drive this reaction and as a consequence deborylation of the benzene ring occurred before the palladium could insert in to the second benzene-bromine bond.

Table 3.2 Summary results for the Suzuki coupling reaction

Attempt	Cat/lig	Base	Solvent	Temp/°C	Time/h	Result
1	$\text{Pd}(\text{PPh}_3)_4$	K_2CO_3	Toluene	110	20	monocoupled
2	$\text{Pd}(\text{AcO})_2/\text{PPh}_3$	K_2CO_3	Tol/ethanol	110	20	unknown
3	$\text{Pd}_2\text{dba}_3/\text{SPhos}$	Na_2CO_3	THF	80	16	unknown
4	$\text{Pd}(\text{PPh}_3)_4$	K_2CO_3	Tol/ethanol	100	28	monocoupled

3.3.2.3 Stille coupling reaction

At this point it was decided that a new route to this coupled product would have to be taken as the Suzuki reaction was not working. It was decided that a Stille reaction, using the 1,4-di(tri-*n*-butylstannyl)benzene **3.15** may be more successful. Therefore an alternative route was devised (Scheme 3.3).



Scheme 3.3 Alternative route to monomer; *Reagents and conditions*: i) Pd(PPh₃)₄, xylene, 170 °C, 20 min, μ W; ii) PPh₃, *o*-DCB, 17h, 150 °C; iii) RBr, aq. NaOH, DMSO.

3.3.2.3.1 Synthesis of 1,4-bis(tri-*n*-butylstannyl)benzene **3.15**

*n*BuLi was slowly added to a solution of 1,4-dibromobenzene, in dry THF under N₂, at -78 °C. This was stirred for 30 min at this temperature and then *n*-Bu₃SnCl was added, dropwise. Once addition was complete, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was worked up and the volatiles removed *in vacuo* to give a crude oil. This was purified by vacuum distillation, to remove the excess *n*-Bu₃SnCl which boiled at 110 °C at 0.07 Torr. The product was collected as a colourless oil in 56 % yield.

3.3.2.3.2 Stille coupling reaction

The first attempt used Pd(PPh₃)₄ as the catalyst and anhydrous xylene as the solvent. The reagents were placed in a microwave vial, along with the 2-bromo-3-nitrothiophene **3.9** and

the stannylbenzene **3.15** starting materials. The reaction was heated at 170 °C for 20 min in the microwave. The crude product was purified by column chromatography (silica gel, hexane: ethyl acetate, 3:1, 2% triethylamine). Unfortunately only starting material was recovered.

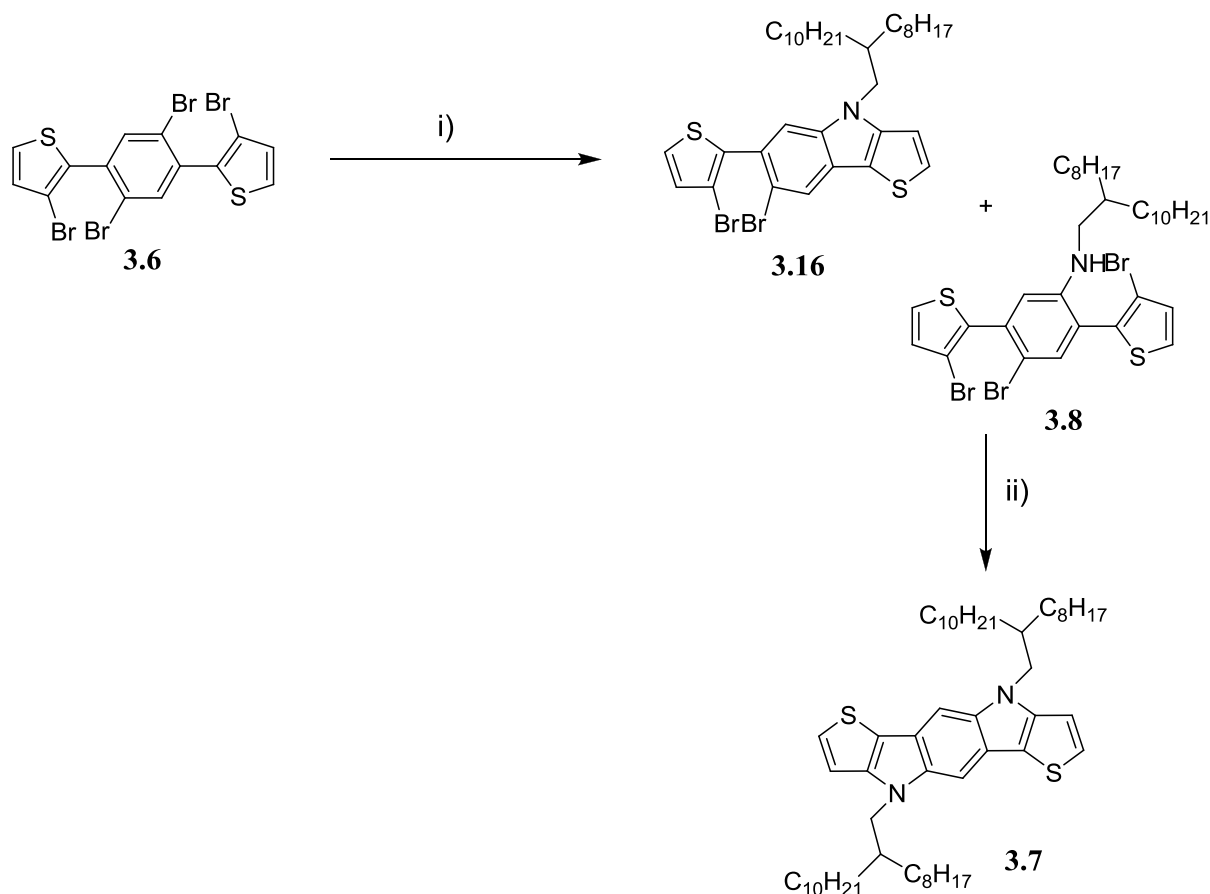
It was unexpected that no coupling occurred, so the reaction was repeated, but under rigorously anhydrous conditions and toluene was used as the solvent. The reaction was heated to 110 °C and monitored by TLC. After 72 h only starting material was present so the reaction was quenched.

It was evident that the Stille coupling was even less successful. Again, the Pd had to insert in to the electron rich thiophene-bromine bond which is unfavourable,⁵³ requiring the use of harsh conditions (e.g. 170 °C in the microwave reactor). As the distannylated benzene was never recovered from the reaction mixture, it is possible that the harsh conditions led to the decomposition of this product by cleavage of the tin groups, eliminating the possibility of a coupling reaction occurring.

3.3.3 Buchwald-Hartwig Amination Revisited

The initial idea involving the Buchwald-Hartwig amination reaction was then revisited. This reaction had been attempted twice in the microwave, using xylene as the solvent but amination only occurred at one of the four bromide sites on the starting material. It was decided that this method would be repeated using less forcing conditions and in a Schlenk tube so as to enable monitoring by TLC and ¹H NMR spectroscopy. This route to the NIDT monomer would also direct the site of ring closure to opposite sides of the molecule. The starting material **3.6** was placed in a clean dry Schlenk and Pd₂dba₃, BINAP, NaOtBu and 2-octyldodecylamine were added. Then dry toluene was added and the reaction mixture was heated to 120 °C for 24 h. TLC (Hex:DCM, 9:1) showed that all the starting material had been consumed and there were two spots very close to one another at R_F 0.41-0.42. Column chromatography (silica gel, 0-10 % DCM in hexane) was carried out on the crude product. Three fractions were collected; ¹H NMR spectroscopy revealed that the first fraction was the

mono-ring closed product **3.16**, the last fraction was the mono-aminated product **3.8** and the middle fraction was therefore a mixture of both (Scheme 3.4).



Scheme 3.4 Synthesis of NIDT: *Reagents and conditions* i) 5 mol % Pd_2dba_3 , 20 mol% BINAP, NaO^tBu , 2-octyldodecylamine, toluene, 120 °C, 24 h; ii) 4 mol% Pd_2dba_3 , 16 mol% BINAP, NaO^tBu , 2-octyldodecylamine, toluene, 120 °C, 24 h.

It was decided that the mixture of the mono-aminated **3.8** and mono-ring closed **3.16** products would be reacted further under the same amination conditions to drive the reaction to completion. The reaction was heated to 120 °C for 20 h. After this time TLC showed only one bright blue spot under UV light (254 nm) with an R_F 0.36 (Hex:DCM, 9:1). Column chromatography (silica gel, hex:DCM (9:1)) was carried out on the crude material and the product **3.7** was recovered as an off white solid with an overall yield of 14 %.

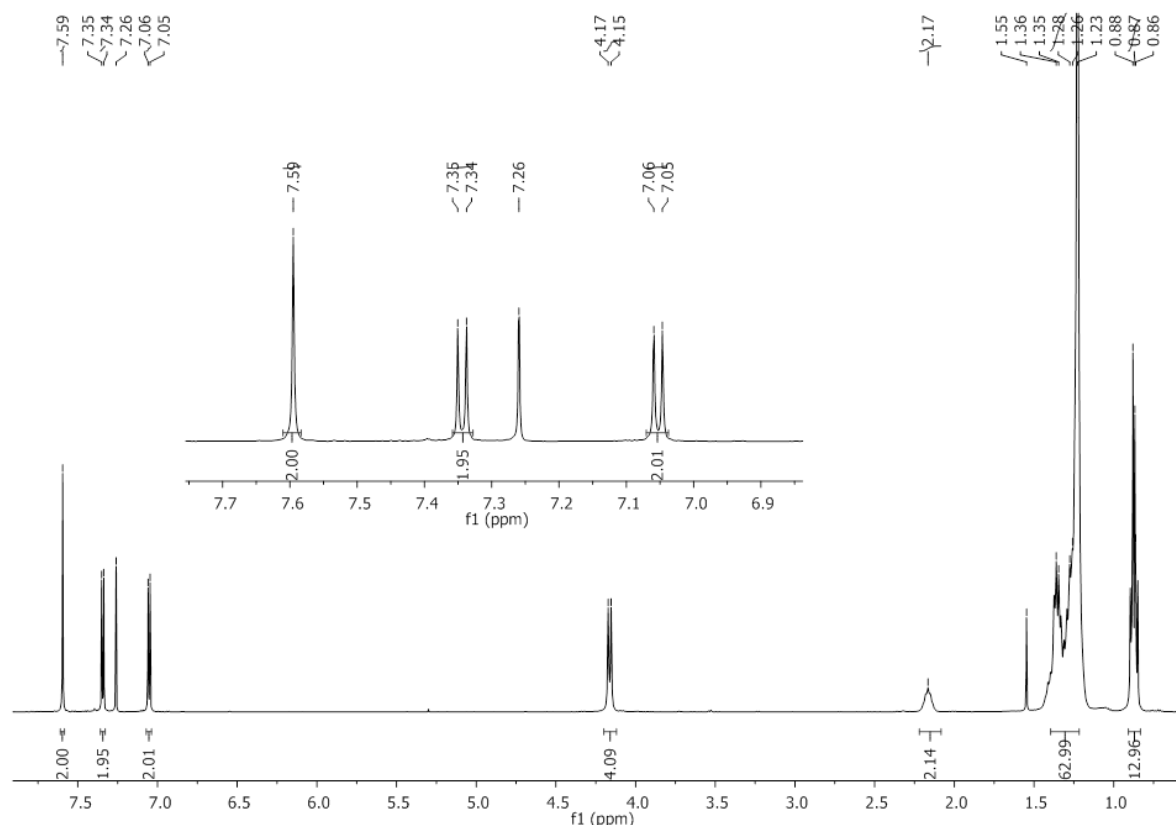


Figure 3.5 ^1H NMR spectrum of NIDT 3.7.

The product was characterised by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis and EI mass spectrometry. The ^1H NMR spectrum (Figure 3.5) shows clearly one singlet at 7.59 ppm, corresponding to the two equivalent protons on the phenyl ring. The two doublets at 7.34 and 7.05 ppm are due to the four protons on the thiophene units. The two protons on each thiophene unit couple with one another to give doublets. The doublet at 4.16 ppm is due to the $-\text{NCH}_2$ protons in the alkyl chains. The multiplet at 2.23-2.10 ppm corresponds to the $-\text{CH}_2\text{CH}-$ of the alkyl chains and the multiplet at 0.90-0.84 ppm is due to the 12 methyl protons on the alkyl chains. Mass spectrometry showed the molecular ion peak at 828 m/z and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy showed the presence of 7 aromatic peaks corresponding to the 14 aromatic carbons; due to the symmetrical nature of the molecule only 7 peaks were observed.

Scheme 3.4 shows the route taken to synthesize the novel NIDT. The first attempt of this reaction gave a very poor overall yield, but once the product had been isolated, it greatly facilitated monitoring of the reaction by ^1H NMR spectroscopy.

3.3.3.1 Optimization of reaction conditions

In order to try and improve the yield it was decided that an excess of base would be used. Previously four equivalents of base were used for every equivalent of starting material, in order to remove all four bromide groups, but if there had been any impurities in the base or if it was consumed in any other side reactions then the reaction could not go to completion. Therefore it was decided that 6 equivalents would be added to the reaction mixture.

The reaction was heated at 120 °C for 24 h before an aliquot was taken from the reaction. A crude ^1H NMR spectrum was run, which showed that the mono-ring closed **3.16** and mono-aminated **3.8** products had been formed in almost equal amounts. Figure 3.6 shows the ^1H NMR spectrum of the mixture after purification by column chromatography. The peak at 8.04 ppm corresponds to the mono-ring closed product **3.16** and the peak at 6.68 ppm corresponds to the mono-aminated product **3.8**. Therefore the reaction could be easily followed. Use of excess base in this part of the reaction showed an improvement in the ratio of **3.16:3.8** from 1:3 to 1:1.2.

The final step had previously proved to be the lowest yielding reaction. Great care was taken to monitor this reaction to try and drive it to completion. Once the mixture of products was isolated it was reacted with 5 equivalents of base and the reaction was made twice as dilute as previous attempts, in order to reduce the possibility of intermolecular coupling and the formation of dimers or trimers etc. The reaction was monitored once more by ^1H NMR spectroscopy and after 8 h the reaction had not reached completion, so more catalyst was added and the reaction was heated for a further 16 h, after which time it had reached around 70 % conversion and the reaction was quenched. The product was purified by column chromatography (silica gel, 0-5 % DCM in hexane) to give a pale yellow oil, with an overall yield of 40 %, which was a great improvement. Therefore a combination of an excess of base

and close monitoring of the reaction progress (adding more catalyst if required) is essential for obtaining reasonable yields in this reaction system.

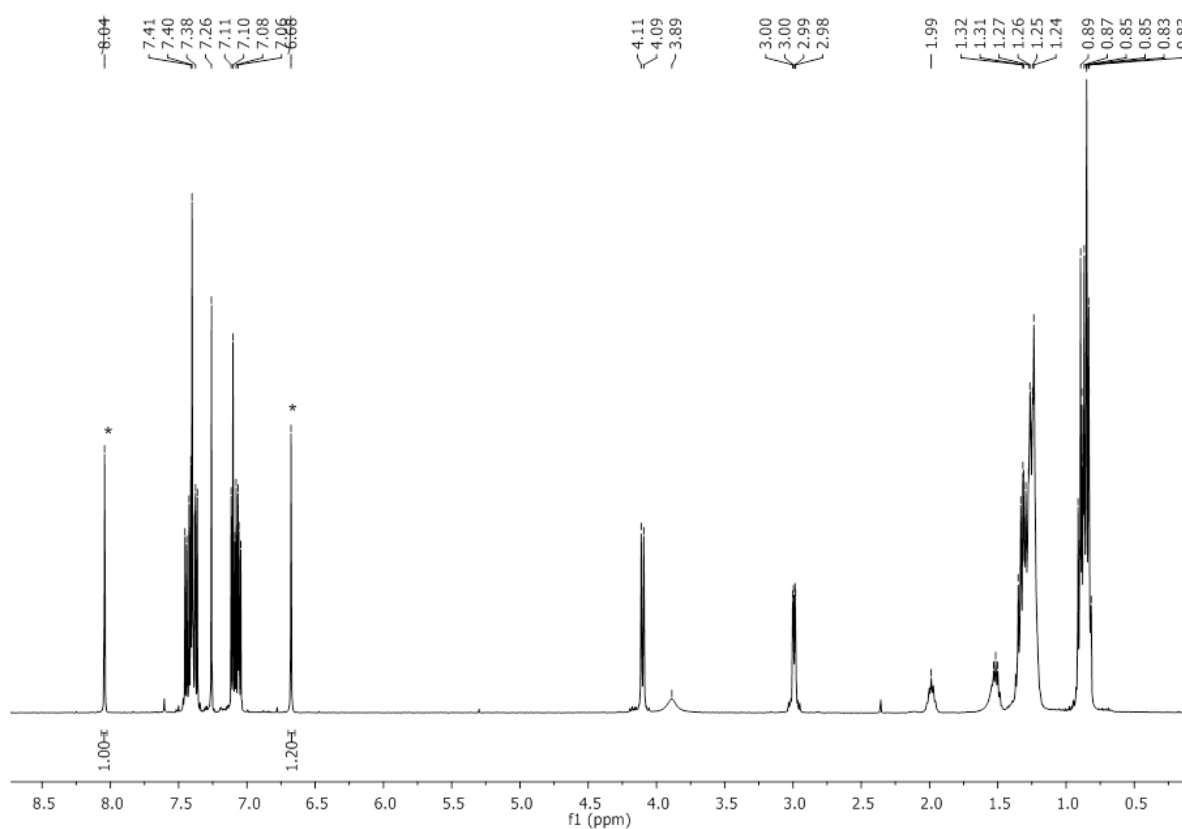


Figure 3.6 ^1H NMR spectrum of the mixture of products **3.16** and **3.8**.

It is also worth noting that in a separate reaction we tried to drive the reaction to the fully ring-closed product in one step, but after 72 h of heating and the addition more catalyst, NIDT was never reached.

Evidence from literature shows that in Buchwald-Hartwig amination reactions, the catalysts and ligands can show a tendency to mono-amine.^{66, 87} Therefore, in order to produce tertiary amines from primary amines, it can sometimes be necessary to perform a second, separate amination reaction.^{66, 87, 88} This observation can help to explain why reaching the fully aminated product can be so difficult. There is also the possibility of the secondary amine reacting intermolecularly with another molecule of starting material to produce polymeric structures.⁶⁶ This could be one possible side reaction which contributes to the low yield. It is also possible that the first amination leads to a deactivation of the benzene ring towards further attack.⁸⁸ The amine group is electron donating and should enhance the electron density of the ring, meaning that the second benzene-bromine bond becomes less favourable

to palladium insertion, explaining the even lower yields obtained from the second amination reaction.

3.3.4 Synthesis of dibromo-NIDT monomer 3.21

Bromination of monomer **3.7** was initially carried out using NBS in dichloromethane at room temperature for 1 h. Unfortunately these conditions were too harsh causing the monomer to decompose to a black solid which precipitated from solution.

Milder conditions were then tried, carrying out the reaction under N₂ using dry THF. The NBS was then added portion-wise at 0 °C. This time the reaction mixture stayed yellow in colour and did not decompose. The crude material was purified by column chromatography (silica gel, hexane) to give an off white solid.

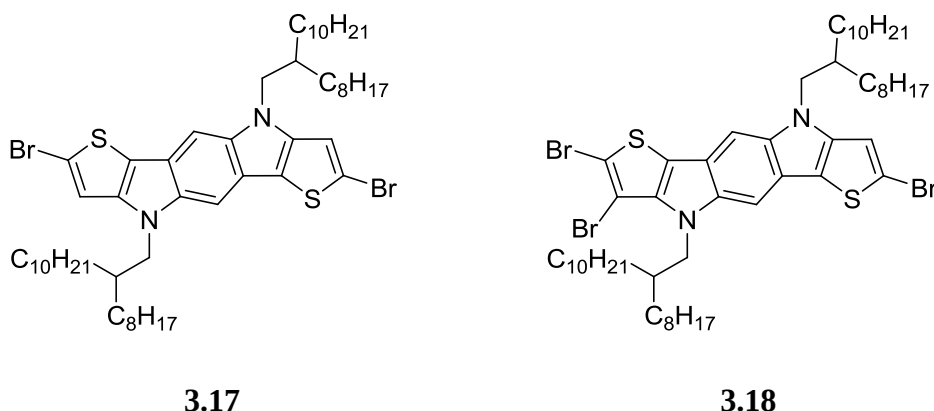


Figure 3.7 Desired dibrominated product **3.17** and over-brominated NIDT unit **3.18**.

Unfortunately, the ¹H NMR spectrum (**Figure 3.8**) showed that the major product was the over-brominated product **3.18**, with three bromines rather than two. It was likely that this was due to the highly electron rich nature of this monomer which makes selective bromination very difficult.

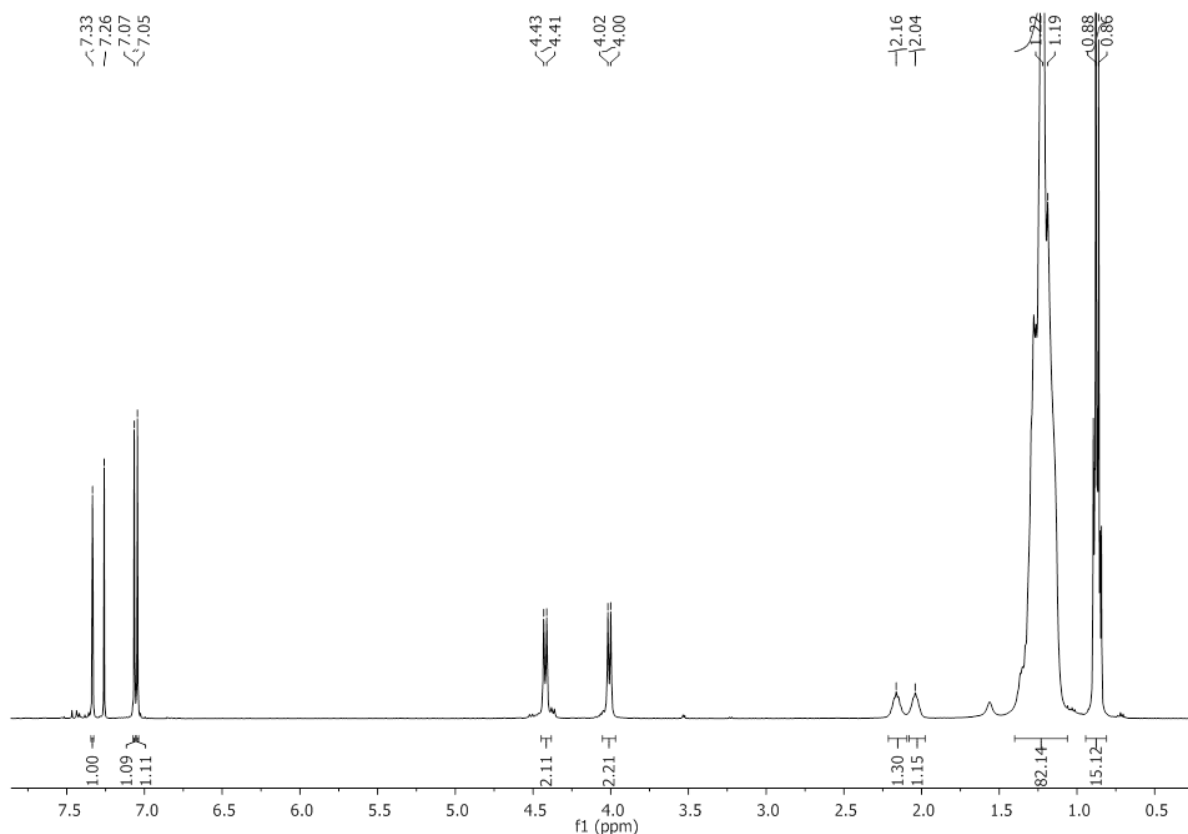
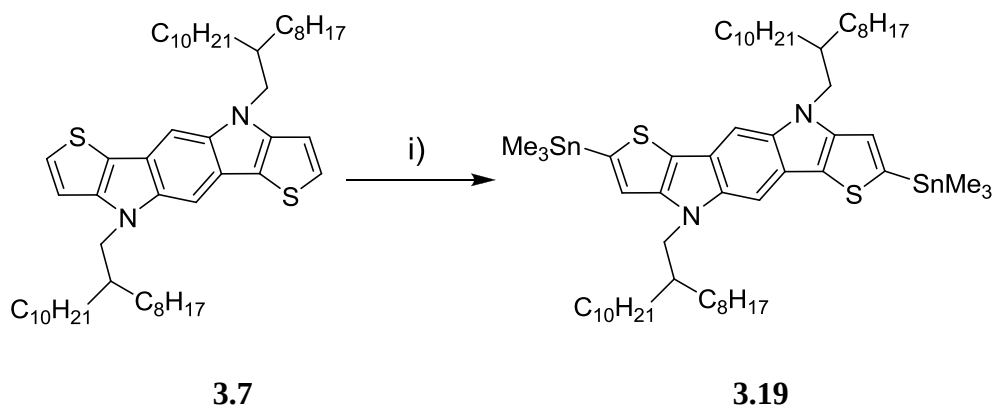


Figure 3.8 ^1H NMR spectrum of the over-brominated product **3.18**.

3.3.5 Synthesis of benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) **3.19**

As the bromination of this monomer proved difficult, it was desirable to make the distannylated monomer. The distannylated NIDT **3.19** was synthesized via direct lithiation of the monomer with *n*BuLi at $-40\text{ }^\circ\text{C}$. After 2 h stirring at this temperature, trimethylstannyl chloride was added over 5 min (Scheme 3.5). The reaction mixture turned from orange/red to pale yellow on addition. After 24 h the reaction was quenched with water and extracted with hexane. The organics were washed with water several times then the volatiles were removed to give a yellow oil (97 %) which solidified in the freezer. No further purification was carried out; column chromatography was not possible as such organo-tin compounds tend to decompose on silica (or alumina), via cleavage of the carbon-tin bond to give the starting material.⁵⁴



Scheme 3.5 Synthesis of distannylated NIDT **3.19**: *Reagents and Conditions*: i) a) *n*BuLi, -40 °C, 2 h; b) Me₃SnCl, -40-25 °C, 24 h.

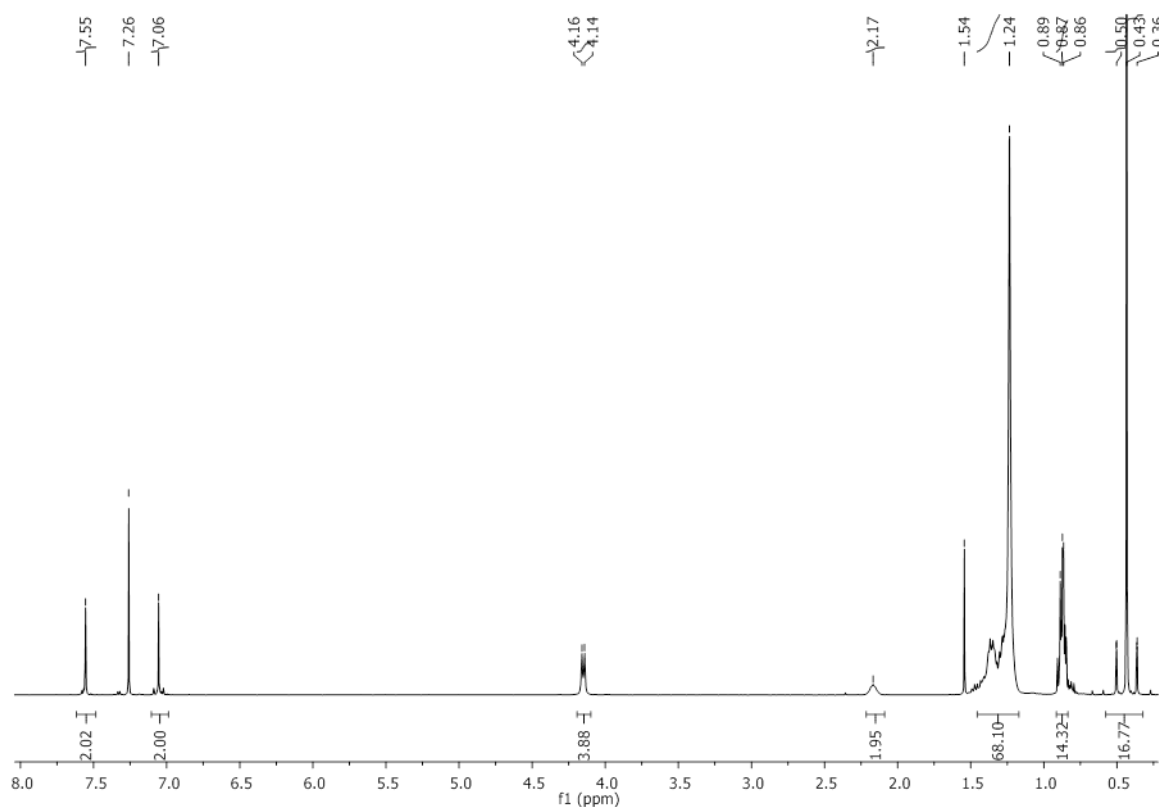


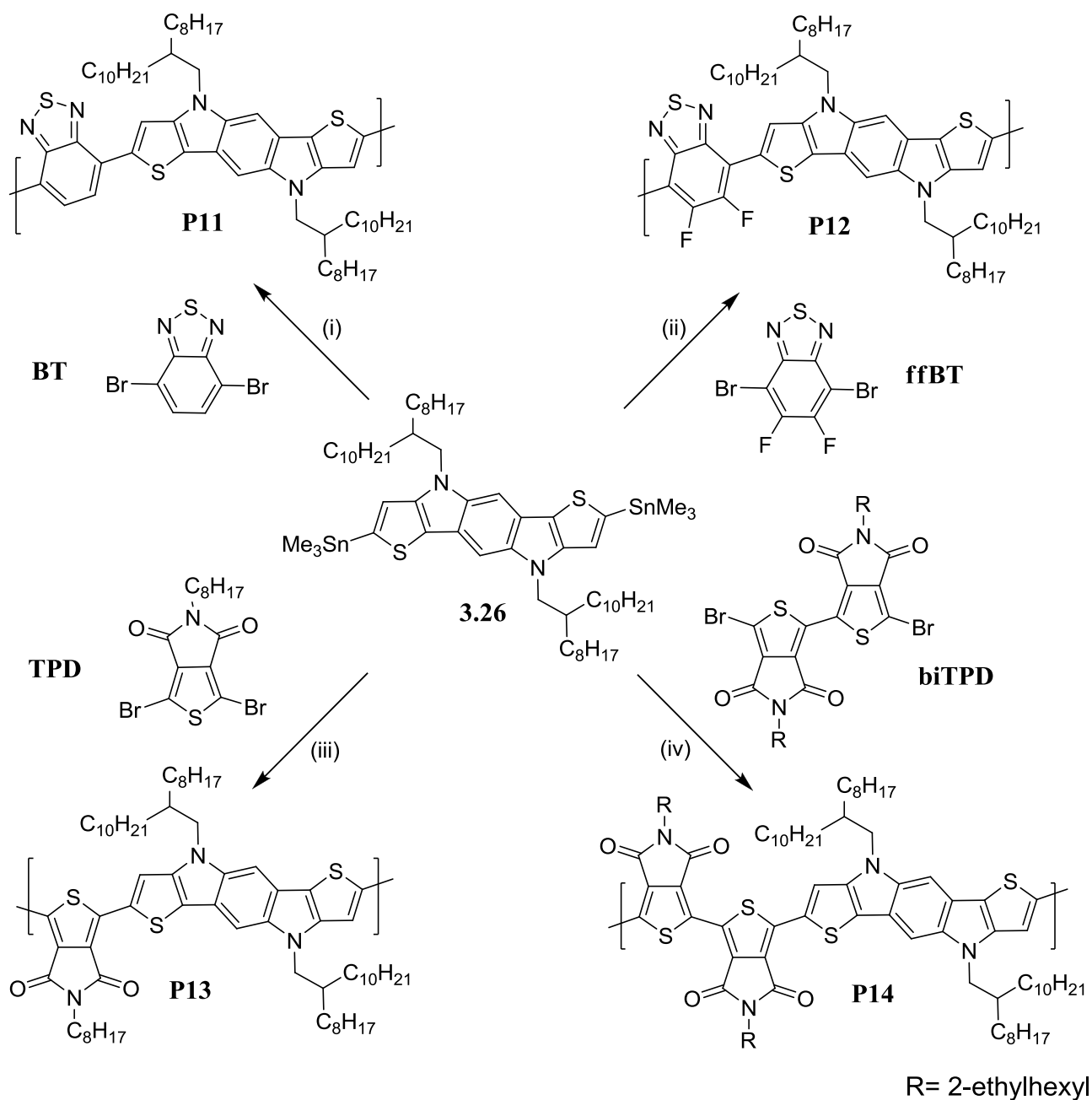
Figure 3.9 ¹H NMR spectrum of the distannylated NIDT **3.19**.

The product was characterized by ¹H NMR spectroscopy, ¹³C{¹H} NMR spectroscopy and ESI mass spectrometry. The ¹H NMR spectrum helped to confirm that the correct product had been isolated (Figure 3.9). Instead of two doublets and a singlet in the aromatic region, we now observe two singlets, each with integrals corresponding to two protons. The singlet at 7.55 ppm corresponds to the protons on the phenyl ring and the singlet at 7.06 ppm

corresponds to the protons on the thiophene rings, next to the trimethyl tin group. A singlet at 0.43 ppm is observed, with two large satellite signals which is due to the 18 methyl protons on the tin groups.

3.4 Polymer Synthesis and Characterization

Having synthesized the distannylated NIDT unit, a series of polymers were synthesized via Stille crossing coupling, with the dibrominated acceptor units. The structures of the polymers are shown in Scheme 3.6. Four acceptor units were chosen for copolymerization: the same units which had previously been co-polymerized with DTP in Section 2.7. The ubiquitous benzothiadiazole (BT) unit is electron deficient and facilitates molecular orbital hybridization with the electron rich NIDT unit, leading to a low band gap polymer which is desirable for enabling efficient photon absorption. The dipole from the benzothiadiazole unit is orthogonal to the backbone and in combination with electron rich co-monomers this has also been shown to enhance π -stacking, leading to materials with very high hole mobilities in OFET devices.⁵⁷ The difluorobenzothiadiazole (ffBT) unit has additional electron withdrawing fluorine groups attached to the 3- and 4-positions of phenyl ring. It is also likely that short contacts will be present between the fluorine of the ffBT and the sulphur from flanking thiophenes of the NIDT unit. These interactions have been shown to enhance coplanarity between coupled units, thus improving π -delocalization and intermolecular.^{31, 89} This was expected to enhance hole mobility in OFET devices.



Scheme 3.6 Reagents and conditions i) 4 mol% Pd(PPh₃)₄, xylene, 180 °C, 40 min, μ W; ii) 2 mol % Pd₂dba₃, 8 mol % P(*o*-tolyl)₃, chlorobenzene, 200 °C, 30 min, μ W; iii) 2 mol% Pd₂dba₃, 8 mol% P(*o*-tolyl)₃, chlorobenzene, 200 °C, 30 min, μ W; iv) 2 mol% Pd₂dba₃, 8 mol% P(*o*-tolyl)₃, chlorobenzene, 200 °C, 30 min, μ W.

The thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit,^{32, 52, 54, 90, 91} was chosen due to the alkyl functionality on the nitrogen, which has a solubilizing influence on the polymer, allowing higher molecular weights to be reached. It also possesses a relatively strong electron withdrawing effect due to the presence of the imide group.⁵⁴ This will encourage electronic

orbital hybridization, leading to a low band gap polymer. A linear alkyl chain on the pyrrolidione was selected in this case to promote crystallinity and therefore good charge transport. The 1,1'-bithienopyrrolodione (biTPD) unit has previously been shown to lower the LUMO level of a polymer significantly in comparison to TPD. The HOMO level of the polymer would also be expected to be slightly reduced which would lead to an increase in V_{oc} , while the reduced band gap would improve photon absorption. This monomer was therefore attractive in order to improve the V_{oc} of photovoltaic devices.⁷⁹

3.4.1 Synthesis of Polymers P11-P14

Polymers **P11**, **P12**, **P13** and **P14** were all synthesized via microwave assisted Stille cross-coupling (Scheme 3.6) of the distannylated NIDT **3.19** with the appropriate dibrominated acceptor unit. The polymers were purified by Soxhlet extraction using acetone, hexane and, finally, chloroform. Each chloroform fraction was concentrated and washed with aqueous sodium diethyldithiocarbamate tetrahydrate to remove any palladium catalyst, then the chloroform fraction was separated and the polymer reprecipitated into methanol. The molecular weights were measured using Gel Permeation Chromatography (GPC), at 80 °C in chlorobenzene.

3.4.1.1 Synthesis of P11

The synthesis of **P11** proved difficult due to its poor solubility. The first attempt involved the use of a $\text{Pd}_2\text{dba}_3/\text{P}(\text{o-tol})_3$ catalyst system and chlorobenzene as the solvent. The reaction mixture was heated for 30 min at 200 °C with an NIDT:BT ratio of 1.03:1. It was expected that the distannylated NIDT may have some minor impurities by studying the ^1H NMR spectrum, so a slight excess was used. This is common when carrying out Stille polymerizations because the trimethyltin compounds are notoriously difficult to purify as they tend to decompose on silica gel and alumina.⁵⁴

Once cooled the viscous, green solution was precipitated in methanol and purified via the method outlined in Section 3.4.1. Unfortunately GPC analysis showed that the polymer had a very low number average molecular weight (M_n) of 5 kDa and PDI of 1.4.

Table 3.3 Conditions used for optimization of molecular weight of P11

Attempt	Catalyst	Solvent	NIDT :BT	Temp (°C)	Time (h)	Heating method	M _n (kDa)	M _w (kDa)
1	Pd ₂ dba ₃ /P(o-tol) ₃	CB	1.03:1	200	0.5	μW	5	7
2	Pd(PPh ₃) ₄	Xylene	1.03:1	180	0.7	μW	3	12
3	Pd(PPh ₃) ₄	Xylene	1:1	180	0.7	μW	6	12
4	Pd(PPh ₃) ₄	Toluene	1:1	120	72	Oil bath	5	11

The reaction was carried out a further 3 times using various conditions (Table 3.3). Unfortunately none of these yielded high molecular weight polymer. The best achievable M_n was 6 kDa with an M_w of 12 kDa. This polymerization employed Pd(PPh₃)₄ as the catalyst and xylene as the solvent. The reactants were present in a 1:1 ratio and heated in the microwave reactor for 40 min at 180 °C. This polymer was obtained in as a green powder in high yield (79 %). This batch was used for all characterization of **P11**.

3.4.1.2 Synthesis of P12, P13 and P14

The polymerization reactions of the distannylated NIDT with the dibromide of ffBT, TPD and biTPD, proceeded in high yields producing materials with moderate number-average molecular weights (Table 3.4), as measured using Gel Permeation Chromatography (GPC), at 80 °C in chlorobenzene.

The starting materials were reacted in a 1.03:1 ratio of with the distannylated monomer in excess. Pd₂dba₃/P(o-tol)₃ was used as the catalyst and chlorobenzene as the solvent. The reaction mixture was heated for 30 min at 200 °C in the microwave and worked up as reported in Section 3.4.1. **P12** was isolated as a green powder in 89 % yield. **P13** and **P14** were isolated as blue powders with respective yields of 79 and 77 %.

Table 3.4 Molecular weight distributions of all four polymers measured by GPC in chlorobenzene at 80 °C

Polymer	M_n (kDa)	M_w (kDa)	PDI	DP
P11	7	12	1.7	7
P12	11	25	2.3	11
P13	12	28	2.3	11
P14	22	57	2.6	16

3.4.2 Polymer Analysis

All four polymers were characterized by ^1H NMR spectroscopy, UV-Vis spectroscopy, Differential Scanning Calorimetry (DSC) and photoelectron spectroscopy in air (PESA). They were also studied computationally, using DFT, in order to give a greater understanding of the energy levels.

3.4.2.1 ^1H NMR spectroscopy

This technique helped to prove that the coupling reactions had indeed taken place. Broadening of the peaks in comparison to the starting materials was observed which is characteristic of a polymeric spectrum. Figure 3.10 shows the ^1H NMR spectrum of **P13**. The broad peaks around 8.6-6.0 ppm are due to the four aromatic protons of the NIDT units. The broad peak between 4.65-3.20 ppm is due to the $-\text{NCH}_2$ protons of the alkyl substituents. The multiplet between 2.40-0.75 ppm corresponds to the remainder of the alkyl protons.

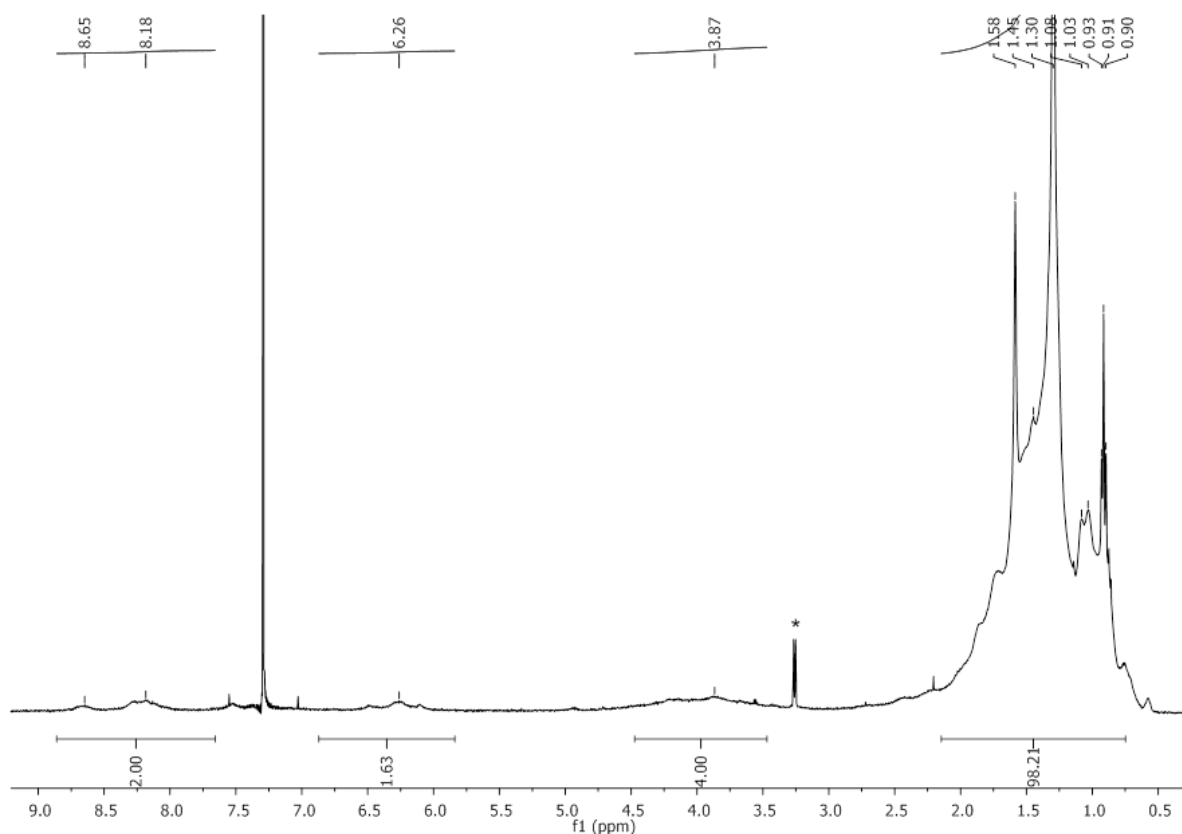


Figure 3.10 ^1H NMR spectrum of **P13** (*solvent impurity).

3.4.2.2 Optical properties

All four polymers showed long wavelength absorption maxima, both in solution and thin film, UV-Vis measurements (Figure 3.11 and Table 3.5). In solution **P11** exhibited an absorption maximum at 770 nm, but on going from solution to thin film **P11** developed a pronounced shoulder on the long wavelength side of the absorption maximum, at around 830 nm, which could be indicative of solid state aggregation effects. For **P12** and **P13** no red shift or shoulder was observed suggesting there is little order gained when going from solution to solid state. In solution **P14** displayed a minor shoulder on the short wavelength side which could be attributed to solution aggregation. In thin film **P14** showed a red shift of 15 nm in its absorption maximum, and the shoulder on the short wavelength side became more pronounced and was attributed to solid state aggregation. The correspondingly low band gaps of these polymers (Table 3.5), estimated from the absorption onset, suggests that these polymers should perform well in organic photovoltaic (OPV) devices.

Table 3.5 Optical properties and energy levels of P11-P14

Polymer	λ_{max} (nm)		E_g (eV) ^c	HOMO (eV)		LUMO (eV)	
	soln. ^a	film ^b		Exp. ^d	Calc. ^f	Exp. ^e	Calc. ^f
P11	770	774, 830	1.4	-4.9	-4.4	-3.5	-3.0
P12	780	785	1.5	-4.9	-4.5	-3.4	-3.1
P13	635	634	1.7	-5.1	-4.6	-3.4	-2.8
P14	680	650, 695	1.6	-5.1	-4.8	-3.5	-3.0

^a Measured in chloroform solution. ^b Spin cast from 5 mg/mL chlorobenzene solution. ^c Estimated from the absorption onset of thin film UV-vis spectra. ^d Measured by ambient photoelectron spectroscopy (PESA). ^e Estimated by addition of E_g to the HOMO. ^f Calculated from the trimer model using Gaussian at the B3LYP/6-31G* level.

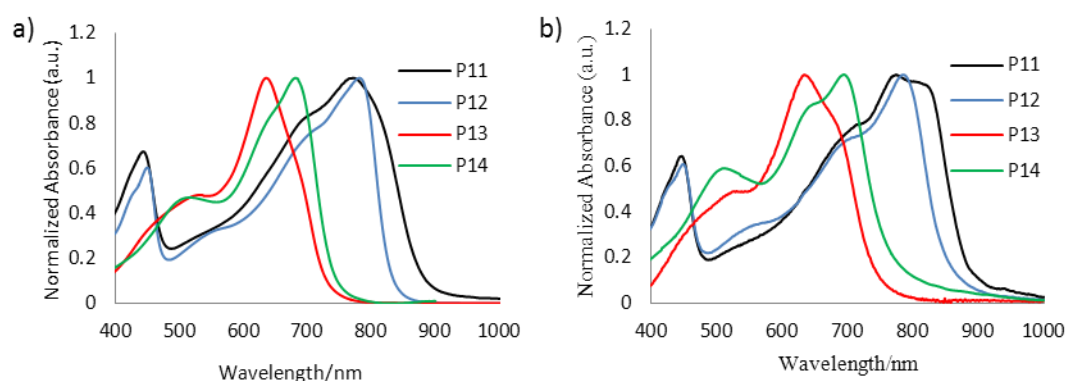


Figure 3.11 a) Solution (in chloroform) UV-Vis spectra of polymers **P11**, **P12**, **P13** and **P14**; b) Thin film (from chlorobenzene) UV-Vis spectra of polymers **P11**, **P12**, **P13** and **P14**.

3.4.2.3 Energy Levels

From studying the UV-Vis absorption spectra it is evident that the molecular orbital energy levels are influenced by the acceptor co-monomer present. In order to further understand the electronic properties of the materials, their trimers were modelled using Gaussian at the B3LYP/6-31G* level.* The side-chain substituents were replaced with methyl groups in order to simplify the calculations, with minimum effect on electronic properties. The HOMO and LUMO wave functions of the trimer model are shown in Figure 3.12.

* All DFT carried out by C. Nielsen, McCulloch group, Imperial College London, London, SW7 2AZ.

P12 differs from **P11** by the addition of two fluorine groups on the BT unit. These F groups were expected to further withdraw electron density and lower both the HOMO and LUMO levels. However, the existence of S-F short contacts was expected to counteract this lowering of the HOMO level by coplanarizing adjacent ring units, leading to a minimal overall effect on the energy levels. The calculated data shows a lowering of the HOMO and LUMO levels by 0.1 eV for **P12** in comparison to **P11**. The experimental data as measured by PESA, exhibits no reduction in the HOMO level. The LUMO level calculated from adding the band gap to the HOMO level, actually shows an increase of 0.1 eV on going from **P11** to **P12**. This is contrary to our prediction and is attributed to be a result of standard experimental error associated with the measurement of the HOMO level and band gap and it is likely that the energy levels are very similar. **P11** and **P12** show a similar density of states distribution for both the HOMO and LUMO wave functions (Figure 3.12). The HOMO calculation showed a broad distribution along the backbone, but the LUMO is mainly located on the acceptor part of the molecule for **P11** and **P12**. The fluorine atoms contribute little to the molecular orbitals and this can help explain why we observe a minimal effect on energy levels.

P13 possesses a strong electron withdrawing imide group and it was predicted to lower the HOMO level by 0.2 eV in comparison to **P11**. Figure 3.12 shows the HOMO and LUMO distributions. The HOMO distribution of **P13** is similar to that of **P11** but they differ significantly in terms of the LUMO wave functions. The LUMO of **P11** is localized on the acceptor unit, whereas the LUMO of **P13** is delocalized across the backbone. It is notable that the imide group of TPD contributes less to the LUMO than the thiazole of BT. Therefore, less of a stabilization of the LUMO was observed. In this case, the experimental and calculated energy levels are in agreement; the HOMO is stabilized and the LUMO is raised on going from **P11** to **P13**.

P14 contains the biTPD unit which has a higher density of electron withdrawing groups than **P13**. This leads to a larger stabilization of the HOMO with respect to **P13** as observed from the calculated data. The experimental data shows little effect on the HOMO (Table 3.5). This could be due to the molecular weight of **P14** being much larger than **P13**, which results in the HOMO being raised, reducing the difference between the HOMO energy levels of **P13** and **P14**,⁷⁰ or simply due to the experimental error associated with the energy level

measurements. The LUMO wave function shows a high density of states around the acceptor unit (Figure 3.12), similar to that observed for **P11** and **P12**, this was expected to stabilize the LUMO level in comparison to **P13**. In both the experimental and calculated data, the stabilization of the LUMO is observed. The biTPD unit therefore has the effect of stabilizing the HOMO but at the same time reducing the band gap.⁷⁹ This is optimal for solar cells as the reduced band gap will increase the solar light harvesting potential and the lower HOMO level will improve the V_{oc} .

It must also be noted that comparison and analysis of the experimental energy levels for **P11**-**P13** is somewhat complicated due to the fact that at low molecular weights the band gap can be molecular weight dependent (especially when the HOMO and LUMO are fully delocalized).⁷⁰

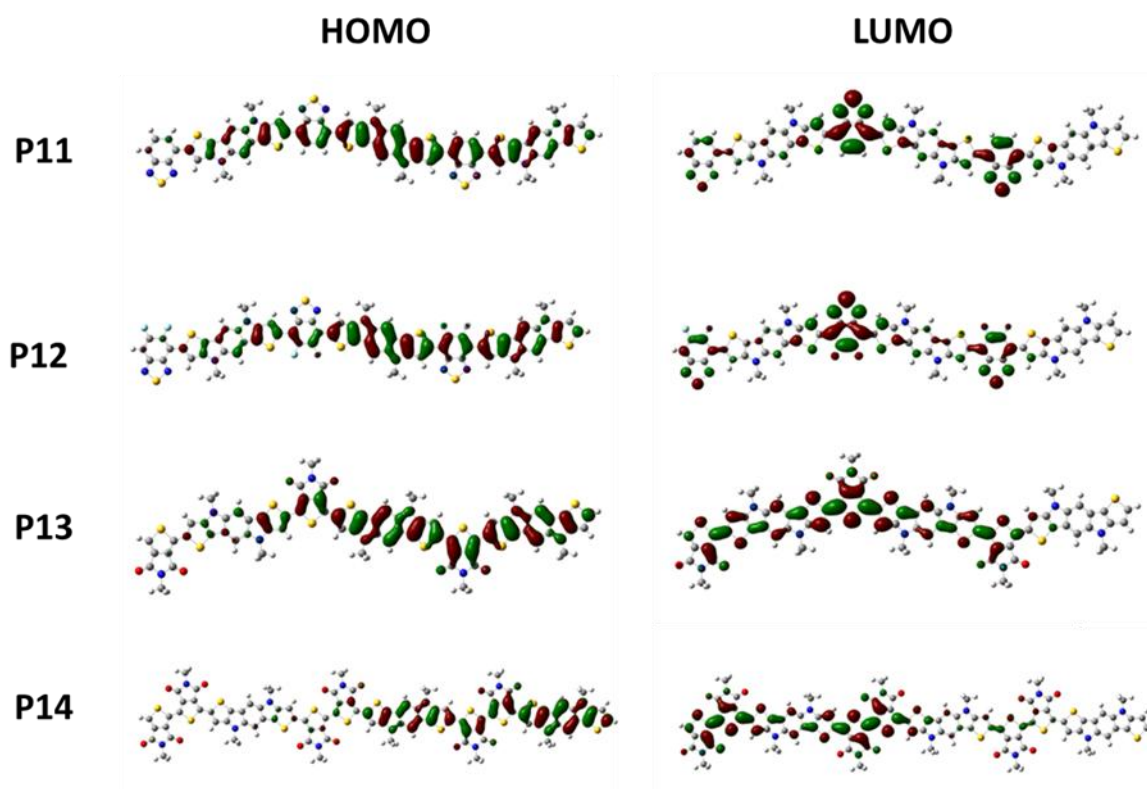


Figure 3.12 The HOMO and LUMO wavefunctions of the trimer model of polymers **P11**, **P12**, **P13** and **P14**.

3.4.3 OFET properties

To measure the p-type charge carrier mobility bottom-gate, top-contact (BG-TC) architecture OFET devices were fabricated on highly doped p-type Si substrates with SiO₂ as the dielectric and n-doped silicon as the common gate. The gold source and drain electrodes were deposited by thermal evaporation and the semiconducting polymer was spin-coated from a hot 1,2-dichlorobenzene solution at 1000 rpm, then annealed at 150 °C or 200 °C for 10 min.* The annealing temperature had minimal effect on performance as all four polymers are amorphous. DSC analysis showed no transitions or decomposition between 40-300 °C (Appendix A).†

The charge carrier mobility was calculated from the transfer characteristics of the device, in the saturation regime, using previously reported procedures.⁷¹ The results are summarized in Table 3.6. Figure 3.14 displays the transfer curves of all four polymers obtained from OFET devices (channel length (*L*)/width (*W*) of 70-200/1000 μm) at a drain voltage (*V_D*) of -5 V and -60 V. The reader is referred to the Appendix A for device output characteristics.

Table 3.6 Summary of OFET device results

Polymer	μ_{sat} (cm ² V ⁻¹ s ⁻¹)	$I_{\text{on/off}}$
P11	0.02	10 ⁴
P12	0.07	10 ⁴
P13	0.01	10 ³
P14	0.001	10 ³

P12 showed the best transfer and output characteristics (Figure 3.13b), with a maximum recorded saturation hole mobility of 0.07 cm²V⁻¹s⁻¹ and a current on/off ratio ($I_{\text{on/off}}$) of 10⁴, obtained from a device with channel length of 100 μm, annealed at 200 °C. **P11** exhibited reasonable mobilities (0.02 cm²V⁻¹s⁻¹) for a device with channel length 200 μm, annealed at 200 °C and displayed an $I_{\text{on/off}}$ of 10⁴. One reason for the lower mobility of **P11** compared to

* OFET fabrication and testing carried out by Youngju Kim, Physics Dept., Imperial College London.

† DCS measurements carried out by Stingelin group, Materials Dept., Imperial College London.

P12 could be the improved interchain charge transport of **P12** caused by the planarization of the backbone by S-F short contact interactions, thus promoting shorter π - π stacking distances, or it could be as a result of the low molecular weight of **P11**. Many studies on P3HT, and other polymers, report that higher molecular weight polymers often exhibit higher mobilities than their lower molecular weight fractions.²⁶

P13 displayed a lower mobility than **P11** and **P12** ($0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) with an on/off ratio of 10^3 . The lower mobility is likely to be due to the weaker π -stacking interactions of the TPD units, which reduces long range molecular order and increases interchain π - π stacking distances. **P14** gave the lowest mobility ($0.001 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) which was as attributed to the branched 2-ethylhexyl units of the biTPD unit which are bulky and suppress π -stacking. **P12** exhibits hole mobilities which are state of the art for bottom gate architecture and within the desirable range for OPV applications.

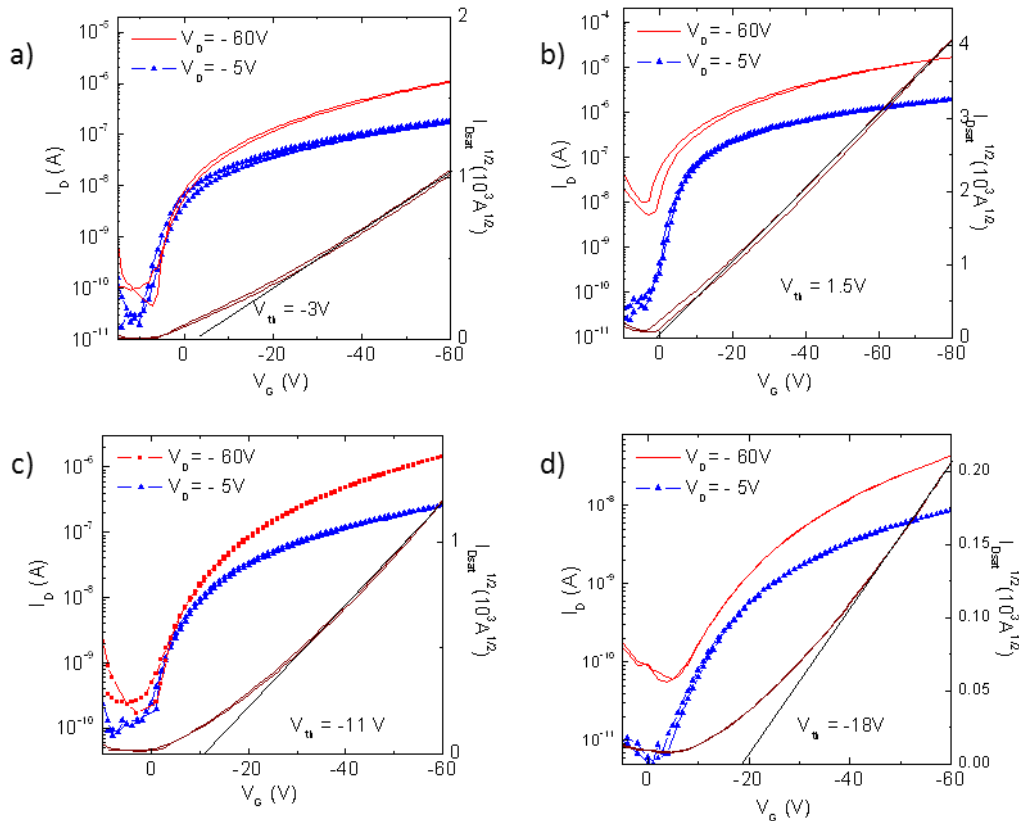


Figure 3.13 Transfer curves of polymers a) **P11**; b) **P12**; c) **P13**; d) **P14** when used as the semiconducting layer in OFET devices.

3.4.4 OPV properties

Solar cells were fabricated with all four polymers using the device structure ITO/PEDOT:PSS/Polymer:PC₇₁BM/Ca/Al.* The *J-V* characteristics are illustrated in Figure 3.14a and the properties are summarized in Table 3.7. The active layers were spin-coated from 1,2-dichlorobenzene (DCB), with a blend ratio of Polymer:PC₇₁BM of 1:3 (w/w). Previous studies on IDT containing polymers have found that the optimum weight ratio of polymer:fullerene blends was at least 1:3.⁵⁶ It has been suggested that the relatively open conformation of the IDT unit allows significant fullerene partitioning within the backbone, and when the fullerene loading exceeds the solubility limit in the polymer, it then phase separates into aggregates, generating the optimal bulk heterojunction morphology.⁵⁶ Having such high fullerene weight requirements also necessitates the use of PC₇₁BM, rather than PC₆₁BM, as an electron acceptor, in order to increase the optical absorption of the blend film.

The morphology of the blended films was studied by tapping-mode atomic force microscopy (AFM). Figure 3.15 shows the AFM images of the blended films, cast from the polymer:fullerene solutions in 1,2-dichlorobenzene.

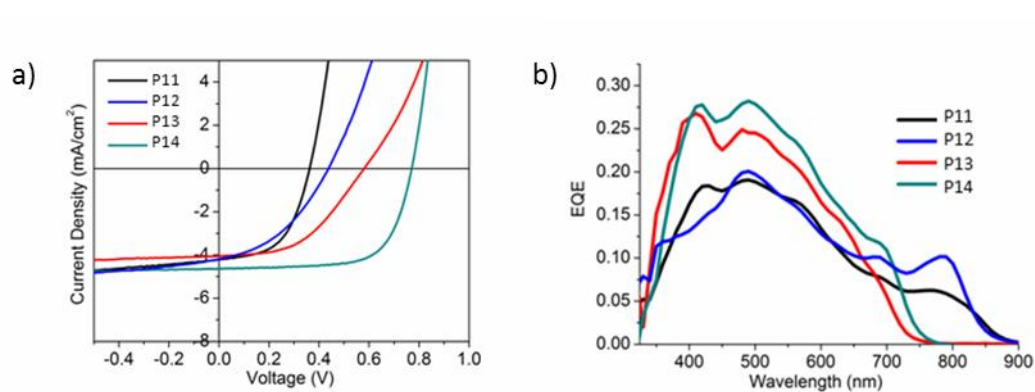


Figure 3.14 a) *J-V* characteristics of polymer(**P11-P14**):PC₇₁BM blends prepared at a blend ratio of 1:3 (w/w); b) EQE curves of polymer(**P11-P14**):PC₇₁BM blends, each prepared at a blend ratio of 1:3 (w/w).

The devices which utilized polymer:fullerene blends of **P11** and **P12** exhibited relatively similar PCE. The **P12** blend had a slightly higher V_{oc} than **P11** suggesting it has a lower lying HOMO level, as predicted by the calculated results. There is, however, a loss in current

* OPV fabrication and testing carried out by S. Ashraf, McCulloch group, Imperial College London, SW7 2AZ.

and FF which leads to the comparable overall performance. The AFM images of the blend of **P11** and **P12** with PC₇₁BM feature large domains. The greater phase segregation and rougher surfaces of the **P11** and **P12** blends presumably arose because of their poor miscibility with PC₇₁BM which can be attributed to their low molecular weight and low alkyl chain density of these copolymers.⁹² These large domain sizes hinder exciton dissociation and charge transport in these devices.

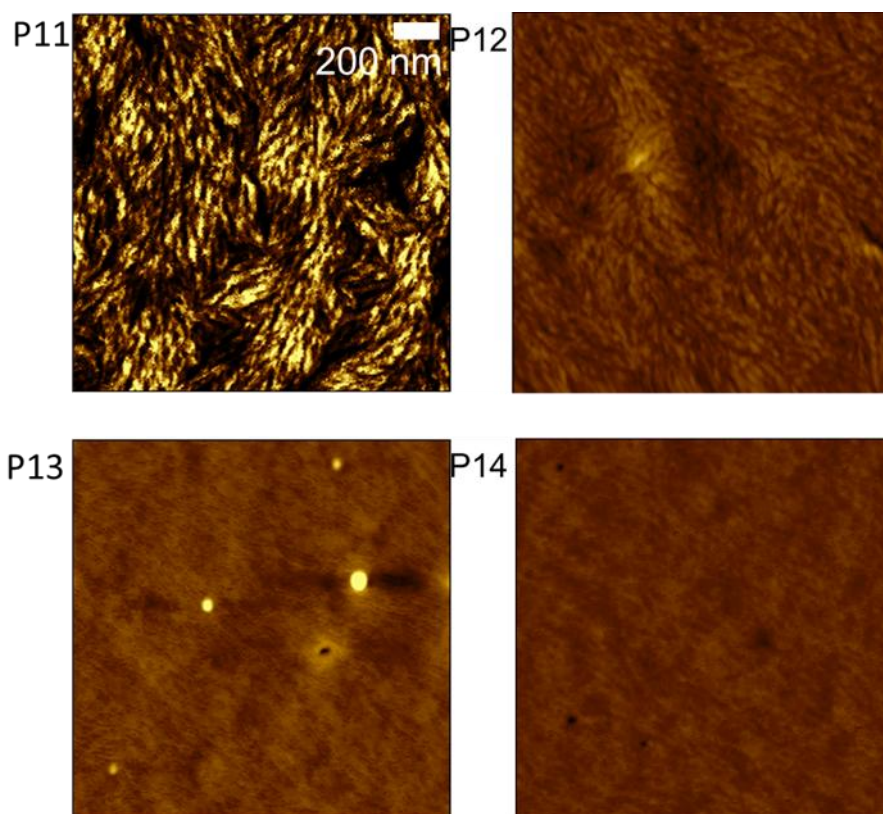


Figure 3.15 AFM topography images (2x2 μm) of polymer(**P11-P14**):PC₇₁BM (1:3 w/w) blend films from *o*-DCB.

Due to their lower lying HOMO levels and therefore higher V_{oc} , **P13** and **P14** performed better than **P11** and **P12**. The J_{sc} values of **P13** and **P14** based devices were very similar, but **P14** exhibited a higher V_{oc} and FF value, leading to an increase in power conversion efficiency from 1.1 % to 2.5 %. Although the experimental HOMO levels are the same for **P13** and **P14**, possibly due to experimental error, the calculated values are in agreement with the increase in V_{oc} observed for **P14**. It has also been shown, in the case of P3HT, that an increase in molecular weight can have a positive impact on J_{sc} , V_{oc} , FF and therefore PCE.⁷⁰

⁹³ As **P14** has a much higher molecular weight than the other polymers, this may explain the marked improvement in performance. Also, the AFM images clearly reveal that the **P14** blend was most homogeneous and smooth, with the lowest root mean square (RMS) roughness of 0.44 nm. This optimum blend morphology clearly contributes to the reason why **P14** has a much improved PCE.^{54, 56, 75, 94}

Table 3.7 Photovoltaic properties of polymer solar cells incorporating P11-P14:PC₇₁BM blends

Polymer: PC ₇₁ BM (1:3)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
P11	4.20	0.36	53.6	0.8
P12	3.69	0.44	40.0	0.7
P13	4.04	0.58	47.8	1.1
P14	4.62	0.77	68.8	2.5

Figure 3.14b shows the external quantum efficiency (EQE) of polymers **P11-P14** as a function of wavelength, which is consistent with the UV–Vis absorption spectra, indicating that all the absorption of the polymers contributed to the conversion. These devices exhibited considerably broad EQE responses extending from the visible to the near Infra-Red (NIR) region, with a maximum intensity ranging between 400 and 500 nm. The higher EQE responses in the visible region can be attributed to the corresponding higher absorbance of the blend, resulting from both the intrinsic absorption of the polymer and the presence of a high content of PC₇₁BM, which absorbs significantly at 400-500 nm. Unfortunately, these devices displayed relatively lower EQE responses at wavelengths above 650 nm because of the modest absorbance of the polymers. The device which employed the **P14** blend exhibited a higher EQE response than that of other polymer blends, with a maximum of 28 % at 490 nm, corresponding to its higher photocurrent.

It was believed that the lower power conversion efficiencies of these polymers in OPV devices was most likely due to the limited molecular weights and sub-optimal phase

separation within the blends, as demonstrated by the AFM images in which we observe large polymer/PC₇₁BM aggregates in the **P11** and **P12** blends.

3.5 Comparison of NIDT with the carbon and silicon analogues

The structure of NIDT was modelled and compared to the carbon analogue (IDT) using Gaussian at the B3LYP/6-31G* level. The calculated energy-minimised conformations of NIDT and IDT are shown in Figure 3.16 and it is clear that the bridging atoms are sp² hybridised for NIDT, with a resultant in-plane bond between the ring nitrogen and the aliphatic carbon, and sp³ hybridised for IDT. This is expected to significantly influence the copolymers microstructure and solubility. The difference in aromaticity is further evidenced by the HOMO distributions of the two structures (Figure 3.16). The lone pair of the nitrogen in NIDT can donate in to the HOMO rendering it fully aromatic, whereas IDT has nodal planes that intersect the bridging carbon atoms, limiting the delocalisation. Although carbon can, to some extent, inductively donate electrons into the π conjugated system, IDT is not a fully aromatic unit. It was therefore expected that this very planar NIDT unit would perform well in OFET devices, as it was likely to have improved π - π stacking interactions.

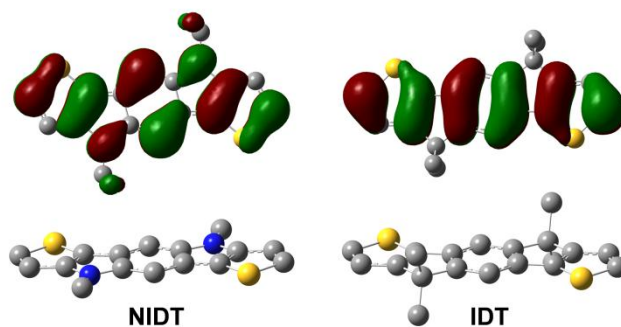


Figure 3.16 Minimum-energy conformations (bottom) and HOMO distributions (top) of the NIDT (left) and IDT (right) monomers optimized using Gaussian at the B3LYP/6-31G* level; all hydrogen atoms are omitted for clarity.

The NIDT unit, with its planar structure and reduced alkyl chain density, unfortunately suffers from a lower solubility, and so most copolymers, without a high degree of compensating solubility from the co-repeat unit, have low molecular weight, as observed experimentally. On the other hand, both the SiIDT and IDT units are highly soluble, and this in turn produces polymers which are highly soluble and can proceed to high molecular weight without precipitation.

Polymer **P11**, with the BT co-monomer, can be compared with the C and Si analogues, which have been reported in the literature.^{56, 65} Table 3.8 compares the molecular weights, absorption maxima and frontier orbital energy levels of all three polymers. As predicted the HOMO level of **P11** (Table 3.8) was raised significantly in comparison to the C and Si analogues which have HOMO levels of -5.3 eV and -5.5 eV respectively,^{56, 65} despite the low molecular weight of **P11**. Also, the band gap of **P11** (1.4 eV) is lower than that observed for the C (1.7 eV) and Si (1.8 eV) analogues.^{56, 65} This reduction in band gap is evident from the UV-Vis absorption maxima; on going from PSiIDT-BT **3.2** to **P11**, the absorption maximum red shifts by 150 nm. This confirms the hypothesis that the addition of the electron donating nitrogen group increases molecular orbital hybridization, raising the HOMO and reducing the band gap.

Table 3.8 Comparison of C, Si and N containing IDT polymers

Polymer	Repeat Unit	Alkyl Chain	M_n (kDa) ^a	M_w (kDa) ^a	$\lambda_{\max}$ (nm) soln. ^b	$\lambda_{\max}$ (nm) film ^c	HOMO (eV) ^d	LUMO (eV) ^e
P11	NIDT	C8C10	7	12	770	774, 830	-4.9	-3.39
3.1 ⁵⁶	IDT	C2C6	40	87	659	660	-5.3	-3.6
3.2 ⁶⁵	SiIDT	C8	30	56	620	634	-5.5	-3.7

^a Determined by GPC using polystyrene standards and chlorobenzene as the eluent. ^b Measured in chloroform solution. ^c Spin cast from 5 mg/mL chlorobenzene solution. ^d Measured by ambient photoelectron spectroscopy (PESA). ^e Estimated by addition of E_g to the HOMO.

The mobility of **P11** was higher than that obtained for the Si analogue ($8 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$),⁶⁵ but much less than that obtained for the C bridging version, which had a mobility of $\sim 0.6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Table 3.9).⁵⁶ The low carrier mobility of the Si analogue may in part be due to the low lying HOMO energy level, which may induce contact resistance at the electrode interface, unless very high work function electrodes, such as platinum are employed.⁶⁵ A strong correlation between the co-monomer and charge carrier mobility was not evident, although the carbon version did seem to perform the best overall, possibly due to its high molecular weight and good energy level alignment with the gold electrodes.

Table 3.9 Summary of OFET and OPV performance of P11, 3.1 and 3.2

Polymer	Repeat unit	Alkyl Chain	μ_h (cm^2/Vs)	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF
P11	NIDT	C8C10	0.02	0.8	0.36	4.2	0.54
3.1 ⁵⁶	IDT	C2C6	0.57	5.5	0.79	11.45	0.49
3.2 ⁶⁵	SiIDT	C8	0.008	4.3	0.88	9.39	0.52

The PIDT-BT **3.1** polymer achieved the highest power conversion efficiency of 5.5 %, ⁵⁶ in part due to its high molecular weight and good blend morphology. The silicon containing polymer, with the lowest energy HOMO, generated the largest open circuit voltage and a maximum PCE of 4.5 % was recorded.⁶⁵ Unfortunately the NIDT containing polymer did not perform well in comparison, with the highest energy HOMO, and therefore the smallest open circuit voltage. The low molecular weight of **P11** and poor blend morphology also had a detrimental effect on PCE.

3.6 Comparison with DTP series

The effect of replacing DTP with the extended ring system, NIDT, was of interest. The energy levels and OPV performance of **P11-P13** were compared to their DTP analogues, **P7-P9**, reported in Chapter 2, Section 2.7.

Unfortunately no significant trends could be identified. The change in the band gaps did not correlate with the change in the J_{sc} , when the DTP unit was replaced with NIDT. Also the reduced HOMO level of the NIDT containing polymers did not manifest itself as an increase in V_{oc} .

The largest difference in PCE was observed between the **P9** and **P13** blends: The **P9** blend exhibited a PCE of 1.41 %, whereas the PCE of the **P13** blend was only 1.10 %. This was attributed to the drop in the fill factor of around 0.1, possibly due to the increased rigidity of the NIDT polymer **P13**: the polymer miscibility with the fullerene may have decreased, leading to a morphology which was less favorable to charge separation and extraction.⁹²

The poor correlation of the results could be due to experimental error. Both the PESA and OPV results of **P11-P13**, were obtained at a different time from **P7-P9**. Any change in the equipment used to measure these values could have an effect on the data collected. A new study of these polymers should be carried out, measuring the required data in the same session, in order to eliminate this problem. This will give a more accurate comparison between DTP and NIDT containing polymers.

3.7 Conclusions

A novel donor monomer NIDT, was synthesized via a double Buchwald-Hartwig amination and fully characterized. The reaction conditions were optimized in order to maximize the yield. The distannylated monomer was then synthesized in high yield.

Four polymers (**P11-P14**) were synthesized via Stille cross-coupling polymerization reactions with the distannylated NIDT unit and the dibromide of the corresponding acceptor unit. All four polymers exhibited long wavelength absorption maxima and correspondingly low band gaps. The polymers containing BT and ffBT had the highest lying HOMO levels. With the introduction of the TPD (and biTPD) units the HOMO level could be lowered.

The polymers were then tested as the semiconducting layer in OFET devices and the donor polymer in bulk heterojunction OPVs. It was evident that the polymers based on BT (**P11** and **P12**) performed best in transistor devices, whereas the TPD containing polymers (**P13** and **P14**) performed best in solar cell devices. Therefore, it is possible to conclude that the performance of the polymer greatly depends on the co-monomer used; very planar units, which have been shown to promote π -stacking, produce polymers which work well in OFETs, whereas the co-monomers which have weaker π -stacking interactions and long solubilizing chains produce polymers which give enhanced OPV performance. Unfortunately the intrinsic problem with NIDT containing polymers is the relatively high energy HOMO levels. This means that the V_{oc} of the devices was always limited with PCBM as the electron acceptor, and therefore high PCEs will never be reached. However, there is scope to improve the mobility of the NIDT polymers in OFETs.

Chapter 4:

Tailoring Pyrroloindacenodithiophene (NIDT) Containing Polymers to Improve Hole Mobility in OFETs

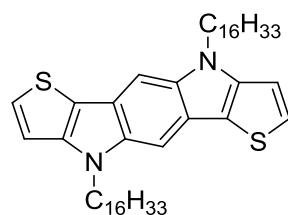
4.1 Introduction

The results obtained in the previous chapter show that the NIDT unit has significant potential for use in OFET devices. When copolymerized with the difluorobenzothiadizole unit, mobilities approaching $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were recorded.⁸¹

It was therefore interesting to see if the hole mobility of a NIDT containing polymer could be improved by using different co-monomers and/or different alkyl substituents on the bridging nitrogens of NIDT.

4.1.1 Strategies for improving mobility

It has been well documented in literature that close π -stacking between polymer chains is crucial for efficient charge transport.^{25, 26} One way of obtaining close π -stacking is to synthesize polymers with conjugated, planar backbones.^{26, 57, 65} The NIDT unit extends π -conjugation due to its rigid, planar structure and aromaticity,⁸¹ however the long branched alkyl chains may disrupt intermolecular order, reducing the mobility. It was therefore worth investigating the effect of replacing the branched alkyl substituents with long linear alkyl chains, such as hexadecyl (**4.1**), in order to reduce the π -stacking distance. Unfortunately, this was likely to reduce the solubility of the resulting polymer, so lower molecular weight polymers were expected.



4.1

Figure 4.1 Pyrroloindacenodithiophene with hexadecyl side chains.

The π -orbital overlap between rings linked by a single bond is maximized when the rings are coplanar.⁸ As mentioned in Section 2.1, conjugation length can be increased by ensuring

minimal steric overlap between substituents on adjacent monomers. Therefore if a BT co-monomer was replaced with a thiophene (T), or thieno[3,2-*b*]thiophene (TT), then the steric twist between units should decrease and the persistence length would be expected to increase.

Thiophene and its alkylated derivatives (namely P3HT) have been used extensively in the synthesis of high mobility, hole conducting materials.^{17, 95, 96} Its electron rich, aromatic nature promotes π -stacking as well as efficient hole transport. Thieno[3,2-*b*]thiophene has been copolymerized with alkylated thiophene units to give PBTTT, a high performance material which can assemble into large crystalline domains on crystallization from a liquid-crystal phase.¹⁶ The introduction of this planar, rigid unit lowers energetic disorder through stiffening of the backbone and promotes close intermolecular π -stacking which aids the formation of highly ordered domains. This structural order gained by the introduction of the TT unit greatly improves the hole mobility in comparison to P3HT.¹⁶ Also as mentioned previously in Section 2.1, TT has been copolymerized with indacenodithiophene, producing a material with a hole mobility of $0.15 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.⁵⁷ It was therefore interesting to investigate the use of TT in the NIDT series. The use of two rigid, planar molecules was expected to lead to close π -sacking, improved conjugation length and in turn, higher mobilities.

Polymer **P13**, which contained the TPD co-monomer, showed promise for use in OFET and OPV devices. It was of interest to see if the mobility and PCE could be further enhanced with the use of linear hexadecyl substituents on the bridging nitrogens of NIDT (Figure 4.1). The straight chains were expected to enhance π -stacking in OFETs and affect the blend morphology in OPV devices.⁵⁶ Substitution of the branched alkyl side chains, for the linear side chains could also have an effect on the energy levels. Li *et al.* report on a cyclopentdithiophene-*co*-thienopyrrolodione (Figure 4.2) copolymer.⁹¹ When the alkyl chain on the TPD moiety was varied (butyl, hexyl, octyl, 2-ethyl hexyl), they discovered that the HOMO and LUMO energy levels lowered with increasing alkyl chain length.⁹¹ Unfortunately an explanation for this observation was not provided.

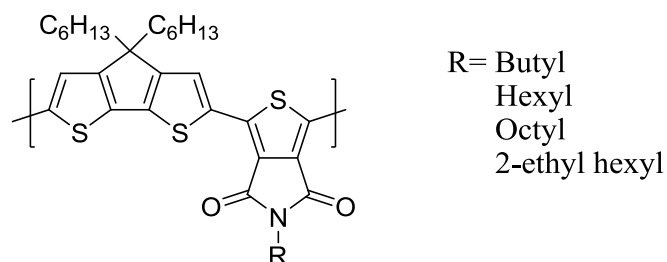


Figure 4.2 Cyclopentadithiophene-co-thienopyrrolodione polymer series.⁹¹

A large amount of research has been carried on diketopyrrolopyrrole (DPP) containing polymers and mobilities approaching $2.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported.^{27, 80, 97} When copolymerized with SiIDT, the resultant copolymer **4.2** exhibited a hole mobility of $0.65 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.⁶⁵ Because of the literature precedent for the use of this monomer in high performance materials, it was of interest to copolymerize NIDT with this unit.

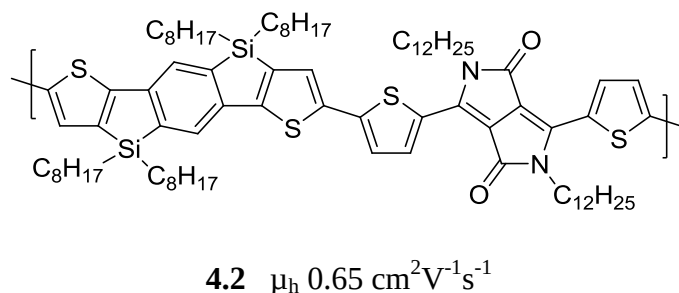


Figure 4.3 PSiIDT-DPP copolymer **4.2**.⁶⁵

4.2 Aim

The aim of this study was to synthesize a series of polymers based on NIDT, which would perform well in OFET devices (Figure 4.4). The branched NIDT monomer would be coupled with thiophene and thieno[3,2-b]thiophene to create two highly planar, electron rich polymers **P15** and **P16**. A NIDT unit with linear hexadecyl substituents **4.1** would be synthesized. This monomer would be stannylated, then copolymerized with thiophene (**P17**) and TPD (**P19**) and compared to the analogous branched NIDT polymers. It would also be copolymerized with a hexadecyl substituted TT unit (**P18**). The hexadecyl units on TT were required in order to improve the solubility of the polymer. Finally the hexadecyl substituted NIDT would be

coupled with DPP (**P20**). All of the polymers will then be tested in OFET devices and **P19** will also be tested in OPVs.

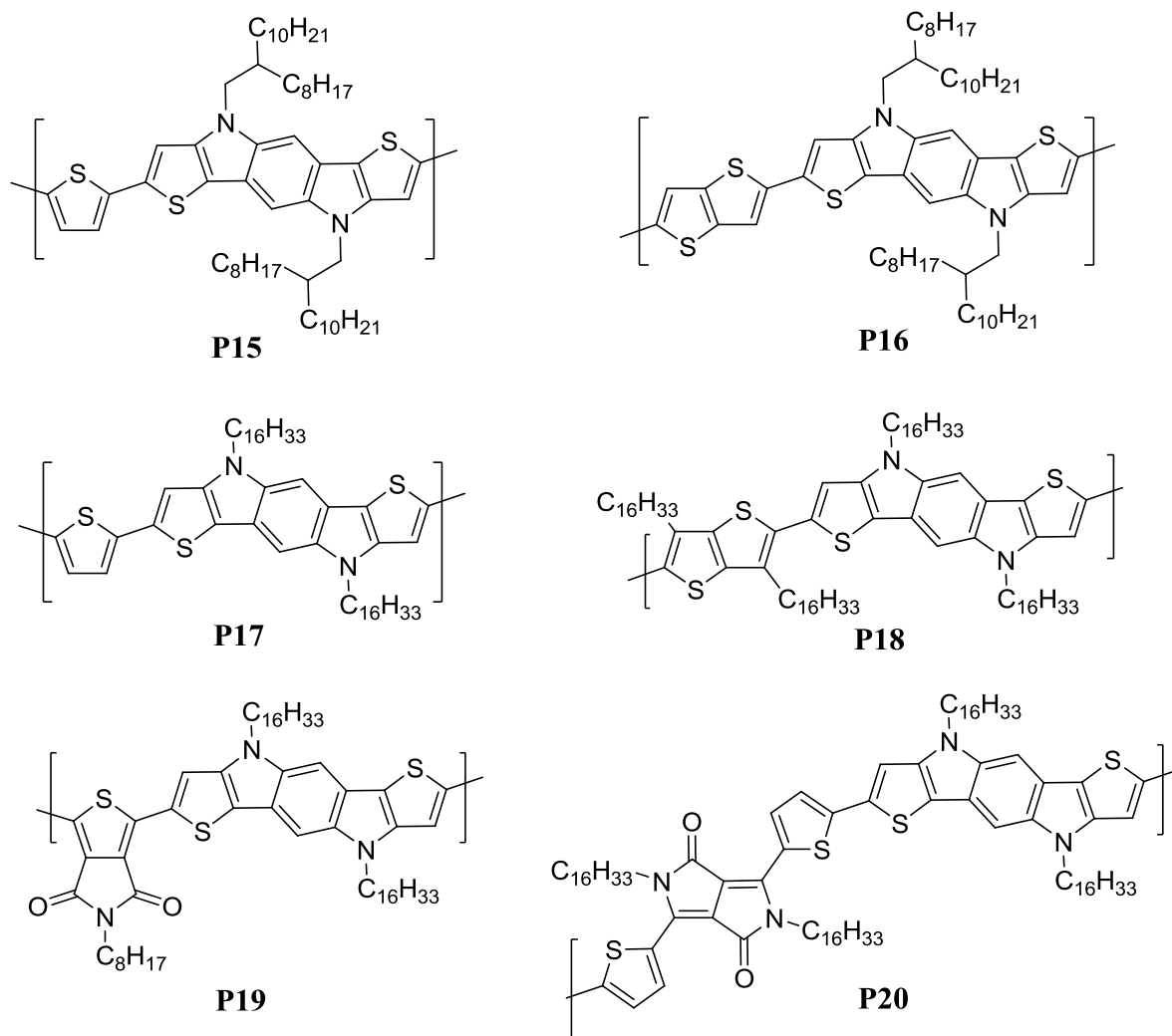
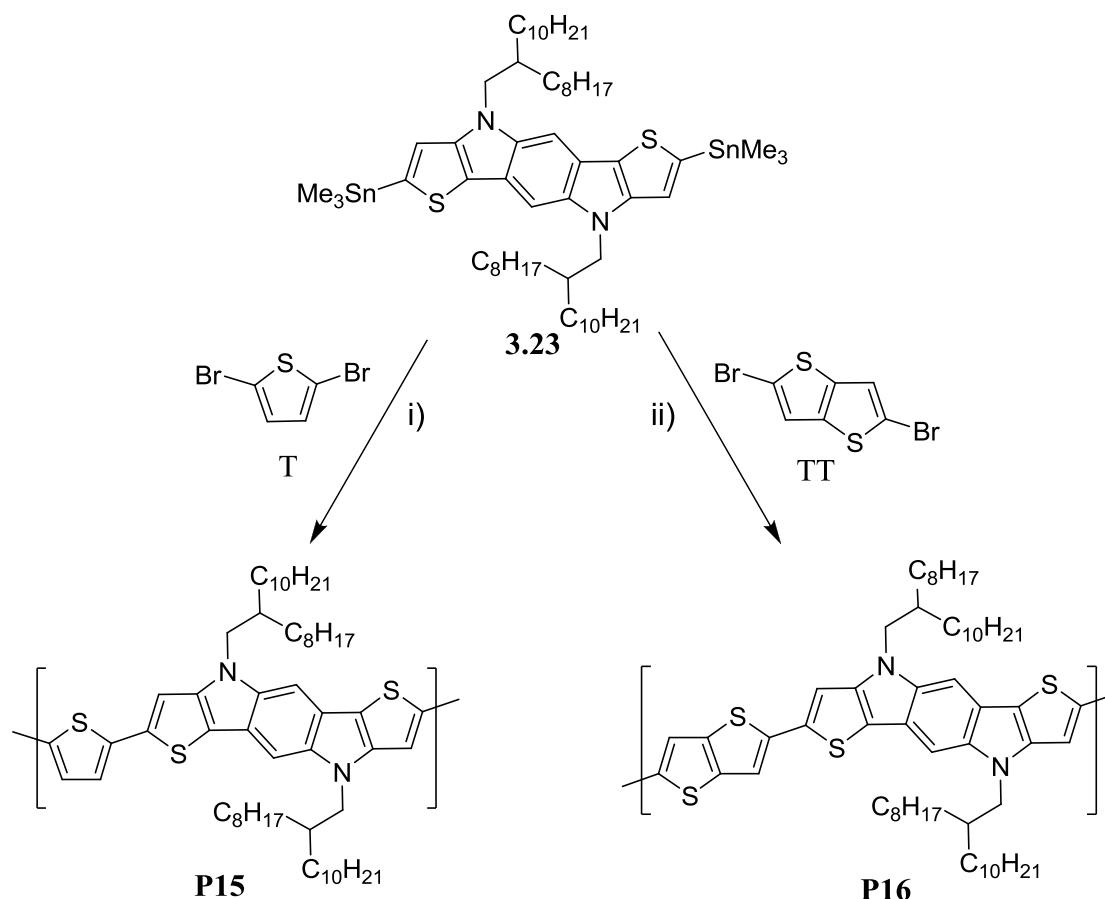


Figure 4.4 Series of NIDT polymers **P15-P20**.

4.3 Polymer Synthesis

4.3.1 Synthesis of P15 and P16

The polymers were synthesized via microwave assisted Stille cross-coupling of the distannylated NIDT **3.23** with the corresponding dibrominated co-monomer (Scheme 4.1). Two electron rich units were chosen for copolymerization: thiophene (**P15**) and thieno[3,2-b]thiophene (**P16**).



Scheme 4.1 Reagents and Conditions i) 2 mol% Pd_2dba_3 , 8 mol% $\text{P}(\text{o-tolyl})_3$, chlorobenzene, 200 °C, 30 min, μW ; ii) 2 mol% Pd_2dba_3 , 8 mol% $\text{P}(\text{o-tolyl})_3$, chlorobenzene, 200 °C, 30 min, μW .

The starting materials were reacted in a 1.03:1 ratio of with the distannylated monomer **3.19** in excess. $\text{Pd}_2\text{dba}_3/\text{P}(\text{o-tolyl})_3$ was used as the catalyst and chlorobenzene as the solvent. The reaction mixture was heated for 30 min at 200 °C in the microwave and once cooled, precipitated in to methanol. The polymers were purified by Soxhlet extraction using acetone, hexane and, finally, chloroform. Each chloroform fraction was concentrated and washed with

aqueous sodium diethyldithiocarbamate tetrahydrate to remove any palladium catalyst, then the chloroform fraction was separated and the polymer reprecipitated into methanol. **P15** was isolated as a dark purple powder in low yield (33 %). Due to the high solubility of this polymer, a lot of mass was lost during extraction. **P16** was isolated as dark purple powder with a moderate yield (52 %). This polymer was markedly less soluble than **P15**, possibly due to the more rigid nature of the backbone.

The molecular weights were measured using Gel Permeation Chromatography (GPC), at 80 °C in chlorobenzene. **P15** had a M_n 33 kDa, M_w 56 kDa, corresponding to a degree of polymerization (DP) of 33; **P16** had a M_n 13 kDa, M_w 28 kDa and DP 13.

The polymers were characterized by ^1H NMR spectroscopy in CDCl_3 . The broadened resonances are characteristic of a polymeric species. For both **P15** and **P16** six aromatic protons are visible between 7.5 and 6.0 ppm, confirming the incorporation of the thiophene/thienothiophene unit in to the polymer.

4.3.2 Synthesis of hexadecyl substituted pyrroloindacenodithiophene 4.1

The hexadecyl substituted NIDT monomer **4.1** was synthesized via the same method used for the synthesis of the branched NIDT **3.10** (Scheme 4.2). The tetrabromo starting material **3.09** was placed in a Schenk tube along with 5 mol% Pd_2dba_3 , 20 mol% BINAP, 6 equivalents of NaO^tBu and 2.2 equivalents of hexadecylamine. Toluene was used as the solvent and the reaction mixture was heated for 24 h at 120 °C, under nitrogen. The crude product was purified by column chromatography (silica gel, hexane). A mixture of the mono-ring closed and mono-aminated products were isolated as expected. This mixture was subjected to the same Buchwald-Hartwig amination conditions, only this time 4 mol% Pd_2dba_3 , 16 mol% BINAP, 5 equivalents of NaO^tBu and 1.1 equivalents of hexadecylamine were used. The fully ring closed product was purified by column chromatography (silica gel, 0-5 % dichloromethane in hexane, R_f 0.32) and isolated in 14 % yield. The yield was lower than that obtained for the branched version, as the final ring closure reaction did not reach full

conversion. This reaction was only carried out once, and it is believed the yield can be improved upon optimization of reaction conditions.

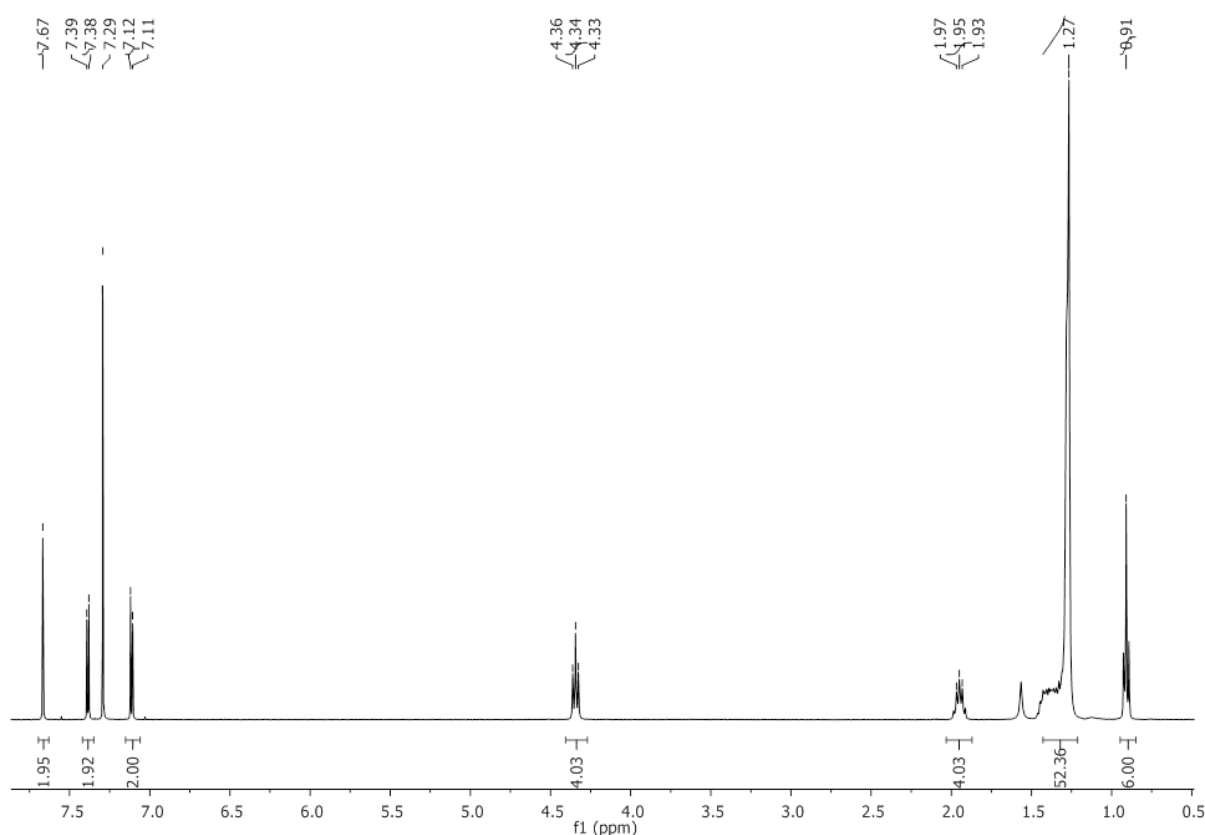
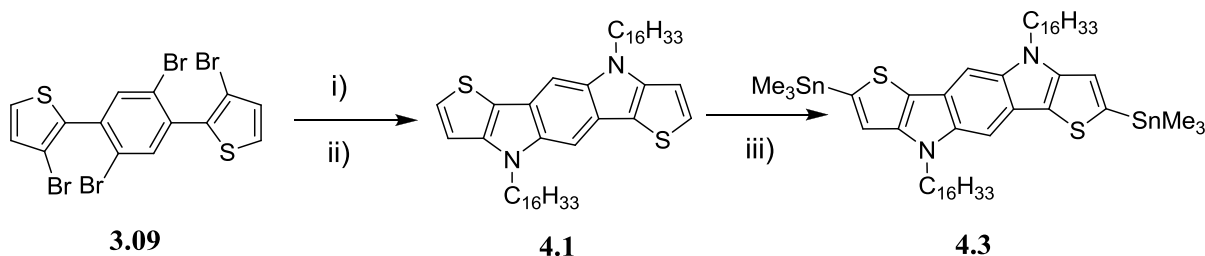


Figure 4.5 ^1H NMR spectrum of hexadecyl substituted NIDT **4.1**.

The product **4.1** was characterized by ^1H NMR spectroscopy, $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, E.I. mass spectrometry and elemental analysis. The ^1H NMR spectrum (Figure 4.5) was similar to that observed for the branched version **3.10**, only fewer peaks were observed in the aliphatic region, as expected.



The stannylation of **4.1** was facile. A lithiation reaction using *n*BuLi at -40 °C, was followed by the addition of trimethyltin chloride, 2 h later. The reaction mixture was allowed to warm to room temperature overnight before being quenched with water. After work up the product was evaporated to dryness and used in the next step without further purification. The distannylated NIDT **4.3** was isolated as a pale brown solid in 90 % yield.

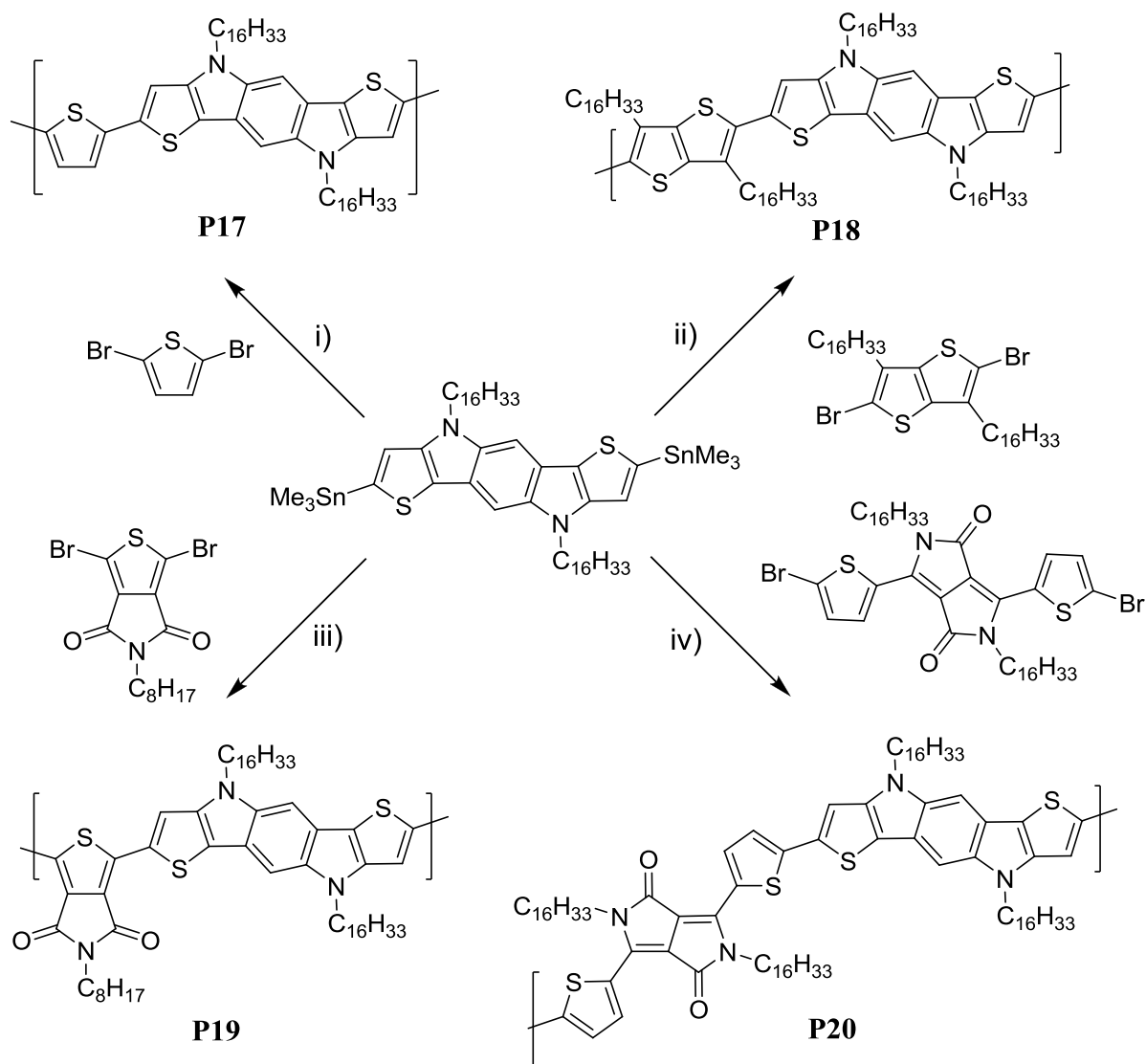
The product formation was supported by ¹H NMR spectroscopy, ¹³C{¹H} NMR spectroscopy, E.I. mass spectrometry and elemental analysis.

4.3.3 Synthesis of P17-P20*

The linear alkyl substituted NIDT series was also synthesized via microwave assisted Stille cross-coupling (Scheme 4.3), using the same conditions as reported for the synthesis of **P15** and **P16**; Pd₂dba₃/P(o-tol)₃ was used as the catalyst, chlorobenzene as the solvent and the reaction mixture was heated for 30 min at 200 °C. The distannylated NIDT **4.3** was used in excess (1.03 equiv.). The polymers were worked up and purified as reported in Section 4.3.1.

P17 was isolated as a purple powder which had poor solubility in organic solvents. A chloroform fraction was obtained (49 %) which possessed low molecular weight polymer (*M_n* 7 kDa, *M_w* 9 kDa) and a chlorobenzene fraction (21 %) was obtained which contained slightly higher molecular weight polymer (*M_n* 8 kDa, *M_w* 11 kDa). Unfortunately, the molecular weight of this polymer was limited by its poor solubility causing it to precipitate from solution before higher molecular weights could be reached.

* Thienothiophene, TPD and DPP supplied by McCulloch group, Chemistry Dept., Imperial College London.



Scheme 4.3 Reagents and conditions: *i-iv*) 2 mol% Pd₂dba₃, 8 mol% P(*o*-tolyl)₃, chlorobenzene, 200 °C, 30 min, μ W.

P18 was isolated as a purple powder which turned orange when dissolved in chloroform or chlorobenzene. This polymer also presented solubility issues, despite the presence of the two hexadecyl side chains on the TT moiety. Once again a low molecular weight chloroform fraction (27 %, M_n 5 kDa, M_w 8 kDa) was obtained, followed by a higher molecular weight chlorobenzene fraction (17 %, M_n 8 kDa, M_w 10 kDa). Due to the very rigid, planar nature of this polymer's backbone, there were solubility issues. Some mass was lost as a fraction the polymer would not dissolve, even in hot dichlorobenzene.

The TPD containing polymer **P19**, was obtained as a blue powder in moderate yield (60 %). This polymer possessed superior solubility in organic solvents and the highest molecular weight fraction was obtained from extraction with chloroform; M_n 10 kDa, M_w 22 kDa. This improvement in solubility is likely due to the more flexible nature of the polymer backbone, combined with the solubilizing influence of the octyl substituent on the TPD unit.

P20 contained the DPP unit with solubilizing hexadecyl substituents on the nitrogens. Using the linear substituents on both co-monomers was expected reduce the π -stacking distance between chains, as there would be no substituents projecting out of the plane of the backbone. This polymer was isolated as a dark blue powder with a 50 % yield obtained from the chloroform fraction. Unfortunately a high molecular weight polymer was not isolated (M_n 5 kDa, M_w 10 kDa), probably because the reaction was carried out on such a small scale, which leads to difficulty in accurate weighing of starting materials and reagents. This reaction should be repeated in the future on a larger scale.

4.3.4 Summary

Table 4.1 Molecular weight distributions of all six polymers measured by GPC in chlorobenzene at 80 °C

Polymer	M_n (kDa)	M_w (kDa)	PDI	DP
P15	33	56	1.7	33
P16	13	28	2.2	13
P17	8	11	1.4	10
P18	8	10	1.3	6
P19	10	22	2.2	10
P20	5	10	2	3

4.4 Optical properties and energy levels of P15-P20

The UV-Vis absorption spectra (Figure 4.6) of **P15** and **P16**, show that both polymers have a defined vibronic structure, indicative of a backbone capable of exhibiting a π -stacked microstructure. **P15** has two major peaks in the solution state, one at 556 nm and the other, more prominent peak, at 587 nm, suggesting a high proportion of polymer aggregates. When going from the solution state to the solid state, the peak on the longer wavelength side becomes more intense and is red shifted by 15 nm, indicating a stronger interchain interaction in the solid state, and a more planar backbone conformation. A similar trend is also observed for **P16**.

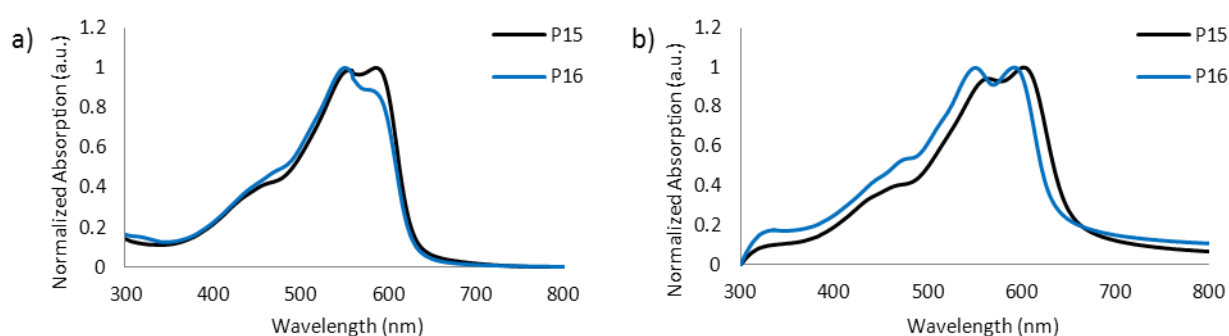


Figure 4.6 a) Solution UV-Vis spectra in chloroform; b) Thin film UV-Vis spectra from chlorobenzene.

The band gaps of the polymers were estimated from the absorption onset and the HOMO levels were estimated via PESA (Table 4.2). **P15** has a lower band gap than **P16**, due to a higher lying HOMO level. The lowering of the HOMO level from **P15** to **P16** is attributed to the reduced electron delocalization along the backbone, due to the larger aromatic stabilization of the TT unit over thiophene.¹⁷ The band gaps are not as low as those recorded for polymers **P11-P14** as they are not donor-acceptor type polymers (the LUMOs are not stabilized) therefore there is less molecular orbital hybridization.

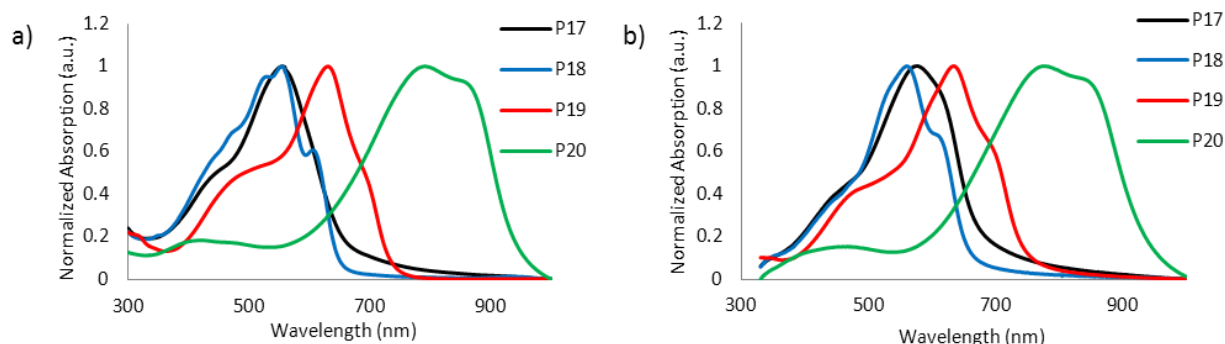


Figure 4.7 a) Solution UV-Vis spectra in chloroform; b) Thin film UV-Vis spectra from chlorobenzene.

The solution and solid state UV-Vis spectra of **P17-P20** are shown in Figure 4.7. When the solution UV-Vis absorption spectrum of **P17** is compared to the branched NIDT analogue (**P15**) only one absorption maximum is observed. When in the solid state, the absorption maximum is red shifted by ~ 22 nm, and a shoulder appears on the long-wavelength side suggesting some solid state aggregation. However, in comparison to **P15**, **P17** appears to have much less solution and solid state aggregation possibly due to the low molecular weight, combined with the high polydispersity of **P17**, which reduces its ability to form aggregates.

In both solution and solid state **P18** has a shoulder on the long-wavelength side of the absorption maximum. There is little difference between the solution and thin film spectra. This could be due to the very rigid nature of the backbone, which only consists of ~ 6 repeat units, resulting in minimal conformational change when going from solution to thin film. Or it could simply be due to the presence of solid particles in the solution, a consequence of the poor solubility of this polymer.

For **P19** we did not observe a red shift or a shoulder suggesting there is little order gained when going from solution to solid state. This is in accordance with what was observed for the branched analogue (**P13**). The absorption maximum for **P19** is also very similar to that recorded for **P13**.

P20, however, exhibited a blue shift in its absorption maximum when going from solution to solid state. The absorption profile does not change much, but instead we see a translation of the absorption spectrum to shorter wavelengths. This could be due to a solvatochromic effect of chloroform on the polymer, which causes it to red shift in solution. In the solid state this effect is no longer present, so the spectra becomes blue shifted. This blue shift has previously been observed for other DPP containing polymers.⁸⁰

Table 4.2 Optical properties and energy levels of P15-P20

Polymer	λ_{max} (nm)		E_g (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^e
	soln. ^a	film ^b			
P15	556, 587	602	1.9	-4.8	-2.9
P16	551	551, 592	2.0	-4.9	-2.9
P17	554	576	1.9	-4.7	-2.8
P18	554	560	1.9	-4.5	-2.6
P19	630	634	1.7	-4.8	-3.1
P20	798	775	1.3	-4.7	-3.4

^a Measured in chloroform solution. ^b Spin cast from 5 mg/mL chlorobenzene solution. ^c Estimated from the absorption onset of thin film UV-Vis spectra. ^d Measured by ambient photoelectron spectroscopy (PESA). ^e Estimated by addition of E_g to the HOMO.

When going from the branched NIDT containing polymers, to their analogous linear NIDT containing polymers, the HOMO and LUMO levels are shifted to higher lying energies, whilst maintaining the same band gap (Table 4.2). The HOMO and LUMO levels of **P15** are 0.1 eV lower than those of **P17**, while the energy levels of **P13** are 0.3 eV lower than **P19**. The lowering of the HOMO level may be due to the increased steric twist experienced when the bulky branched substituents are used. This steric twist would reduce π -conjugation, leading to a lower lying HOMO. It is apparent that the side chains present on the NIDT unit can greatly affect the energy levels of the resulting polymers. As mentioned in Section 4.1.1, Li *et al.* observed a change in the energy levels when the alkyl chain on the TPD moiety of their polymer was varied,⁹¹ so this phenomenon is not unique to the NIDT polymers.

Comparison of the very low molecular weight polymers, **P17** and **P18**, with each other and other higher molecular weight polymers, is difficult as the polymer energy levels are molecular weight dependent at such low DPs. The effect that end groups have on the polymers properties will also be much more significant, therefore a clear explanation cannot be given for the differences observed in their energy levels.

4.5 Differential Scanning Calorimetry^{*}

All six polymers were subjected to differential scanning calorimetry (DSC) between 40-300 °C in order to assess if they possessed any crystallinity. For polymers **P15-P18**, no transitions were observed, suggesting they are amorphous materials. For **P19** a glass transition (T_g) was observed at 185 °C, but no crystallization or melting peaks were observed, indicating that this polymer is also amorphous.

However, for **P20** a melting transition (T_m) appeared at 48 °C and a crystallization transition (T_c) was observed at 42 °C. From integration of the areas under the melt and crystallization transition peaks, the degree of crystallization was calculated and found to be 15 %.

4.6 OFET properties of P15-P20

To measure the p-type charge carrier mobility of the polymers bottom gate-bottom contact (BG-BC) architecture devices were fabricated. Si/SiO₂ substrates with lithographically patterned gold electrodes (purchased from Fraunhofer IPMS) were cleaned and UV/ozone treated before they were modified with HMDS. Polymer solutions (5 mg/ml in chlorobenzene) were spin coated on the pre-printed substrate at 3000 rpm for 3 min, then annealed at 200 °C for 30 min.[†] Annealing above the T_m for **P20** allowed the polymer to reach its optimum morphology upon cooling.

^{*} DSC carried out by Stingelin Group, Materials Dept, Imperial College London. See Appendix A for DSC curves.

[†] OFET fabrication and testing carried out by Eun-Ho Sohn, Physics Dept., Imperial College London. See Appendix A.

The charge carrier mobility was calculated from the transfer characteristics of the device, in the saturation regime, using previously reported procedures.⁷¹ The results are summarized in Table 4.3. Figure 4.8 displays the transfer curves of all six polymers obtained from OFET devices (channel length (*L*)/width (*W*) of 0.02/10 mm) at a drain voltage (*V_D*) of -80 V.

4.6.1 P15 versus P16

The aim of this study is to draw a comparison between the use of a thiophene unit and a thienothiophene unit as a co-monomer for NIDT. From analysis of the transfer curves and calculated mobility values it is clear that **P15** performs better than **P16**. **P15** has a hole mobility which is one order of magnitude greater than that recorded for **P16**. It also has a lower threshold voltage and larger on/off current ratio.

Table 4.3 Summary of OFET device results

Polymer	μ_{sat} (cm ² V ⁻¹ s ⁻¹)	<i>V_{th}</i> (V)	<i>I_{on/off}</i>
P15	0.004	-14	10 ⁵
P16	0.0004	-19	10 ⁴
P17	0.0005	-25	10 ⁵
P18	0.0005	4	10 ⁴
P19	0.002	10	10 ⁵
P20	0.04	16	10 ⁶

This result was unexpected. The replacement of a thiophene unit with a thienothiophene unit should lower energetic disorder through stiffening of the backbone and promote close intermolecular π -stacking, leading to improved hole mobility.^{16, 17, 57} However, it was possible that the thiophene containing polymer **P15** performed better due to its superior molecular weight. **P15** had a degree of polymerization (DP) of 33, whereas **P16** had a DP of 13. When the thiophene was replaced with the rigid, planar TT unit the solubility was compromised and in turn the molecular weight fell substantially. As discussed previously, the molecular weight of a polymer can have a significant effect on OFET performance.^{9, 10, 70, 93,}

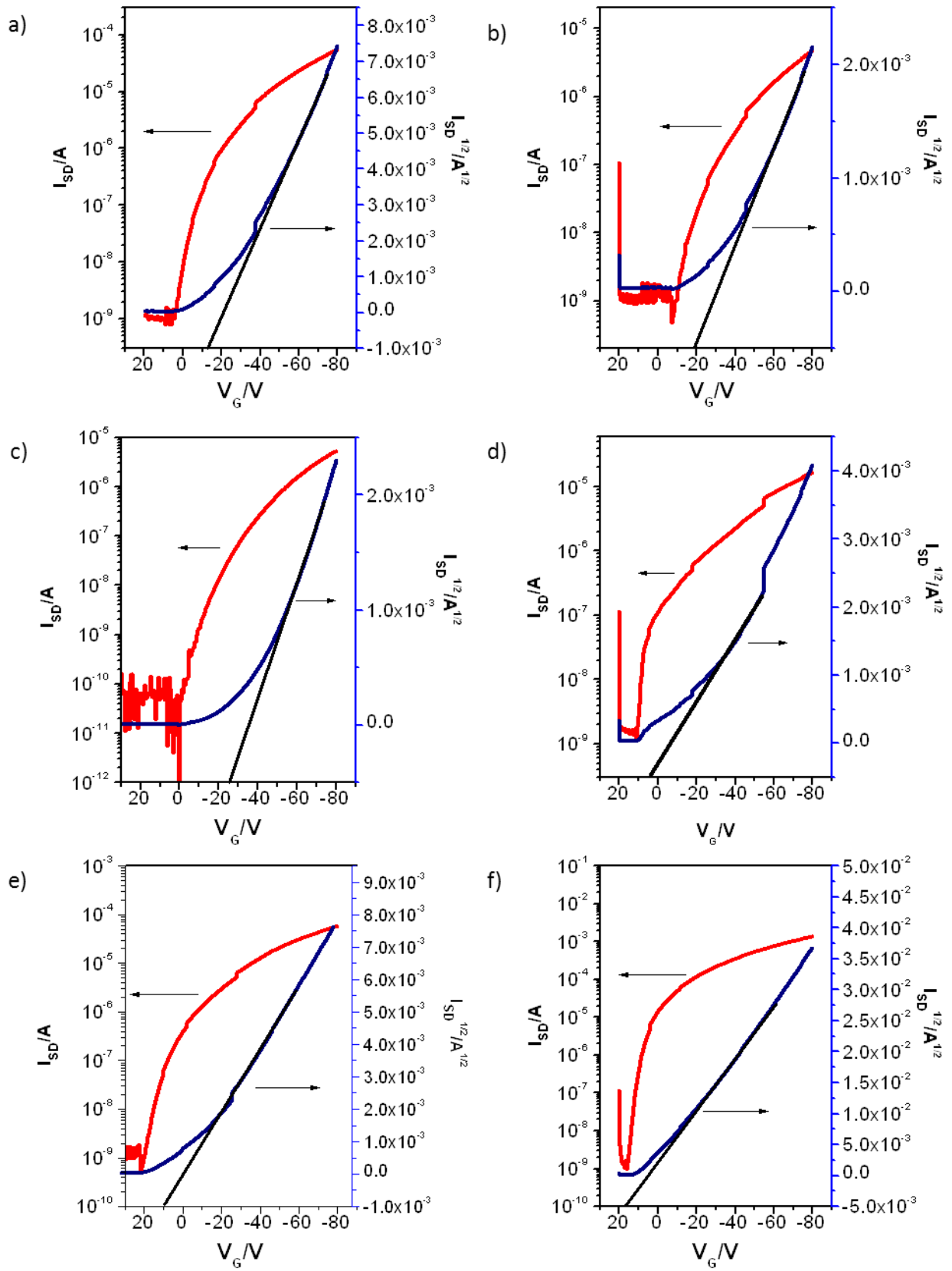


Figure 4.8 Transfer curves of polymers a) **P15**; b) **P16**; c) **P17**; d) **P18**; e) **P19**; f) **P20** when used as the semiconducting layer in OFET devices.

4.6.2 P15 versus P17

This investigation aims to compare the performance of a polymer containing the branched NIDT monomer **P15**, with one containing the linear NIDT monomer **P17**. In this case **P15** outperforms **P17**, with its superior mobility, lower threshold voltage and high on/off current ratio.

With the introduction of the linear alkyl chains the local structural order was expected to improve due to improved π -stacking, leading to enhanced inter-chain charge transport. Unfortunately, any enhancement in charge transport was once again out-weighed by the drop in molecular weight on going from **P15** to **P17**. The solubility of **P17** was greatly reduced with the introduction of the linear alkyl chains on the NIDT moiety, leading to a low molecular weight polymer with a DP of 10. This drop in molecular weight was expected, but not to this extent and the effect it would have on mobility was underestimated.

4.6.3 Highest performing polymer P20

Polymer **P20** performed best out of all the polymers containing the hexadecyl NIDT unit. With the incorporation of the DPP unit, the mobility was improved by over 1 order of magnitude (Table 4.3). **P20** also had the lowest threshold voltage (18 V) and the highest on/off current ratio (10^6).

This result was expected as there has been a lot of literature precedent for the use of DPP containing polymers in high performance OFETs.^{65, 99, 100} It is believed that even higher mobilities could be reached if the molecular weight of this polymer was increased. Work in this area is on-going.

In order to optimize the performance of **P20**, a TG-BC device was fabricated. Gold source/drain contacts were evaporated onto cleaned Corning glass substrates, followed by functionalization with PFBT monolayer. Polymer solution (7 mg/ml in chlorobenzene) was spin coated on top of the electrodes at 3000 rpm for 3 min, then annealed at 200 °C for 30

min. CYTOP was spin coated on top of the polymer at 2000 rpm for 1 min, then annealed at 100 °C for 30 min before the Al top gate was evaporated on to the surface.

The charge carrier mobility was calculated from the transfer characteristics of the device, in the saturation regime. Figure 4.9b displays the transfer curve obtained from the OFET device (channel length (L)/width (W) of 40/1000 μm) at a drain voltage (V_D) of -80 V. The reader is referred to Appendix A for device output characteristics.

Analysis of the results showed a drop in mobility of **P20** from 0.04 to 0.002 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, when the TG-BC device was tested. It is worth noting however, that zero hysteresis is observed when this architecture is employed (Figure 4.9). BG-TC devices are currently being fabricated to see if the mobility can be improved further.

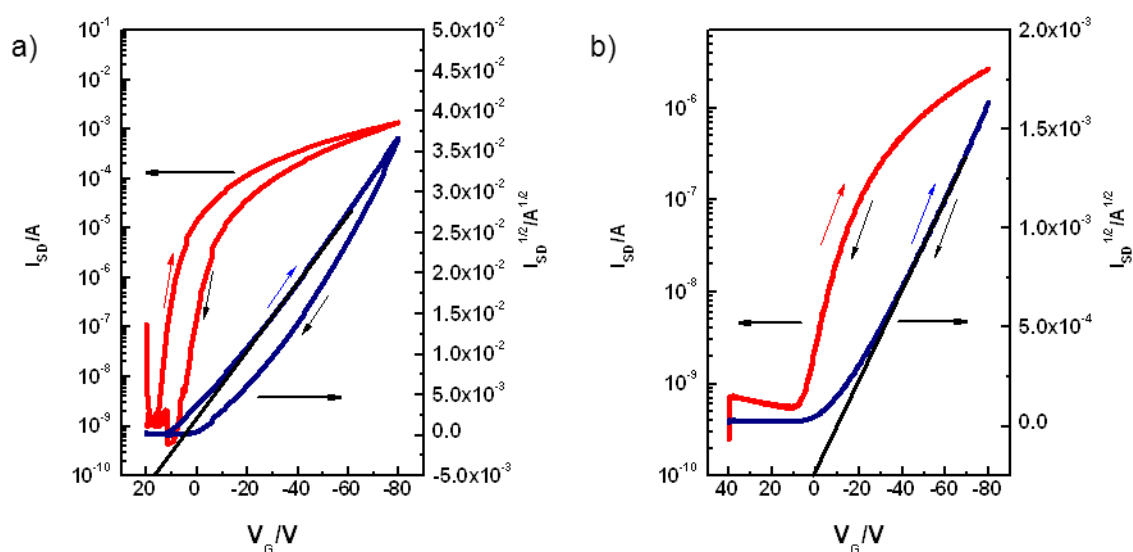


Figure 4.9 Transfer curves of polymer **P20** when used in a) BG-BC; b) TG-BC architecture OFET device.

4.7 OPV properties of P19

The OPV performance of **P19** was of interest as it could be compared to the branched version, **P13**. This will give insight in to whether the branched or linear NIDT containing polymers perform better in OPVs.

A solar cell was fabricated with **P19** using the device structure ITO/PEDOT:PSS/**P19**:PC₇₁BM/Ca/Al.* The *J-V* characteristics are illustrated in Figure 4.10 and the properties are summarized in Table 4.4. The active layer was spin-coated from 1,2-dichlorobenzene (DCB), with a blend ratio of Polymer:PC₇₁BM of 1:3 (w/w).

Table 4.4 Photovoltaic properties of polymer solar cells incorporating polymer:PC₇₁BM blends

Polymer	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	FF	PCE (%)
P19	4.08	0.46	0.51	0.96
P13 (Chap 3)	4.04	0.58	0.48	1.10

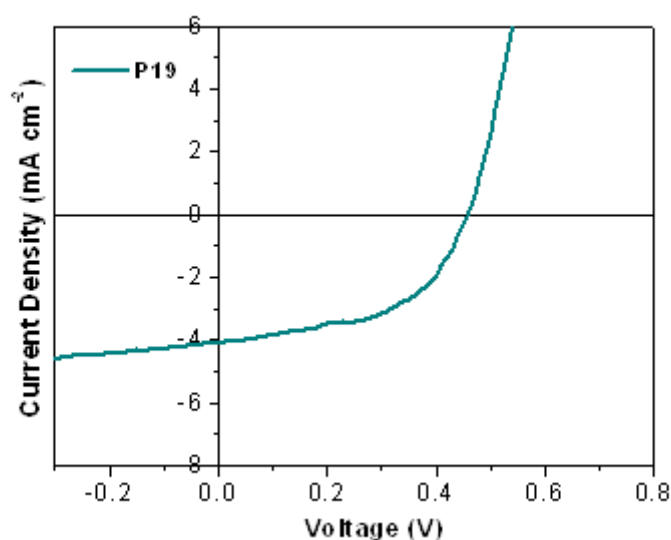


Figure 4.10 *J-V* characteristics of **P19**:PC₇₁BM blend prepared at a blend ratio of 1:3 (w/w).

* OPV fabrication and testing carried out by S. Ashraf, McCulloch group, Imperial College London, SW7 2AZ.

As previously mentioned the λ_{max} values, and therefore band gaps, are very similar for **P13** and **P19**. This results in a J_{sc} which is comparable for both blends. The fill factor of the blends are also very similar, suggesting any change in morphology has not had a detrimental effect. However, due to the higher HOMO level of **P19**, the V_{oc} has decreased from 0.58 to 0.46 V. Ultimately it was this reduction in V_{oc} which led to the reduced PCE of the **P19** blend.

4.8 Conclusions

A novel NIDT monomer with linear hexadecyl substituents was synthesized, along with six novel polymers which were characterized by ^1H NMR spectroscopy, UV-Vis spectroscopy, PESA and DSC.

The OFET performance of the polymers were tested. It was found that the solubility of these polymers dictated the molecular weights which could be reached. Therefore, when the solubility was compromised by the introduction of the TT unit or the hexadecyl NIDT unit, the molecular weight fell significantly. This fall in molecular weight had a detrimental effect on the hole mobility of the polymers.

Polymer **P20** was the highest performing polymer when tested in OFET devices. Its hole mobility was over one order of magnitude higher than the other polymers. This was due to the introduction of the DPP unit which has excellent hole transport properties. The initial results look promising and work is on-going to optimize this polymers performance.

In terms of OPV performance, the introduction of the hexadecyl NIDT unit in to the polymer led to a decrease in V_{oc} . This was attributed to the higher lying HOMO level of the hexadecyl NIDT containing polymer. With the introduction of the linear substituent it is likely that the polymer backbone became more planar, resulting in improved molecular orbital hybridization and a rise in the HOMO level.

Chapter 5: Experimental Procedures

5.1 OFET device fabrication

Chapter 2

Bottom-gate, bottom-contact devices were fabricated using Si/SiO₂ substrates with lithographically patterned gold electrodes which were cleaned by sonication in acetone and IPA. Electrodes were treated with a self-assembled monolayer by immersion in a pentafluorobenzenethiol (PFBT) solution in IPA (1:1000) and then rinsed with neat IPA. Polymer solutions (10 mg/ml in chlorobenzene) were spin coated on the pre-printed substrate at 1500 rpm for 0.5 min and annealed at 100 °C for 2 min.

Top-gate, bottom-contact devices were fabricated using Au/PFBT electrodes on glass with CYTOP as the dielectric. The polymer solutions (10 mg/ml in chlorobenzene) were spin coated on to the cleaned substrate at 2000 rpm for 30 sec. Devices were annealed at 140 °C for 10 min prior to CYTOP deposition. An aluminium gate was then evaporated on to the surface of the dielectric.

Top-gate, bottom-contact devices were fabricated using Au/MoO₃ electrodes on glass with CYTOP as the dielectric. The polymer solutions (10 mg/ml in chlorobenzene) were spin coated on to the cleaned substrate at 2000 rpm for 30 sec. Devices were annealed at 100 °C for 5 min prior to CYTOP deposition. An aluminium gate was then evaporated on to the surface of the dielectric.

Chapter 3

Bottom-gate, top-contact devices were fabricated on highly doped p-type Si with 400 nm SiO₂ dielectric layer. Si/SiO₂ was treated with OTS or HMDS depending on wettability of each polymer. For source and drain electrodes, 60 nm Au electrodes were deposited by thermal evaporation. Polymer films were spin cast from hot 1,2-dichlorobenzene solution (5 mg/mL) at 1000 rpm and annealed at 150 °C or 200 °C for 10 min. All procedures/measurements were carried out in a dry nitrogen filled glove box.

Chapter 4

Bottom gate-bottom contact (BG-BC) architecture devices were fabricated on Si/SiO₂ substrates with lithographically patterned gold electrodes (purchased from Fraunhofer IPMS). They were cleaned and UV/ozone treated before they were modified with HMDS. Polymer solutions (5 mg/ml in chlorobenzene) were spin coated on the pre-printed substrate at 3000 rpm for 3 min, then annealed at 200 °C for 30 min.

Top-gate, bottom contact devices were fabricated using gold source/drain contacts which were evaporated onto cleaned Corning glass substrates, followed by functionalization with PFBT monolayer. Polymer solutions (7 mg/ml in chlorobenzene) were spin coated on top of the electrodes at 3000 rpm for 3 min, then annealed at 200 °C for 30 min. CYTOP was spin coated on top of the polymer at 2000 rpm for 1 min, then annealed at 100 °C for 30 min before the Al top gate was evaporated on to the surface.

5.2 OPV device fabrication

ITO-coated glass substrates were cleaned with acetone and isopropyl alcohol, followed by drying and oxygen plasma treatment. A 30 nm layer of PEDOT:PSS (AI4083) was spin-coated onto the plasma-treated ITO substrate and annealed at 150 °C for 30 min. An active layer consisting of 1:3 blend of polymer (10 mg/mL) and PC₇₁BM (30 mg/mL, Solenne) dissolved in *o*-dichlorobenzene (*o*-DCB) was spin-coated on the PEDOT:PSS layer and then Ca (30 nm)/Al (100 nm) cathode was finally deposited by thermal evaporation under high vacuum (10⁻⁶ mbar) through a shadow mask. The pixel size, defined by the spatial overlap of the ITO anode and Ca/Al cathode, was 0.045 cm². The device characteristics were obtained using a xenon lamp at AM1.5 solar illumination (Oriel Instruments). AFM was carried out using an Agilent 5500 Atomic Force Microscope and post processing Pico Image software.

5.3 Materials

Unless otherwise stated, all reactions were conducted under nitrogen, using a nitrogen filled dual manifold and standard Schlenk line techniques. All solvents and reagents were obtained from commercial sources (Aldrich, Acros, Thermo Fisher, VWR) and used as received, unless otherwise stated. Where required, toluene, diethyl ether and THF were dried by distillation from Na-benzophenone. Flash column chromatography was performed on Merck Kieselgel 60 (230-400 mesh) silica. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick Merck 5715 Kieselgel 60 F₂₅₄ silica gel plates and observed under 254 nm or 366 nm ultraviolet light.

5.4 Measurements

¹H NMR spectra were measured on a Bruker Av-400 (400 MHz) instrument and ¹³C{¹H} NMR were measured on a Bruker Av-400 (100 MHz). Chemical shifts are reported in ppm, relative to the residual protons in the deuterated solvents. All spectra were analysed using MestreNova v6.2.1 software, from *MestreLab*. UV-Vis spectra were recorded at 289 K on a UV-1601 Shimadzu UV-Vis spectrometer. Solution UV-Vis spectra were carried out in chloroform solutions at concentrations of $\sim 10^{-5}$ M. Thin films of polymers were spin coated from chlorobenzene solutions with a concentration of 5 mg/mL, on a Laurell spin coater at 2000 rpm for 1 min. Photoelectron spectroscopy in air (PESA) measurements were made using a Riken Keiki AC-II at CSIRO Materials Science and Engineering, Australia. Electrospray (ESI) mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. Electron Ionization (EI) mass spectrometry was performed on a Micromass Autospec Premier instrument. Elemental Analyses were determined by Mr. Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7. GPC data was collected using an Agilent Technologies 1200 series instrument, with two mixed B columns, in series, at 80 °C and using chlorobenzene as the eluent, at a flow rate of 1 mL/min. The instrument was calibrated using narrow polydispersity polystyrene standards. DSC measurements were carried out by the Materials Department, Imperial College London, using a Star SW 9.20. Measurements were made between 40-300 °C at a scan rate of 10 °C/min.

5.5 Experimental Section

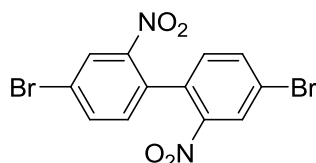
5.5.1 Polymerization Method A

An oven dried 5 mL microwave vial was charged with the appropriate distannylated monomer (1-1.1 equiv), the appropriate dibrominated monomer (1 equiv) and $[\text{Pd}(\text{PPh}_3)_4]$ (4 mol%). The cap was placed on the vial and dry toluene was added. The reaction mixture was purged with argon for 20 min, before being heated in an oil bath at 120 °C for 72 h. Once the reaction had cooled the viscous liquid was precipitated in acidic methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone (12 h), hexane (12 h) and chloroform (24 h). The chloroform fraction was vigorously stirred with aqueous sodium diethyldithiocarbamate tetrahydrate at 50 °C for 1 h, then the organic layer was separated and washed with water, then dried (MgSO_4). The chloroform solution was concentrated and reprecipitated in methanol. The product was collected by filtration and dried *in vacuo*.

5.5.2 Polymerization Method B

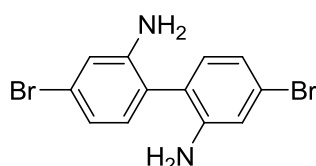
An oven dried 5 mL microwave vial was charged with the appropriate distannylated monomer (1-1.1 equiv), the appropriate dibrominated monomer (1 equiv), $[\text{Pd}_2\text{dba}_3]$ (2 mol%) and tri-*o*-tolylphosphine (8 mol%). The cap was placed on the vial and dry chlorobenzene was added. The reaction mixture was then purged with argon for 20 min before being placed in the microwave and subjected to the following conditions: 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, 180 °C for 2 min and 200 °C for 30 min. Once the reaction had cooled, the viscous liquid was precipitated in acidic methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate at 50 °C for 1 h, then the organic layer was separated and washed with water, then dried (MgSO_4). The chloroform fraction was concentrated and reprecipitated in methanol. The product was collected by filtration and dried *in vacuo*.

5.5.3 Experimental for Chapter 2

Synthesis of 4,4'-dibromo-2,2'-dinitrophenyl²² 2.7

A 1 L round bottomed flask, equipped with a stirrer bar, was charged with 2,5-dibromonitrobenzene (90.00 g, 320.40 mmol), copper powder (48.60 g, 763.2 mmol) and DMF (360 mL). The suspension was heated to 125 °C and stirred for 3 h. The solution was allowed to cool to room temperature then toluene (400 mL) was added. The solution was filtered through celite and the volatiles removed under reduced pressure. The resulting brown solid was washed with methanol (300 mL) and recovered by filtration. The solid was redissolved in toluene (500 mL) with heating, and the resulting suspension was filtered through celite once more. Toluene was removed under reduced pressure to yield the *title* compound (53.16 g, 82 % [Lit. Yield: 88 %]²²) as a yellow solid.

m.p. 148-149 °C [Lit. 150 °C]²²; δ_H (400 MHz, CDCl₃) 8.41 (2H, d, $^4J_{HH}$ = 4 Hz, ArH), 7.85 (2H, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 4 Hz, ArH), 7.18 (2H, d, $^3J_{HH}$ = 8 Hz, ArH); The data is in agreement with literature values.²²

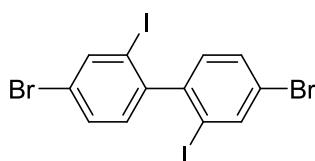
Synthesis of 4,4'-dibromobiphenyl-2,2'-diamine²² 2.8

4,4'-Dibromo-2,2'-dinitrophenyl (53.16 g, 132.23 mmol) was dissolved in stirring absolute ethanol (600 mL). Aqueous HCl (380 mL, 37 % w/w) was added to the solution, followed by cautious addition of tin powder (62.73 g, 528.94 mmol), over 15 min. The reaction mixture was heated to 100 °C and stirred at this temperature for 2 h. The solution was allowed to cool to room temperature, then it was poured into ice water (ca. 2000 mL). KOH pellets were added slowly until the mixture became pH basic (pH > 9). The product was extracted with

diethyl ether (1000 mL), then the organic layer was washed with brine (500 mL) and dried (MgSO_4). The volatiles were removed, under reduced pressure, to yield a dark brown semi-solid. This was washed with hot petroleum ether (3 x 500 mL) to yield the *title* compound (39.86 g, 88 % [Lit. Yield: 92 %]²²) as a light brown solid.

m.p. 118-119 °C [Lit. 118-119 °C]²²; δ_{H} (400 MHz, CDCl_3) 6.96 (6H, m, ArH), 3.77 (4H, brs, NH_2); The data is in agreement with literature values.²²

Synthesis of 4,4'-dibromo-2,2'-diiodobiphenyl 2.9



Method A⁵⁹

A 3-necked round bottomed flask equipped with a low temperature thermometer was charged with 4,4'-dibromobiphenyl-2,2'-diamine (0.50g, 1.34 mmol), aqueous HCl (4.5 mL 37% w/w), H_2O (20 mL) and acetonitrile (40 mL). The mixture was warmed and stirred until the diamine was dissolved, then cooled to -10 °C. Upon cooling, a yellow precipitate was observed. A solution of sodium nitrite (0.46 g, 6.70 mmol) in H_2O (2.5 mL) was cooled to 0 °C and added slowly to the reaction mixture, while maintaining the reaction temperature between -10 and -5 °C. The reaction was stirred at this temperature for 1 h. A solution of KI (2.22 g, 13.35 mmol) in H_2O (5 mL) was cooled to 0 °C and added drop-wise, with vigorous stirring, to the reaction mixture, whilst maintaining the reaction temperature between -15 and -10 °C. Once addition was complete the reaction was warmed to room temperature and then heated to 80 °C for 20 h. The reaction mixture was allowed to cool, before being extracted with chloroform (3 x 50 mL). The combined organic phases were washed with aq. $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL) and brine (100 mL), dried (MgSO_4) and evaporated to dryness. Purification by column chromatography (silica gel, hexane, R_{F} = 0.33) followed by recrystallisation from hexane yielded the *title* compound (0.24 g, 30 % [Lit. yield: 58 %]⁵⁹) as a white solid.

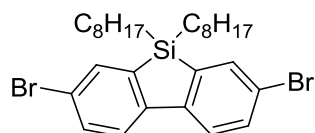
m.p. 90 °C [Lit. 89-90 °C]²²; δ_{H} (400 MHz, CDCl_3) 8.10 (2H, d, $^4J_{\text{HH}} = 2$ Hz, ArH), 7.58 (2H, dd, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 2$ Hz, ArH), 7.06 (2H, d, $^3J_{\text{HH}} = 8$ Hz, ArH); The data is in agreement with literature values.⁵⁹

Method B

4,4'-Dibromobiphenyl-2,2'-diamine (10.30 g, 30.0 mmol) was added to a solution of *p*-toluenesulfonic acid (34.40 g, 180 mmol) in acetonitrile (300 mL). The resulting yellow suspension of amine salt was cooled to 10 °C. A solution of sodium nitrite (8.30 g, 120 mmol) and KI (2.49 g, 150 mmol) in H_2O (40 mL) was added drop-wise to the reaction mixture, with vigorous stirring, whilst maintaining the reaction temperature between 10 and 15 °C. Once addition was complete, the reaction mixture was allowed to reach room temperature, then it was warmed to 80 °C for 20 h. Once the reaction had cooled, it was diluted with H_2O (600 mL) and NaHCO_3 was added drop-wise until pH 9-10 was reached. The product extracted with chloroform (6 x 250 mL). The combined organic phases were washed with aq. $\text{Na}_2\text{S}_2\text{O}_3$ (4 x 250 mL) and brine (4 x 250 mL), dried (MgSO_4) and evaporated to dryness. Purification by column chromatography (silica gel, hexane, $R_{\text{F}} = 0.33$) followed by recrystallisation from hexane yielded the *title* compound (4.45 g, 26 %) as a white solid.

m.p. 89-90 °C [Lit. 89-90 °C]²²; δ_{H} (400 MHz, CDCl_3) 8.10 (2H, d, $^4J_{\text{HH}} = 2$ Hz, ArH), 7.58 (2H, dd, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 2$ Hz, ArH), 7.06 (2H, d, $^3J_{\text{HH}} = 8$ Hz, ArH); The data is in agreement with literature values.²²

Synthesis of 2,7-dibromo-9,9-di-*n*-octyldibenzosilole²² 2.10



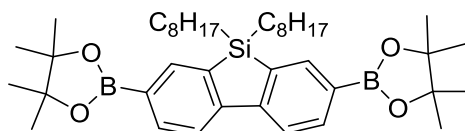
An oven-dried 3-necked flask was charged with 4,4'-dibromo-2,2'-diiodobiphenyl (3.00g, 5.30 mmol) and dry THF (75 mL) under a N_2 atmosphere. The solution was cooled to -90 °C using an ethanol/ liquid nitrogen cooling bath. *t*-Butyllithium (12.8 mL, 21.8 mmol, 1.7 M in

hexanes) was added drop-wise, while maintaining the temperature at $-90\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for a further 30 min at this temperature, then di-*n*-octyldichlorosilane (3.87 mL, 11.2 mmol) was added drop-wise to the reaction. The mixture was stirred for 20 h, allowing it to warm to room temperature. A few drops of distilled water were added to quench the reaction and the THF/water was removed *in vacuo*. The crude product was extracted with diethyl ether (3 x 75 mL) and the combined organic layers were washed with aq. $\text{Na}_2\text{S}_2\text{O}_3$ (2 x 75 mL) and brine (2 x 75 mL), dried (MgSO_4) and evaporated to dryness to give a yellow oil. Purification by column chromatography (silica gel, hexane, $R_F = 0.42$) yielded the *title* compound (1.59 g, 53 % [Lit. yield: 52 %]²²) as a colourless oil.

δ_{H} (400 MHz, CDCl_3) 7.70 (2H, d, $^4J_{\text{HH}} = 2\text{ Hz}$, ArH), 7.64 (2H, d, $^3J_{\text{HH}} = 8\text{ Hz}$, ArH), 7.55 (2H, dd, $^3J_{\text{HH}} = 8\text{ Hz}$, $^4J_{\text{HH}} = 2\text{ Hz}$, ArH), 1.43-1.19 (24H, m, CH_2), 0.99-0.95 (4H, m, CH_2), 0.90 (6H, t, $^3J_{\text{HH}} = 7\text{ Hz}$, CH_3); The data is in agreement with literature values.²²

Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralane-2-yl)-9,9-

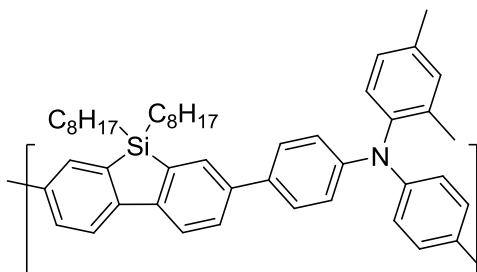
dioctyldibenzosilole²² 2.11



An oven-dried Schlenk tube was charged with 2,7-dibromo-9,9-dioctyldibenzosilole (2.00 g, 3.54 mmol) and dry THF (30 mL), under a N_2 atmosphere. The solution was cooled to $-78\text{ }^{\circ}\text{C}$, then *t*-Butyllithium (8.81 mL, 15.0 mmol, 1.7 M in hexanes) was added dropwise, while maintaining the temperature at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for a further 30 min at this temperature, then 2-isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaboralane (1.81 mL, 8.87 mmol) was added dropwise to the reaction. The mixture was stirred for 20 h, warming to room temperature. A few drops of distilled water were added to quench the reaction and the THF/water was removed *in vacuo*. The crude product was extracted with diethyl ether (3 x 75 mL) and the combined organic layers were washed with brine (110 mL), dried (MgSO_4) and evaporated to dryness to give an off white solid. Purification by recrystallization (ethanol) yielded the *title* compound (1.76 g, 76 % [Lit. yield: 86 %]²²) as a white solid.

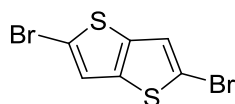
m.p. 116-117 °C [Lit. 116-117 °C]²²; δ_{H} (400 MHz, CDCl_3) 8.08 (2H, s, ArH), 7.90 (4H, quartet, $^3J_{\text{HH}} = 8$ Hz, ArH), 1.40 (24H, s, OCCH_3), 1.35-1.19 (24H, m, CH_2), 0.98-0.94 (4H, m, CH_2), 0.87 (6H, t, $^3J_{\text{HH}} = 7$ Hz, CH_3); The data is in agreement with literature values.²²

Synthesis of poly(9,9-di-n-octyldibenzosilole-co-2,4-dimethyltriarylamine) P1



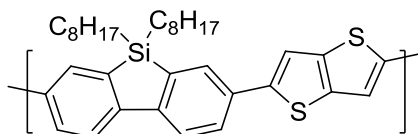
A multi-neck round bottomed flask was charged with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralane-2-yl)-9,9-dioctyldibenzosilole (400 mg, 0.61 mmol), 4,4-dibromo-2,4-dimethyltriarylamine (262 mg, 0.61 mmol), $[\text{Pd}(\text{OAc})_2]$ (7 mg, 0.05 mmol), aqueous tetraethylammonium hydroxide (20 % solution in water, 5 mL) and toluene (20 mL). The mixture was degassed for 10 minutes with nitrogen. Tricyclohexylphosphine tetrafluoroborate (46 mg, 0.13 mmol) was then added and the mixture was degassed, while stirring, for a further 30 minutes. The reaction was then heated to 100 °C and stirred at this temperature for 72 h under nitrogen. The reaction mixture was allowed to cool, then it was added dropwise to a flask of cold, vigorously stirring methanol (200 mL). The resulting yellow precipitate was filtered and redissolved in toluene. This was then washed with sodium diethylthiocarbamate (400 mg in 75 mL H_2O) to remove the palladium. The organic layer was separated, dried (MgSO_4) and filtered through a plug of silica. The solution was then concentrated to 10 mL and re-precipitated in methanol. The yellow precipitate was recovered and subjected to Soxhlet extraction with acetone (12 h), hexane (12 h) and chloroform (24 h). The chloroform fraction was concentrated and re-precipitated in methanol to yield the *title* compound (148 mg, 38 %) as a yellow solid.

GPC analysis in chlorobenzene: M_n 29 kDa, M_w 75 kDa; δ_{H} (400 MHz, CDCl_3) 7.91-7.00 (17H, m, ArH), 2.41 (3H, s, ArCH_3), 2.12 (3H, s, ArCH_3), 1.58 (6H, s, OCCH_3), 1.37-1.08 (24H, m, CH_2), 1.05-0.42 (10H, m, CH_2); λ_{max} (CHCl_3) 379 nm.

Synthesis of 2,5-dibromothieno-(3,2-*b*)-thiophene¹⁰¹ 2.13

A 100 mL round bottomed flask was charged with thieno-(3,2-*b*)-thiophene (1.5 g, 10.6 mmol), chloroform (25 mL) and glacial acetic acid (12 mL). Once all the thieno-(3,2-*b*)-thiophene had dissolved, *n*-bromosuccinimide (4.0 g, 22.5 mmol) was added, in small portions, over 30 min, in the dark. The reaction was allowed to stir for a further 3 h at room temperature. The reaction mixture was washed with 5 % aq. NaHCO₃ (2 x 50 mL) and water (3 x 50 mL). The organic layer was dried (MgSO₄) and the volatiles removed *in vacuo* to yield the *title* compound (2.9 g, 92 % [Lit. Yield 96 %]¹⁰¹) as a yellow crystalline solid.

m.p. 117-118 °C [Lit. 117-119 °C]⁶¹; δ_{H} (400 MHz, CDCl₃) 7.18 (2H, s, *ArH*). The data is in agreement with literature values.^{61, 101}

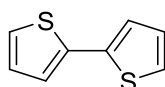
Synthesis of poly(9,9-di-*n*-octyldibenzosilole-co-thieno[3,2-*b*]thiophene) P2

A two-necked round bottomed flask was charged with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralane-2-yl)-9,9-dioctyldibenzosilole (250 mg, 0.38 mmol), 2,5-dibromothieno-(3,2-*b*)-thiophene (112 mg, 0.38 mmol), [Pd(OAc)₂] (4.2 mg, 0.019 mmol), aqueous tetraethylammonium hydroxide (20% solution in water, 3 mL) and toluene (12 mL). The mixture was degassed for 10 minutes with nitrogen. Tricyclohexylphosphine tetrafluoroborate (28 mg, 0.076 mmol) was then added and the mixture was degassed while stirring for a further 30 minutes. The reaction was then heated to 110 °C and stirred at this temperature for 72 h under nitrogen. The reaction mixture was allowed to cool then it was added dropwise to a flask of cold, vigorously stirring methanol. The resulting yellow/green precipitate was filtered and redissolved in chloroform. This was then washed with sodium diethylthiocarbamate (400 mg in 75 mL H₂O) to remove palladium. The organic layer was separated, dried (MgSO₄) and filtered through a plug of silica. The solution was then concentrated to 10 mL and reprecipitated in methanol. The yellow precipitate was recovered

and subjected to Soxhlet extraction with acetone (12 h), hexane (12 h) and chloroform (24 h). The chloroform fraction was concentrated and reprecipitated in methanol to yield the *title* compound as (150 mg, 42 %) a yellow solid.

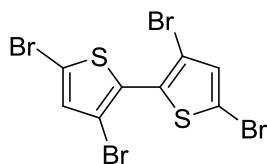
GPC analysis in chloroform: M_n 38 kDa, M_w 75 kDa; δ_H (400 MHz, $CDCl_3$) 8.50-6.10 (6H, bs, ArH), 1.8-0.5 (34H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 405 nm.

Synthesis of 2,2'-bithiophene⁶³ 2.18



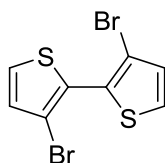
A 3-necked 250 mL round bottomed flask was charged with 2-bromothiophene (50 g, 0.30 mol) and dry diethyl ether (140 mL). This was then transferred into a dry flask containing magnesium turnings (8.85 g, 0.36 mol) activated with iodine in dry diethyl ether (100 mL). The reaction was then refluxed for 1h and left to cool for 20 h, under nitrogen. The resultant Grignard reagent was then transferred, via cannula, to a flask containing 2-bromothiophene (42 g, 0.26 mol) and $[NiCl_2(dppp)]$ (1.38 g, 2.54 mmol) in diethyl ether (100 mL) at 5 °C. The mixture was stirred overnight at room temperature, before being cooled to 0 °C and treated with saturated NH_4Cl solution (200 mL). The ether layer was collected, washed with 10 % sodium thiosulphate solution (200 mL) and brine (200 mL) and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a crude red liquid. Column chromatography (silica gel, hexane) yielded the title compound (20.02 g, 43 % [Lit. yield 72 %]⁶³) as a yellow solid.

δ_H (400 MHz, $CDCl_3$) 7.35-7.17 (4H, m, ArH), 7.03-7.13 (2H, m, ArH); The data is in agreement with literature values.⁶³

Synthesis of 3,3',5,5'-tetrabromo-2,2'-bithiophene¹⁰² 2.19

A 250 mL 3-necked round bottomed flask equipped with a dropping funnel and reflux condenser connected to a KOH bubbler, was charged with 2,2'-bithiophene (7.34 g, 44.2 mmol), chloroform (60 mL) and glacial acetic acid (25 mL). This solution was cooled to 5 °C. Bromine (9.06 mmol) was placed in the dropping funnel and added dropwise to the reaction mixture over 1 h, while maintaining the temperature between 5-10 °C. On addition of the bromine, the reaction mixture turned green in colour. Once the bromine had been added, the reaction was stirred at 25 °C for 2 h, then it was heated to 65 °C, overnight, until no more HBr was produced. The reaction mixture, which was now yellow in colour, was extracted with chloroform (2 x 150 mL). The combined extracts were washed with sodium thiosulphate (200 mL) and brine (200 mL) and dried (MgSO₄). The volatiles were removed *in vacuo* to give a yellow solid. This was dissolved in hot ethanol and filtered when hot to remove insoluble material. The ethanol was then removed *in vacuo* to yield the title compound (11.37 g, 53 % [Lit. yield 77 %]¹⁰²) as a pale yellow solid.

m.p. 138-139 °C [Lit. 137-138 °C]¹⁰³; δ_{H} (400 MHz, CDCl₃) 7.05 (s, 2H, ArH); The data is in agreement with literature values.^{102, 103}

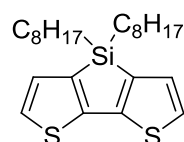
Synthesis of 3,3'-dibromo-2,2'-bithiophene¹⁰² 2.14

A 250 mL round bottomed flask was charged with zinc dust (3.09 g, 47.3 mmol), ethanol (65 mL), water (7 mL), acetic acid (16 mL) and HCl (0.33 mL, 12 M). This was heated to 80 °C and then 3,3',5,5'-tetrabromo-2,2'-bithiophene (6 g, 12.5 mmol) was added in 6 portions over 30 mins to the refluxing mixture. The reaction was stirred at this temperature for a further 2 h before being cooled to room temperature. The reaction mixture was filtered to remove zinc and the residue was washed with ethanol. The solvent was removed *in vacuo* to give a yellow

solid. This was dissolved in diethyl ether (100 mL) and water was added (50 mL). The aqueous layer was extracted with ether (2 x 50 mL) and the combined organics were washed with aq KOH (50 mL) and brine (100 mL) and dried (MgSO₄). The volatiles were removed *in vacuo* to give a yellow solid. This was then dissolved in hexane and a spatula full of charcoal was added, turning the solution a paler yellow. The solution was filtered through celite and evaporated to dryness to give the title compound (3.52 g, 87 % [Lit. yield 90 %]¹⁰²) as a yellow solid.

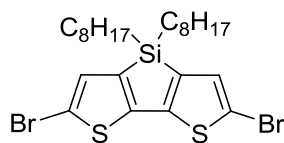
m.p 97-99 °C [Lit. 98-100 °C]¹⁰³; δ_H (400 MHz, CDCl₃) 7.41 (2H, d, $^3J_{HH}$ = 5.39 Hz, ArH), 7.09 (2H, d, $^3J_{HH}$ = 5.39 Hz, ArH); The data is in agreement with literature values.^{102, 103}

Synthesis of 9,9-di-*n*-octyldithienosilole¹⁰² 2.15



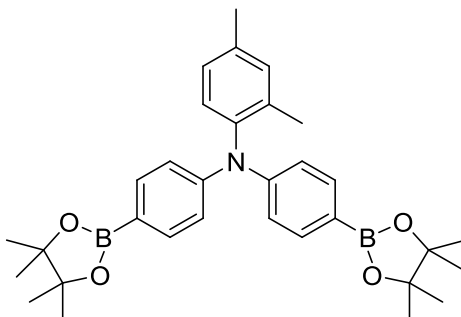
An oven-dried 3-necked flask was charged with dry THF (75 mL), under a N₂ atmosphere. This was cooled to -78 °C using an acetone/dry ice cooling bath. *n*-Butyllithium (6.4 mL, 10.2 mmol, 1.6 M in hexanes) was added, slowly to the THF. A solution of 3,3'-dibromobithiophene (1.50 g, 4.62 mmol) in dry THF (30 mL) was then added dropwise to the flask while maintaining the temperature at -78 °C. The reaction mixture was stirred for a further 30 min at this temperature, then di-*n*-octyldichlorosilane (1.74 mL, 5.08 mmol) was added dropwise to the reaction. The mixture was stirred overnight, warming to room temperature. A few drops of distilled water were added to quench the reaction and the THF/water was removed *in vacuo*. Water was added (10 mL) and the crude product was extracted with diethyl ether (3 x 50 mL) and the combined organic layers were washed with brine (150 mL), dried (MgSO₄) and evaporated to dryness to give a yellow oil. Purification by column chromatography (silica gel, hexane, R_F = 0.43) yielded the *title* compound (1.24 g, 64 % [Lit. yield: 68 %]¹⁰²) as a pale yellow oil.

δ_H (400 MHz, CDCl₃) 7.20 (2H, d, $^3J_{HH}$ = 4 Hz, ArH), 7.06 (2H, d, $^3J_{HH}$ = 4 Hz, ArH), 1.41-1.20 (24H, m, CH₂), 0.93-0.85 (10H, m, CH₂); The data is in agreement with literature values.¹⁰²

Synthesis of 2,6-dibromo-9,9-di-n-octyldithienosilole¹⁰² 2.16

9,9-Di-n-octyldithienosilole (800 mg, 1.91 mmol) was placed in a round bottomed flask and dissolved in dichloromethane (17 mL). The n-bromosuccinimide (748 mg, 4.20 mmol) was added in 3 portions over 5 min to the flask. This was allowed to stir for 30 min at room temperature. Water (7 mL) was added to the reaction mixture and the organic layer was separated from the aqueous layer. The aqueous layer was then extracted with diethyl ether (2 x 20 mL). The combined organics were washed with brine (50 mL), dried (MgSO_4) and the volatiles removed, *in vacuo*, to give a yellow oil with some white solid in it. This was then purified by column chromatography (silica gel, hexane, R_F 0.60) to yield the *title* compound (1.05 g, 90 % [Lit. yield 91 %]¹⁰²) as a yellow/green oil.

δ_H (400 MHz, CDCl_3) 6.99 (2H, s, ArH), 1.40-1.20 (24H, m, CH_2), 0.91-0.85 (10H, m, CH_2 and CH_3); δ_C (400 MHz, CDCl_3) 141, 132, 111, 33, 32, 29.2, 29.1, 24, 23, 14, 12; EI (m/z) 576, 464, 351, 272; The data is in agreement with literature values.¹⁰²

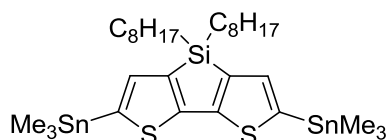
2,4-Dimethyl-4,4'-(4,4',5,5'-tetramethyl-1,3,2-dioxaboralane-2-yl)triarylamine⁶⁴ 2.19

An oven-dried Schlenk tube was charged with 4,4'-dibromo-2,4-dimethyltriarylamine (700 mg, 1.86 mmol) and dry THF (20 mL), under a N_2 atmosphere. The solution was cooled to -78 °C, then *n*-Butyllithium (2.55 mL, 4.09 mmol, 1.6 M in hexanes) was added dropwise, while maintaining the temperature at -78 °C. The reaction mixture was stirred for a further 30 min at this temperature, then 2-isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaboralane (0.95 mL, 4.65 mmol) was added dropwise to the reaction. The mixture was stirred overnight,

warming to room temperature. A few drops of distilled water were added to quench the reaction and the THF/water was removed *in vacuo*. The crude product was extracted with dichloromethane (3 x 50 mL) and the combined organic layers were washed with brine (100 mL), dried (MgSO₄) and evaporated to dryness to give an off white solid. Purification by two consecutive recrystallizations (hexane) yielded the *title* compound (267 mg, 27 % [Lit. yield: 55 %⁶⁴]) as an off white solid.

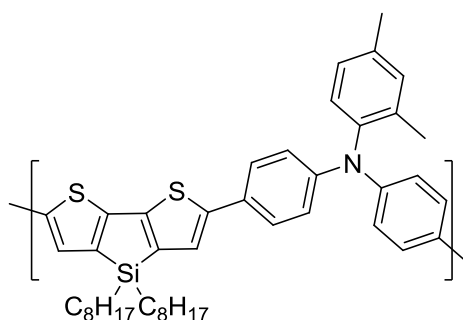
δ_{H} (400 MHz, CDCl₃) 7.64-7.01 (11H, m, ArH), 2.34 (3H, s, CH₃), 2.04 (3H, s, CH₃), 1.40 (24H, s, OC(CH₃)₂); The data is agreement with the literature values.⁶⁴

Synthesis of 2,6-bis(trimethylstannyl)-9,9-n-octyldithienosilole 2.20



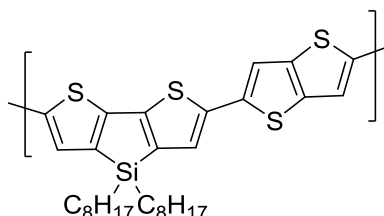
A clean dry Schlenk tube was charged with 9,9-di-*n*-octyldithienosilole (1.10 mg, 2.60 mmol) which was dissolved in dry THF (6 mL). The solution was cooled to – 40 °C with an acetonitrile/dry ice bath, then *n*-BuLi (4.9 mL, 7.88 mmol, 1.6 M solution in hexanes) was added, dropwise, to the flask. Once addition was complete, the solution was left to stir for a further 2 h at 0 °C. The reaction mixture was cooled to -40 °C and trimethyltin chloride (9.1 mL, 9.1 mmol, 1 M solution in THF) was added, in one portion. The reaction was allowed to warm to room temperature, overnight. The reaction was quenched with water (10 mL) and hexane (20 mL) was added. The organic layer was separated and washed with water (4 x 20 mL). The organic layer was then dried (MgSO₄) and the volatiles were removed *in vacuo*. The pale green oil (1.70 g, 89 %) was dried under high vacuum for 2 h. The product was used in the next step without further purification.

δ_{H} (400 MHz, CDCl₃) 7.12 (2H, s, ArH), 1.55-1.22 (24H, m, CH₂), 0.95-0.86 (10H, m, CH₂ and CH₃), 0.41 (18H, s, -SnMe₃). The data is in agreement with literature values.²⁴

Synthesis of poly(9,9-di-n-octyldithienosilole-co-2,4-dimethyltriarylamine) P3

2,6-Bis(trimethylstannyl)-9,9-n-octyldithienosilole (200 mg, 0.270 mmol), 4,4'-dibromo-2,4-dimethyltriarylamine (112 mg, 0.260 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (12 mg, 0.011 mmol) were added to the vial, followed by dry toluene (0.7 mL). Polymerization method **A** was followed to afford the *title* compound (40 mg, 21 %) as green powder.

GPC analysis in chloroform: M_n 3.5 kDa, M_w 7 kDa; δ_H (400 MHz, CDCl_3) 7.51-6.80 (13H, m, ArH), 2.39 (3H, s, ArCH₃), 2.06 (3H, s, ArCH₃), 1.42-0.97 (24H, m, CH₂), 0.96-0.42 (10H, m, CH₂); λ_{max} (CHCl_3) 451 nm.

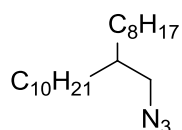
Synthesis of poly(9,9-di-n-octyldithienosilole-co-thieno[b-3,2]thiophene) P4

An oven dried 5 mL microwave vial, equipped with a stirrer bar, was charged with 2,6-dibromo-9,9-di-n-octyldithienosilole (200 mg, 0.35 mmol), di(trimethylstannyl)-thieno[b-3,2]thiophene (162 mg, 0.35 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (4.04 mg, 3.5 μmol). The cap was placed on the vial and the vial was placed under consecutive cycles of vacuum and nitrogen for 10 min. Then anhydrous xylene (3 mL) was added to the vial and the system purged with nitrogen. The vial was placed in the microwave for 2 min at 120 °C, 2 min at 140 °C and 40 min at 170 °C. Once cool, the vial was removed from the microwave and a viscous dark blue product was observed. This was dissolved in chloroform and poured in to methanol (300 mL). The dark blue precipitate was collected by filtration and purified by Soxhlet extraction using the following extraction solvents: acetone for 16 h, hexane for 20 h, chloroform for 48

h. The chloroform fraction was concentrated and reprecipitated in methanol. The product was collected as a dark blue powder (171 mg, 88 %).

GPC analysis in chlorobenzene: M_n 10 kDa, M_w 16 kDa; δ_H (400 MHz, $CDCl_3$) 7.20-6.50 (4H, bs, ArH), 1.9-0.5 (34H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 576 nm.

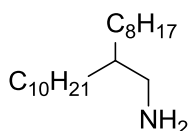
Synthesis of 2-octyl-1-dodecylazide 2.23



An oven dried 500 mL round bottomed flask was charged with 2-octyl-1-dodecanol (18.5g, 22 mL, 62 mmol), triphenylphosphine (22.6 g, 87 mmol), diisopropylazodicarboxylate (17.6 g, 17 mL, 87 mmol) and diphenylphosphoryl azide (24g, 19 mL, 87 mmol). The flask was placed under nitrogen and dry THF (250 mL) was added. The reaction mixture was stirred overnight, at room temperature, under nitrogen. Then, the volatiles were removed under reduced pressure, water was added (200 mL) and the product was extracted with hexane (4 x 200 mL). The combined organic fractions were washed with brine (400 mL), dried ($MgSO_4$) and the volatiles removed *in vacuo*. The viscous yellow oil was purified by column chromatography (silica gel, hexane, R_F 0.35) to give the azide as a colourless oil (12.5 g, 62 %).

δ_H (400 MHz, $CDCl_3$) 3.26 (2H, d, $^3J_{HH} = 5$ Hz, $-CH_2N_3$), 1.61-1.56 (1H, m, $-NCH_2CH-$), 1.39-1.22 (32H, m, $-CH_2-$), 0.91 (6H, t, $^3J_{HH} = 5$ Hz, $-CH_3$).

Synthesis of 2-octyl-1-dodecylamine 2.24

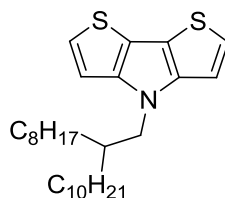


A 500 mL oven dried round bottomed flask, equipped with a reflux condenser, was charged with 2-octyl-1-dodecylazide (16.50 g, 50.9 mmol). The flask was purged with nitrogen before dry diethyl ether (250 mL) and lithium aluminium hydride (72 mL, 72 mmol, 1M solution in

diethyl ether) were added to the solution. The reaction mixture was heated for 2 h at 60 °C, then cooled to room temperature. The reaction was quenched with 15 % sodium hydroxide solution (100 mL), then the organic layer was separated and washed with water (3 x 100 mL). The organic layer was dried (MgSO_4) and the volatiles removed *in vacuo* to give the product as a colourless liquid (13.32 g, 88 %).

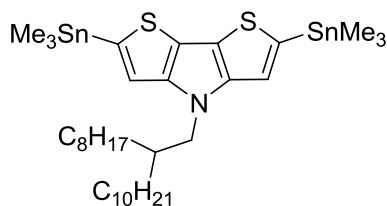
δ_{H} (400 MHz, CDCl_3) 2.64 (2H, d, $^3J_{\text{HH}} = 5$ Hz, $-\text{CH}_2\text{N}-$), 1.40-1.22 (33H, m, CH and CH_2), 1.12 (2H, bs, NH_2), 0.90 (6H, t, $^3J_{\text{HH}} = 5$ Hz, CH_3). The data is in agreement with the literature values.⁶⁸

Synthesis of 9-n-(2-octyl-1-dodecyl)dithienopyrrole 2.25



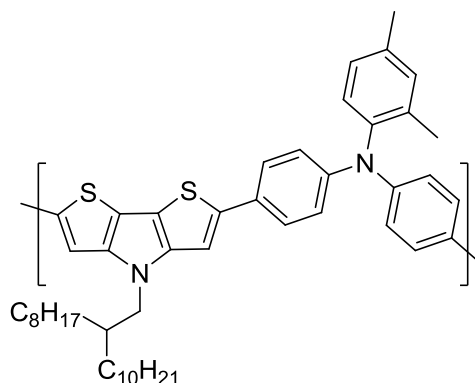
A clean dry Schlenk tube was charged with 3,3'-dibromo-2,2'-bithiophene (1.00 g, 3.09 mmol), Pd_2dba_3 (84 mg, 0.093 mmol), BINAP (231 mg, 0.37 mmol), NaO^tBu (891 mg, 9.27 mmol) and 2-octyl-1-dodecylamine (898 mg, 3.34 mmol). Three consecutive vacuum/nitrogen cycles were carried, before adding dry toluene (10 mL). The reaction mixture was heated to 120 °C for 24 h. The reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 x 30 mL). The combined organics were washed with brine (50 mL) and dried (MgSO_4). The volatiles were removed to *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, ethyl acetate: hexane, 1:19, $R_{\text{F}} = 0.34$) yielded the *title* compound (500 mg, 35 %) as a yellow solid.

(Found: C, 73.23; H, 9.92; N, 2.95. $\text{C}_{28}\text{H}_{45}\text{NS}_2$ requires: C, 73.14; H, 9.86; N, 3.05 %); δ_{H} (400 MHz, CDCl_3) 7.11 (2H, d, $^2J_{\text{HH}} = 5.2$ Hz, ArH), 6.98 (2H, d, $^2J_{\text{HH}} = 5.2$ Hz, ArH), 4.05 (2H, d, $-\text{NCH}_2\text{CH}-$), 1.93-1.79 (2H, m, $-\text{NCH}_2\text{CH}-$), 1.39-1.21 (32 H, m, $-\text{CH}_2-$), 0.92 (6H, t, $-\text{CH}_3$); δ_{C} (100 MHz, CDCl_3) 145.3, 122.7, 114.6, 111.1, 51.8, 39.1, 31.8, 31.6, 29.9, 29.6, 29.5 (d), 29.4, 26.4, 22.7 9d), 14.2; EI (m/z) 459 [M^+].

Synthesis of 2,6-bis(trimethylstannyl)-9-n-(2-octyl-1-dodecyl)dithienopyrrole 2.26

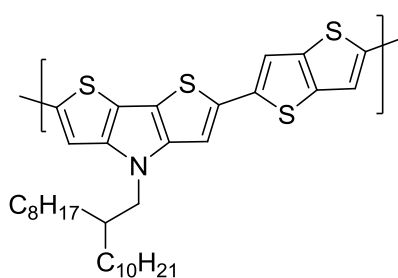
A clean dry Schlenk tube was charged with 9-n-(2-octyl-1-dodecyl)dithienopyrrole (390 mg, 0.85 mmol) which was dissolved in dry THF (10 mL). The solution was cooled to $-40\text{ }^{\circ}\text{C}$ with an acetonitrile/dry ice bath, then *n*-BuLi (1.6 mL, 2.54 mmol, 1.6 M solution in hexanes) was added, dropwise, to the flask. Once addition was complete, the solution was left to stir for a further 2 h at $0\text{ }^{\circ}\text{C}$. The reaction mixture was cooled to $-40\text{ }^{\circ}\text{C}$ and trimethyltin chloride (3 mL, 3 mmol, 1 M solution in THF) was added in one portion. The reaction was allowed to warm to room temperature, overnight. The reaction was quenched with water (10 mL) and hexane (20 mL) was added. The organic layer was separated from the aqueous layer and washed with water (4 x 20 mL). The organic layer was then dried (MgSO_4) and the volatiles were removed *in vacuo*. The yellow oil was dried under high vacuum for 2 h, then placed in the freezer where it solidified to give a yellow solid (610 mg, 91 %). The product was used in the next step without further purification.

(Found: C, 52.07; H, 7.76; N, 1.70. $\text{C}_{34}\text{H}_{61}\text{NS}_2\text{Sn}_2$ requires: C, 51.99; H, 7.87; N, 1.78 %) δ_{H} (400 MHz, CDCl_3) 6.96 (2H, s, ArH), 4.04 (2H, d, $-\text{NCH}_2\text{CH}-$), 2.08-1.98 (2H, m, $-\text{NCH}_2\text{CH}-$), 1.39-1.21 (32 H, m, $-\text{CH}_2-$), 0.88 (6H, t, $-\text{CH}_3$), 0.40 (18 H, s, $-\text{Sn}(\text{CH}_3)_3$); δ_{C} (100 MHz, CDCl_3) 145.3, 122.7, 114.6, 111.1, 51.8, 38.1, 31.9 (d), 31.6, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.5, 22.7 (d), 14.2; ESI (m/z) 786 [M^+].

Synthesis of poly(9-*n*-(2-octyl-1-dodecyl)dithienopyrrole-co-dimethyltriarylamine) P5

2,6-Di(trimethylstannyl)-9-*n*-(2-octyl-1-dodecyl)dithienopyrrole (200 mg, 0.250 mmol), 4,4'-dibromo-2,4-dimethyltriarylamine (108 mg, 0.250 mmol), [Pd₂dba₃] (3.4 mg, 3.750 μmol) and tri-*o*-tolylphosphine (4.6 mg, 0.015 mmol) were added to the vial, followed by dry chlorobenzene (0.8 mL). Polymerization method **B** was used to afford the *title* compound (55 mg, 30 %) as an orange powder.

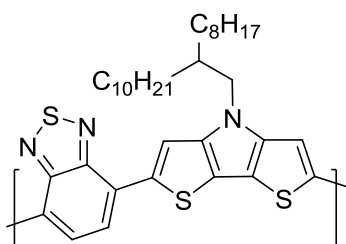
GPC (chlorobenzene 80 °C): M_n 7 kDa, M_w 15 kDa; δ_H (400 MHz, CDCl₃) 7.56-6.97 (13H, m, ArH), 4.07 (2H, bs, -NCH₂-), 2.40-2.38 (3H, m, CH₃), 2.09-2.05 (3H, m, CH₃), 1.60 (1H, bs, -NCH₂-CH-), 1.40-1.15 (32H, m, CH₂), 0.91-0.86 (6H, m, CH₃); λ_{max} (CHCl₃) 448 nm.

Synthesis of poly(9-*n*-(2-octyl-1-dodecyl)dithienopyrrole-co-thieno(3,2-*b*)thiophene) P6

2,6-Di(trimethylstannyl)- 9-*n*-(2-octyl-1-dodecyl)dithienopyrrole (200 mg, 0.250 mmol), 2,5-dibromo-thieno(3,2-*b*)thiophene (76 mg, 0.250 mmol), [Pd₂dba₃] (3.4 mg, 3.750 μmol) and tri-*o*-tolylphosphine (4.6 mg, 0.015 mmol) were added to the vial, followed by dry chlorobenzene (0.8 mL). Polymerization method **B** was followed to afford the *title* compound (40 mg, 27 %) as a purple powder.

GPC (chlorobenzene 80 °C): M_n 3 kDa, M_w 5 kDa; δ_H (400 MHz, $CDCl_3$) 7.80-6.70 (4H, m, ArH), 3.75 (2H, bs, $-NCH_2CH-$), 1.45-0.75 (39H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 596 nm.

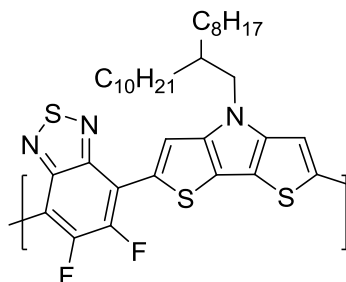
Synthesis of poly(9-*n*-(2-octyl-1-dodecyl)dithienopyrrole-co-benzo[c][1,2,5]thiadiazole) P7



An oven dried 5 mL microwave vial was charged with 2,6-di(trimethylstannyl)- 9-*n*-(2-octyl-1-dodecyl)dithienopyrrole (210 mg, 0.267 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (79 mg, 0.267 mmol) and $[Pd(PPh_3)_4]$ (12 mg, 0.011 mmol). The cap was placed on the vial and dry *o*-xylene (0.8 mL) was added. The reaction mixture was purged with argon for 20 min, before being placed in the microwave and subjected to the following conditions: 100 °C for 2 min, 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min and 180 °C for 40 min. Once the reaction had cooled, the viscous green liquid was precipitated in acidic methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate at 50 °C for 1 h, then the organic layer was separated and washed with water, then dried ($MgSO_4$). The chloroform solution was concentrated and reprecipitated in methanol. The green precipitate (80 mg, 51 %) was collected by filtration.

GPC (chlorobenzene 80 °C): M_n 10 kDa, M_w 18 kDa; δ_H (400 MHz, $CDCl_3$) 8.30-6.60 (4H, bs, ArH), 3.90-3.20 (2H, bs, $-NCH_2-$), 1.80-0.50 (39H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 726 nm.

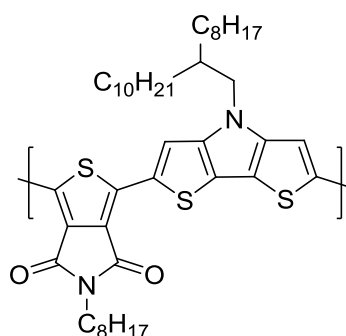
Synthesis of poly(9-*n*-(2-octyl-1-dodecyl)dithienopyrrole-co-5,6-difluoro-benzo[*c*][1,2,5]thiadiazole) P8



2,6-Di(trimethylstannyl)- 9-*n*-(2-octyl-1-dodecyl)dithienopyrrole (210 mg, 0.267 mmol), 4,7-dibromo-5,6-difluoro-benzo[*c*][1,2,5]thiadiazole (79 mg, 0.267 mmol) and [Pd(PPh₃)₄] (12 mg, 0.011 mmol) were added to the vial, followed by dry toluene (0.8 mL). Polymerization method **A** was followed and a green precipitate (32 mg, 19 %) was collected by filtration. The Soxhlet thimble was then placed into hot chlorobenzene to dissolve the high molecular weight fraction. The solution was then filtered hot, concentrated and reprecipitated in methanol to give the *title* compound (15 mg, 9 %) as a green powder.

GPC (chlorobenzene 80 °C): Chloroform fraction: M_n 6kDa, M_w 10 kDa; Chlorobenzene fraction: M_n 9 kDa, M_w 17 kDa; δ_H (400 MHz, CDCl₃) 8.30-7.50 (2H, bs, ArH), 3.90-3.20 (2H, bs, -NCH₂-), 1.80-0.50 (39H, m, CH₂ and CH₃); λ_{max} (CHCl₃) 726 nm.

Synthesis of poly(9-*n*-(2-octyl-1-dodecyl)dithienopyrrole-co-5-octylthieno[3,4-*c*]pyrrole-4,6-dione) P9

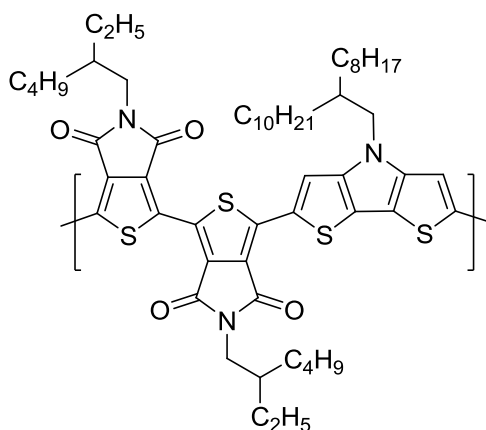


2,6-Di(trimethylstannyl)- 9-*n*-(2-octyl-1-dodecyl)dithienopyrrole (200 mg, 0.250 mmol), 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione (106 mg, 0.250 mmol), [Pd₂dba₃] (3.4 mg, 3.75 μ mol) and tri-*o*-tolylphosphine (4.6 mg, 0.015 mmol) were placed in a vial, followed by

dry chlorobenzene (0.8 mL). Polymerization method **B** was followed to afford the *title* compound (75 mg, 42 %) as a dark blue powder.

GPC (chlorobenzene 80 °C): M_n 7 kDa, M_w 12 kDa; δ_H (400 MHz, $CDCl_3$) 8.70-7.80 (2H, bs, *ArH*), 4.50-3.60 (4H, m, $-NCH_2-$), 2.20-0.70 (54H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 617 nm.

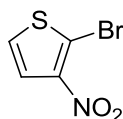
Synthesis of poly(9-*n*-(2-octyl-1-dodecyl)dithienopyrrole-co-5,5'-di-2-ethylhexyl 1-4*H*,4'*H* 1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(*5H*, 5'*H*)-tetrone) P10



2,6-Di(trimethylstannyl)-9-*n*-(2-octyl-1-dodecyl)dithienopyrrole (200 mg, 0.250 mmol), 3,3'-dibromo-5,5'-di-2-ethylhexyl 1-4*H*,4'*H* 1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(*5H*, 5'*H*)-tetrone (152 mg, 0.220 mmol) and $[Pd(PPh_3)_4]$ (10 mg, 8.88 μ mol) were added to the vial, followed by dry toluene (1 mL). Polymerization method **A** was followed and the *title* compound (74 mg, 30 %) was isolated as a dark blue powder.

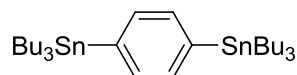
GPC (chlorobenzene 80 °C): M_n 7 kDa, M_w 9 kDa; δ_H (400 MHz, $CDCl_3$) 8.80-7.90 (2H, bs, *ArH*), 4.40-3.50 (6H, m, $-NCH_2-$), 2.00-0.5 (69H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 624 nm.

5.5.4 Experimental for Chapter 3

Synthesis of 2-bromo-3-nitrothiophene⁸⁵ 3.9

A 3-necked 100 mL round bottomed flask equipped, with a low temperature thermometer and dropping funnel, was charged with 2-bromothiophene (0.89 mL, 9.20 mmol) and acetic anhydride (49 mL). This was cooled to -5 °C using a salt/ice water bath. Once cooled, HNO₃ (1.6 mL, 22.5 mmol, 69 %) in acetic anhydride (3 mL) was added dropwise, to the solution over 30 min., this was stirred for a further 1 h at -5 °C, before being left in the freezer for 20 h. Water (20 mL) and diethyl ether (30 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 mL). The combined extracts were washed with brine (100 mL) and dried (MgSO₄). The volatiles were removed *in vacuo* to give a orange/red oil. The crude material was purified by column chromatography (silica gel, hexane: diethyl ether, 9:1, R_F= 0.57) to give a yellow/orange solid, which was recrystallized from hexane to give yellow crystals (1.09 g, 57 % [Lit. yield 75 %]⁸⁵).

m.p. 77-78 °C ; δ_{H} (400 MHz, CDCl₃) 7.70 (1H, d, ³J_{HH}= 4.4 Hz, ArH), 7.10 (1H, d, ³J_{HH}= 4.4 Hz, ArH). The data is in agreement with literature values.⁸⁵

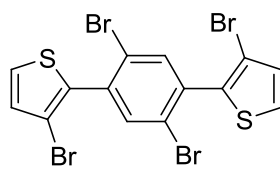
Synthesis of 1,4-bis(tri-*n*-butylstannyl)benzene¹⁰⁴ 3.15

t-Butyllithium (22 mL, 35.3 mmol, 1.6 M in pentanes) was added dropwise to a stirred solution of 1,4-dibromobenzene (2.00 g, 8.40 mmol) in dry THF (50 mL), at -78 °C over 30 min. This was stirred for a further 45 min at -78 °C, over which time a yellow precipitate was observed. SnBu₃Cl (6.80 mL, 25.3 mmol) was added dropwise to the reaction mixture over 15 min. The reaction mixture was then allowed to warm to room temperature, overnight. The reaction was quenched with a saturated solution of NH₄Cl (2 mL). The volatiles were removed *in vacuo* then more water was added (10 mL) and the aqueous layer was extracted

with diethyl ether (3 x 50 mL). The combined organics were washed with brine (100 mL), dried (MgSO_4) and the volatiles removed *in vacuo*. The colourless oil was dissolved in hexane (50 mL) and filtered through a plug of silica gel. The volatiles were removed once more, then the oil was purified by vacuum distillation. The excess SnBu_3Cl was removed by vacuum distillation (110 °C at 0.07 Torr) and the pure product remained in the flask as a colourless oil (2.89 g, 52 % [Lit. yield 67 %]¹⁰⁴).

δ_{H} (400 MHz, CDCl_3) 7.41 (4H, s, ArH), 1.55 (12H, p, $^3J_{\text{HH}} = 7.3$ Hz, $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$), 1.34 (12H, hex, $^3J_{\text{HH}} = 7.4$ Hz, $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$), 1.04 (12H, t, $^3J_{\text{HH}} = 7.4$ Hz, $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$), 0.89 (18 H, t, $^3J_{\text{HH}} = 7.4$ Hz, $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$). The data is in agreement with literature values.¹⁰⁴

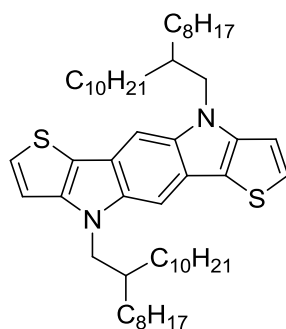
Synthesis of 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene)⁶⁵ 3.6



An oven dried round bottom flask was charged with 1,4-dibromo-2,5-diiodobenzene (5.86 g, 12.02 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (0.693 g, 0.6 mmol), under nitrogen. (3-Bromothiophen-2-yl)zinc(II) bromide (52 mL, 26 mmol, 0.5 M in THF) was added and the resulting mixture was stirred at 65 °C for 8 h. The mixture was then cooled to room temperature and quenched with a saturated NH_4Cl solution (30 mL). The precipitate was filtered and washed with water (20 mL) and diethyl ether (30 mL). The title compound was dried in vacuum and isolated as a white solid (4.76 g, 71 % [Lit. yield 73 %]⁶⁵).

δ_{H} (400 MHz, CDCl_3) 7.74 (2H, s, ArH), 7.45 (2H, d, $^3J_{\text{HH}} = 5.4$ Hz, ArH), 7.12 (2H, d, $^3J_{\text{HH}} = 5.3$ Hz, ArH). The data was in agreement with the literature values.⁶⁵

Synthesis of benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b*]thiophene 3.7



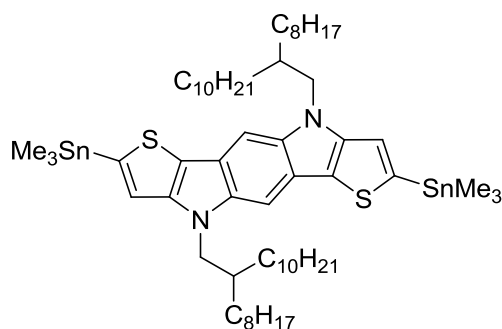
A dry Schlenk tube was charged with 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) (1.10 g, 1.97 mmol), [Pd₂dba₃] (90 mg, 98.5 μmol), BINAP (245 mg, 0.39 mmol) and NaO^tBu (1.01 g, 10.48 mmol). Three consecutive vacuum/nitrogen cycles were carried out on the contents of the Schlenk tube, before adding 2-octyl-1-dodecylamine (1.29 g, 4.33 mmol) and dry toluene (40 mL). The reaction mixture was heated to 120 °C for 24 h. The reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 x 100 mL). The combined organic fractions were washed with brine (200 mL) and dried (MgSO₄). The volatiles were removed to *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, 0-5 % CH₂Cl₂/Hexane) yielded a mixture of mono-ring-closed and mono-aminated product as a colourless oil (915 mg).

This mixture (910 mg) was placed in a Schlenk tube, along with [Pd₂dba₃] (45 mg, 0.05 mmol), BINAP (122 mg, 0.20 mmol) and NaO^tBu (586 mg, 6.1 mmol). Three consecutive vacuum/nitrogen cycles were carried out on the contents of the Schlenk tube, before adding 2-octyl-1-dodecylamine (361 mg, 1.22 mmol) and dry toluene (40 mL). The reaction mixture was heated to 120 °C and monitored using TLC. Once the reaction had reached completion (24 h) the reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 x 100 mL). The combined organics were washed with brine (200 mL) and dried (MgSO₄). The volatiles were removed to *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, 0-5 % CH₂Cl₂/Hexane, R_F 0.32) yielded the *title* compound (638 mg, 40 % overall yield) as a pale yellow solid;

(Found: C, 78.28; H, 10.78; N, 3.28. C₅₄H₈₈N₂S₂ requires: C, 78.20; H, 10.70; N, 3.38 %); δ_H (400 MHz, CDCl₃) 7.59 (2H, s, ArH), 7.34 (2H, d, ²J_{HH} = 5.2 Hz, ArH), 7.05 (2H, d, ²J_{HH} =

5.2 Hz, *ArH*), 4.16 (4H, d, $^3J_{\text{HH}} = 7.2$ Hz, $-\text{NCH}_2-$), 2.23-2.10 (2H, m, $-\text{NCH}_2\text{CH}-$), 1.44-1.18 (64 H, m, $-\text{CH}_2-$), 0.90-0.84 (12H, m, $-\text{CH}_3$); δ_{C} (100 MHz, CDCl_3); 146.7, 138.1, 125.7, 119.3, 114.9, 110.8, 98.3, 50.1, 38.2, 31.9, 31.9, 31.8, 30.0, 29.6, 29.6, 29.4, 29.3, 26.5, 22.7, 22.7, 14.2; m/z (EI) 828.6 [M^+], 829.6, 830.6.

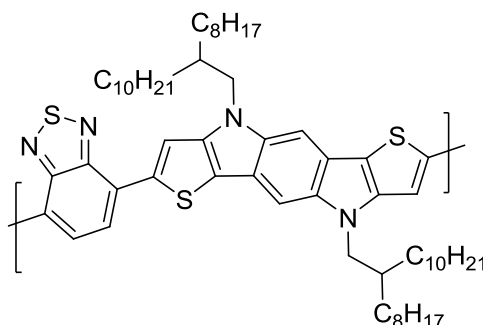
Synthesis of benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) 3.19



A dry Schlenk tube was charged with benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (630 mg, 0.75 mmol) and dissolved in dry THF (10 mL). The solution was cooled to -40 °C with an acetonitrile/dry ice bath, then *n*BuLi (1.6 mL, 2.56 mmol, 1.6 M solution in hexanes) was added, dropwise, to the flask. Once the addition was complete, the solution was left to stir for a further 2 h at 0 °C. The reaction mixture was cooled to -40 °C and trimethyltin chloride (3 mL, 3 mmol, 1 M solution in THF) was added in one portion. The reaction was allowed to warm to room temperature, overnight. The reaction was quenched with water (10 mL) and hexane (20 mL) was added. The organic layer was separated and washed with water (4 x 20 mL). The organic layer was then dried (MgSO_4) and the volatiles were removed *in vacuo*. The yellow oil was dried under high vacuum for 8 h, then placed in the freezer to give a yellow solid (950 mg, 97 %). The product was used in the next step without further purification.

δ_{H} (400 MHz, CDCl_3): 7.62 (2H, s, *ArH*), 7.10 (2H, s, *ArH*), 4.19 (4H, d, $^3J_{\text{HH}} = 7.2$ Hz, $-\text{NCH}_2-$), 2.15-2.10 (2H, m, $-\text{NCH}_2\text{CH}-$), 1.51-1.24 (64 H, m, $-\text{CH}_2-$), 0.96-0.88 (12H, m, CH_3), 0.48 (18H, s, SnMe_3); δ_{C} (100 MHz, CDCl_3) 149.2, 139.2, 138.6, 121.0, 119.1, 117.7, 98.5, 49.9, 38.2, 31.9, 30.1, 29.7, 29.4, 26.4, 22.7, 14.2; m/z (EI) 1154.6 [M^+].

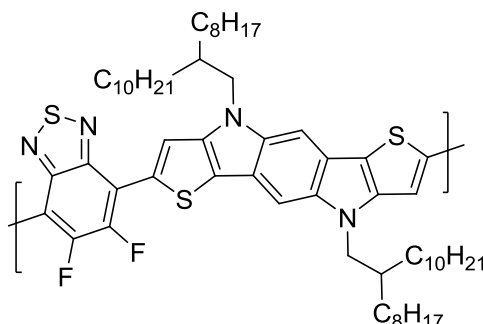
Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene-*co*- benzo[*c*][1,2,5]thiadiazole) P11



An oven-dried 5 mL microwave vial was charged with benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (250 mg, 0.216 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (64 mg, 0.216 mmol) and [Pd(PPh₃)₄] (10 mg, 8.58 μmol). The cap was placed on the vial and dry *o*-xylene (0.8 mL) was added. The reaction mixture was purged with argon for 20 min, before being placed in the microwave and subjected to the following conditions: 100 °C for 2 min, 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min and 180 °C for 40 min. Once the reaction had cooled, the viscous green liquid was precipitated in acidified methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate, at 50 °C for 1 h, then the organic layer was separated and washed with water, then dried (MgSO₄). The chloroform was concentrated and reprecipitated in methanol. The dark green precipitate (140 mg, 79 %) was collected by filtration.

GPC (chlorobenzene 80 °C): M_n 7 kDa, M_w 10 kDa; δ_H (400 MHz, CDCl₃) 7.90 (4H, bs, ArH), 6.30 (2H, bs, ArH), 4.40-3.50 (4H, m, -NCH₂-), 2.40-0.30 (78H, m, CH₂ and CH₃); λ_{max} (CHCl₃) 770 nm.

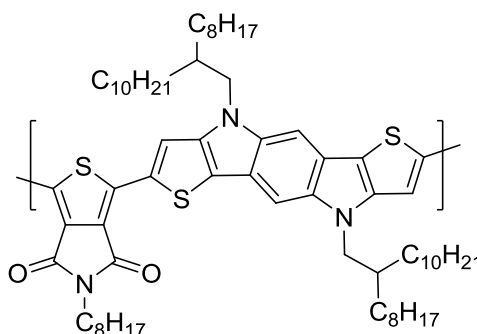
Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene-co-5,6-difluoro-benzo[*c*][1,2,5]thiadiazole) P12



Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (200 mg, 0.173 mmol), 4,7-dibromo-5,6-difluoro-benzo[*c*][1,2,5]thiadiazole (55 mg, 0.168 mmol), [Pd₂dba₃] (2.3 mg, 2.52 μmol) and tri-*o*-tolylphosphine (3.1 mg, 0.01 mmol) were added to the vial, followed by dry chlorobenzene (1.2 mL). Polymerization method **B** was used to afford the *title* compound (160 mg, 89 %) as a dark green powder.

GPC (chlorobenzene 80 °C): M_n 11 kDa, M_w 25 kDa; δ_H (400 MHz, CDCl₃) 8.25 (2H, bs, ArH), 6.70 (2H, bs, ArH), 4.50-3.60 (4H, m, -NCH₂-), 2.90-0.5 (78H, m, CH₂ and CH₃); λ_{max} (CHCl₃) 780 nm.

Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene-co-5-octylthieno[3,4-*c*]pyrrole-4,6-dione) P13

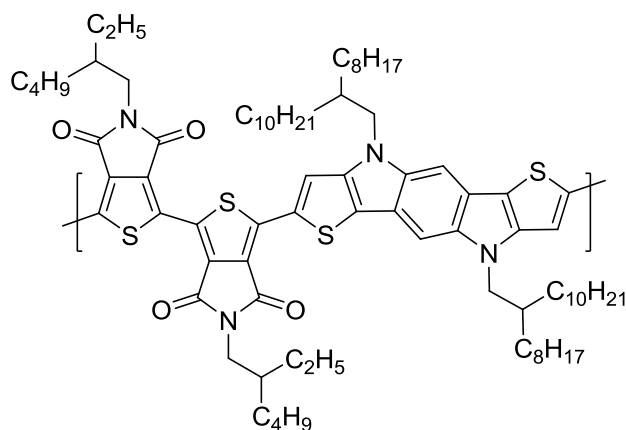


Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (200 mg, 0.173 mmol), 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione (71 mg, 0.168 mmol), [Pd₂dba₃] (2.3 mg, 2.52 μmol) and tri-*o*-tolylphosphine (3.1 mg, 0.01 mmol) were

added to the vial, followed by dry chlorobenzene (1 mL). Polymerization method **B** was followed and the *title* compound (150 mg, 79 %) was isolated as a dark blue powder.

GPC (chlorobenzene 80 °C): M_n 12 kDa, M_w 28 kDa; δ_H (400 MHz, $CDCl_3$) 8.18 (2H, bs, ArH), 6.26 (2H, bs, ArH), 4.65-3.20 (4H, m, $-NCH_2-$), 2.40-0.75 (95H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 635 nm.

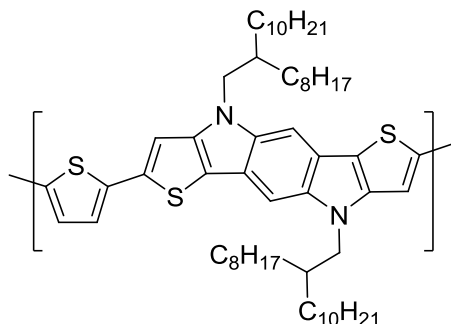
Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene-*co*-5,5'-di-2-ethylhexyl 1-4*H*,4'*H* 1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(5*H*, 5'*H*)-tetrone) P14



Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (210 mg, 0.182 mmol), 3,3'-dibromo-5,5'-di-2-ethylhexyl 1-4*H*,4'*H* 1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(5*H*, 5'*H*)-tetrone (125 mg, 0.182 mmol), $[Pd_2dba_3]$ (2.5 mg, 2.73 μ mol) and tri-*o*-tolylphosphine (3.3 mg, 0.01 mmol) were added to the vial, followed by dry chlorobenzene (1 mL). Polymerization method **B** was employed and the *title* compound (190 mg, 77 %) was isolated as a dark blue powder.

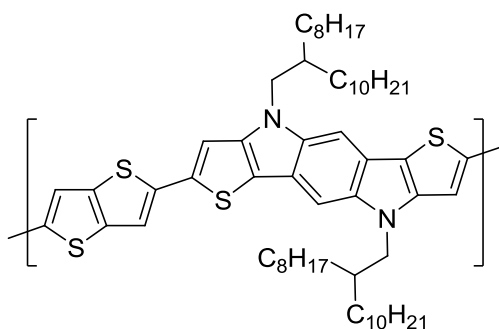
GPC (chlorobenzene 80 °C): M_n 22 kDa, M_w 57 kDa; δ_H (400 MHz, $CDCl_3$) 8.40 (2H, bs, ArH), 6.50 (2H, bs, ArH), 4.50-3.25 (8H, m, $-NCH_2-$), 2.40-0.50 (108H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 695 nm.

5.5.5 Experimental for Chapter 4

Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene-co-thiophene) P15

Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (100 mg, 0.087 mmol), 2,5-dibromothiophene (20 mg, 0.084 mmol), [Pd₂dba₃] (1.2 mg, 1.26 μmol) and tri-*o*-tolylphosphine (1.5 mg, 5.04 μmol) were added to the vial, followed by dry chlorobenzene (0.5 mL). Polymerization method **B** was employed and the *title* compound (27 mg, 33 %) was isolate as a dark purple powder.

GPC (chlorobenzene 80 °C): M_n 33 kDa, M_w 56 kDa; δ_H (400 MHz, CDCl₃) 7.20-6.55 (6H, bs, ArH), 4.25-3.50 (2H, bs, -NCH₂-), 2.05 (1H, bs, -NCH₂CH-), 1.29 (32H, s, CH₂), 0.90 (12H, s, CH₃); λ_{max} (CHCl₃) 556, 587 nm.

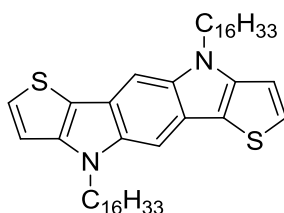
Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene-co-thieno(3,2-*b'*)thiophene) P16

Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b'*]thiophene) (100 mg, 0.087 mmol), 2,5-dibromo-thieno(3,2-*b'*)thiophene (25 mg, 0.084 mmol), [Pd₂dba₃] (1.2 mg, 1.26 μmol) and tri-*o*-tolylphosphine (1.5 mg, 5.04 μmol) were added to the vial,

followed by dry chlorobenzene (0.5 mL). Polymerization method **B** was followed and the *title* compound (45 mg, 52 %) was isolated as a dark purple precipitate.

GPC (chlorobenzene 80 °C): M_n 13 kDa, M_w 28 kDa; δ_H (400 MHz, $CDCl_3$) 7.50-6.65 (6H, m, ArH), 4.30-3.20 (4H, m, $-NCH_2CH-$), 2.20-0.55 (45H, m, CH_2 and CH_3); λ_{max} ($CHCl_3$) 551 nm.

Synthesis of benzo[1,2-*b*:4,5-*b'*]bis(4-(hexadecyl)-4*H*-amino[3,2-*b*]thiophene) 4.1



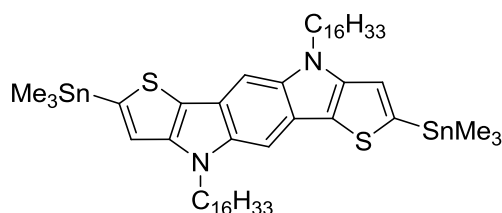
A dry Schlenk tube was charged with 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) (2.00 g, 3.60 mmol), $[Pd_2dba_3]$ (165 mg, 0.18 mmol), BINAP (448 mg, 0.72 mmol) and NaO^tBu (1.90 g, 19.80 mmol). Three consecutive vacuum/nitrogen cycles were carried out on the contents of the Schlenk tube, before adding hexadecylamine (1.91 g, 7.92 mmol) and dry toluene (40 mL). The reaction mixture was heated to 120 °C for 24 h. The reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 x 100 mL). The combined organic fractions were washed with brine (200 mL) and dried ($MgSO_4$). The volatiles were removed to *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, 0-5 % CH_2Cl_2 /Hexane) yielded a mixture of mono ring-closed and mono-aminated product as a colourless oil (2.35 mg).

This mixture (2.30 mg) was placed in a Schlenk tube, along with $[Pd_2dba_3]$ (117 mg, 0.13 mmol), BINAP (319 mg, 0.51 mmol) and NaO^tBu (1.54 mg, 16.0 mmol). Three consecutive vacuum/nitrogen cycles were carried out on the contents of the Schlenk tube, before adding hexadecylamine (850 mg, 3.25 mmol) and dry toluene (30 mL). The reaction mixture was heated to 120 °C and monitored using TLC. Once the reaction had reached completion (20 h) the reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 x 100 mL). The combined organics were washed with brine (200 mL) and dried ($MgSO_4$). The volatiles were removed to *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, 0-5 %

CH₂Cl₂/Hexane) yielded the *title* compound (370 mg, 14 % overall yield) as a pale yellow solid.

(Found: C, 77.13; H, 9.99; N, 3.85. C₄₆H₇₂N₂S₂ requires: C, 77.03; H, 10.12; N, 3.91 %); δ_H (400 MHz, CDCl₃) 7.66 (2H, s, ArH), 7.38 (2H, d, $^2J_{HH}$ = 5.2 Hz, ArH), 7.11 (2H, d, $^2J_{HH}$ = 5.2 Hz, ArH), 4.34 (4H, t, $^3J_{HH}$ = 7.2 Hz, -NCH₂-), 1.97-1.90 (4H, m, -NCH₂CH₂-), 1.40-1.21 (52 H, m, -CH₂-), 0.94-0.86 (6H, m, -CH₃); δ_C (100 MHz, CDCl₃); 146.3, 137.7, 125.8, 119.4, 115.0, 110.6, 98.2, 45.6, 31.9, 29.7, 29.6, 29.5, 29.4 (d), 27.3, 22.7, 14.2; *m/z* (EI) 716 [M⁺], 717, 718.

Synthesis of benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(hexadecyl)-4*H*-amino[3,2-*b*]thiophene) 4.3

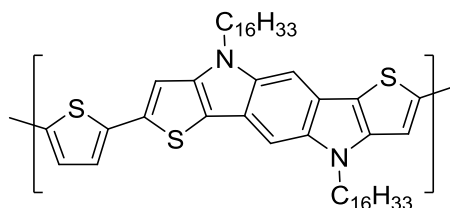


A dry Schlenk tube was charged with benzo[1,2-*b*:4,5-*b'*]bis(hexadecyl)-4*H*-amino[3,2-*b*]thiophene) (350 mg, 0.49 mmol) and dissolved in dry THF (5 mL). The solution was cooled to – 40 °C with an acetonitrile/dry ice bath, then *n*BuLi (0.92 mL, 1.46 mmol, 1.6 M solution in hexanes) was added, dropwise, to the flask. Once the addition was complete, the solution was left to stir for a further 2 h at 0 °C. The reaction mixture was cooled back down to - 40 °C and trimethyltin chloride (1.72 mL, 1.72 mmol, 1 M solution in THF) was added in one portion. The reaction was allowed to warm to room temperature, overnight. The reaction was quenched with water (10 mL) and ethyl acetate (50 mL) was added. The organic layer was separated from the aqueous layer and washed with water (4 x 20 mL). The organic layer was then dried (MgSO₄) and the volatiles were removed *in vacuo* to give a pale brown solid (460 mg, 90 %). The product was used in the next step without further purification.

(Found: C, 60.00; H, 8.58; N, 2.61. C₅₂H₈₈N₂S₂Sn₂ requires: C, 59.90; H, 8.51; N, 2.69 %) δ_H (400 MHz, CDCl₃) 7.59 (2H, s, ArH), 7.10 (2H, s, ArH), 4.29 (4H, t, $^3J_{HH}$ = 7.2 Hz, -NCH₂-), 1.97-1.89 (4H, m, -NCH₂CH-), 1.45-1.21 (52 H, m, -CH₂-), 0.89 (6H, t, $^3J_{HH}$ = 7.2 Hz, CH₃),

0.44 (18H, s, SnMe_3); δ_{C} (100 MHz, CDCl_3) 148.7, 139.5, 138.2, 121.2, 119.2, 117.5, 98.4, 45.5, 32.0, 29.7(d), 29.5, 29.4, 27.3, 22.7, 14.2; m/z (EI) 1041.4 [M^+], 1042.5, 1043.4.

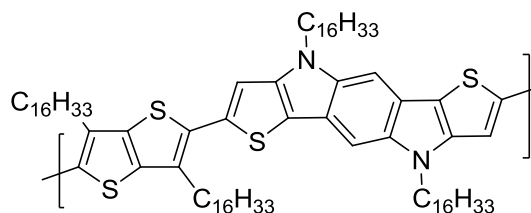
Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene-co-thiophene) P17



Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene) (80 mg, 0.077 mmol), 2,5-dibromothiophene (18 mg, 0.075 mmol), $[\text{Pd}_2\text{dba}_3]$ (1.03 mg, 1.13 μmol) and tri-*o*-tolylphosphine (1.37 mg, 4.50 μmol) were added to the vial, followed by dry chlorobenzene (0.5 mL). Polymerization method **B** was followed and a dark purple precipitate (31 mg, 49 %) was collected from the chloroform fraction. The Soxhlet thimble was then placed into hot chlorobenzene to dissolve the high molecular weight fraction. The solution was then filtered hot, concentrated and reprecipitated in methanol to give the *title* compound (13 mg, 21 %) as a purple powder.

GPC (chlorobenzene 80 °C): Chloroform fraction: M_n 7 kDa, M_w 9 kDa; Chlorobenzene fraction: M_n 8 kDa, M_w 11 kDa; δ_{H} (400 MHz, CDCl_3) 7.70-6.80 (6H, bs, ArH), 4.40-3.75 (4H, bs, - NCH_2), 2.00-0.70 (62H, m, CH_2 and CH_3); λ_{max} (CHCl_3) 554 nm.

Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene-co-3,6-hexadecyl-thieno(3,2-*b'*)thiophene) P18

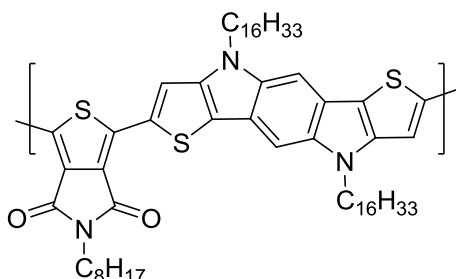


Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene) (80 mg, 0.077 mmol), 2,5-dibromo-3,6-hexadecyl-thieno(3,2-*b'*)thiophene (56 mg, 0.075 mmol),

[Pd₂dba₃] (1.03 mg, 1.13 μmol) and tri-*o*-tolylphosphine (1.37 mg, 4.50 μmol) were added to the vial, followed by dry chlorobenzene (0.5 mL). Polymerization method **B** was followed and a dark purple precipitate (28 mg, 27 %) was collected from the chloroform fraction. The Soxhlet thimble was then placed into hot chlorobenzene to dissolve the high molecular weight fraction. The solution was then filtered hot, concentrated and reprecipitated in methanol to give the *title* compound (17 mg, 17 %) as a purple powder.

GPC (chlorobenzene 80 °C): Chloroform fraction: M_n 5 kDa, M_w 8 kDa; Chlorobenzene fraction: M_n 8 kDa, M_w 10 kDa; δ_H (400 MHz, CDCl₃) 7.80-6.70 (6H, m, ArH), 3.53-3.52 (8H, m, -NCH₂-), 2.05-1.22 (112H, CH and CH₂), 0.95-0.83 (12H, m, CH₃); λ_{max} (CHCl₃) 554 nm.

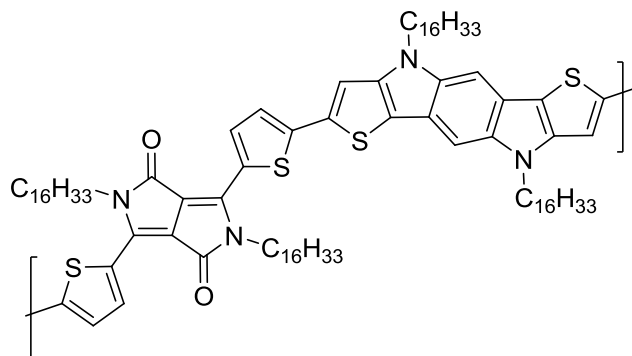
Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene-co-5-octylthieno[3,4-*c*]pyrrole-4,6-dione) P19



Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene) (200 mg, 0.173 mmol), 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione (80 mg, 0.188 mmol), [Pd₂dba₃] (2.6 mg, 2.82 μmol) and tri-*o*-tolylphosphine (3.4 mg, 0.011 mmol) were added to the vial, followed by dry chlorobenzene (0.7 mL). Polymerization method **B** was followed and the *title* compound (112 mg, 60 %) was isolated as a dark blue powder.

GPC (chlorobenzene 80 °C): M_n 10 kDa, M_w 22 kDa; δ_H (400 MHz, CDCl₃) 8.40-7.5 (2H, bs, ArH), 6.40-5.40 (2H, bs, ArH), 4.65-3.00 (6H, m, -NCH₂-), 2.00-0.70 (77H, m, CH₂ and CH₃); λ_{max} (CHCl₃) 630 nm.

Synthesis of poly(benzo[1,2-*b*:4,5-*b'*]bis(4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene-co-2,5-di-*n*-hexadecyl-3,6-dithiophen-2-yl-pyrrolo[3,4-*c*]pyrrole-1,4-dione) P20



Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(hexadecyl)-4*H*-amino[3,2-*b'*]thiophene) (50 mg, 0.050 mmol), 3,6-bis-(5-bromo-thiophen-2-yl)-2,5-di-*n*-hexadecyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (42 mg, 0.047 mmol), [Pd₂dba₃] (0.60 mg, 0.69 μmol) and tri-*o*-tolylphosphine (0.80 mg, 2.62 μmol) were added to the vial and dry chlorobenzene (0.5 mL). Polymerization method **B** was followed and the *title* compound (35 mg, 50 %) was isolated as a dark blue powder.

GPC (chlorobenzene 80 °C): M_n 5 kDa, M_w 10 kDa; δ_H (400 MHz, CDCl₃) 8.10-6.20 (8H, m, ArH), 4.40-4.0 (8H, m, -NCH₂), 2.10-0.80 (124H, m, CH₂ and CH₃); λ_{max} (CHCl₃) 789 nm.

Chapter 6: Conclusions and Future Work

In **Chapter 2** six novel semi-conducting polymers **P1-P6** were synthesized and their energy levels probed by UV-Vis spectroscopy and PESA. It was found that those with thiophene-thiophene links (**P4** and **P6**) had the most red shifted absorption and higher lying HOMO levels. OFET devices were fabricated using gold source and drain electrodes, with polymers **P1** and **P4**. This study showed that the hole mobility of a device could be increased by two orders of magnitude by the use of co-monomers with flanking thiophenes and planar, conjugated co-monomers, such as TT.

Polymer **P4** (Scheme 6.1) showed the promise for use in OFET devices and further device optimization should be carried out in the future in order to maximize hole mobility.

Four low band gap polymers **P7-P10** were then synthesized, all employing dithienopyrrole as the electron rich unit. They were tested as the donor polymer in polymer:fullerene BHJ solar cells. **P9** exhibited the highest PCE due to its low lying HOMO level and high fill factor of 0.61, which was possibly due to a blend morphology which was conducive to charge separation and charge extraction.

Polymer **P9** (Scheme 6.1) should be investigated further for use in OPV devices. The PCE is limited by the low J_{sc} and if this could be improved by adding an electron transport layer, for example, then the efficiency would greatly improve.

In **Chapter 3** a novel donor monomer NIDT, was synthesized via a double Buchwald-Hartwig amination and fully characterized. The reaction conditions were optimized in order to maximize the yield. Four low band gap polymers (**P11-P14**) were synthesized containing the NIDT unit. The polymers containing BT and ffBT had the highest lying HOMO levels. With the introduction of the TPD (and biTPD) units the HOMO level could be lowered.

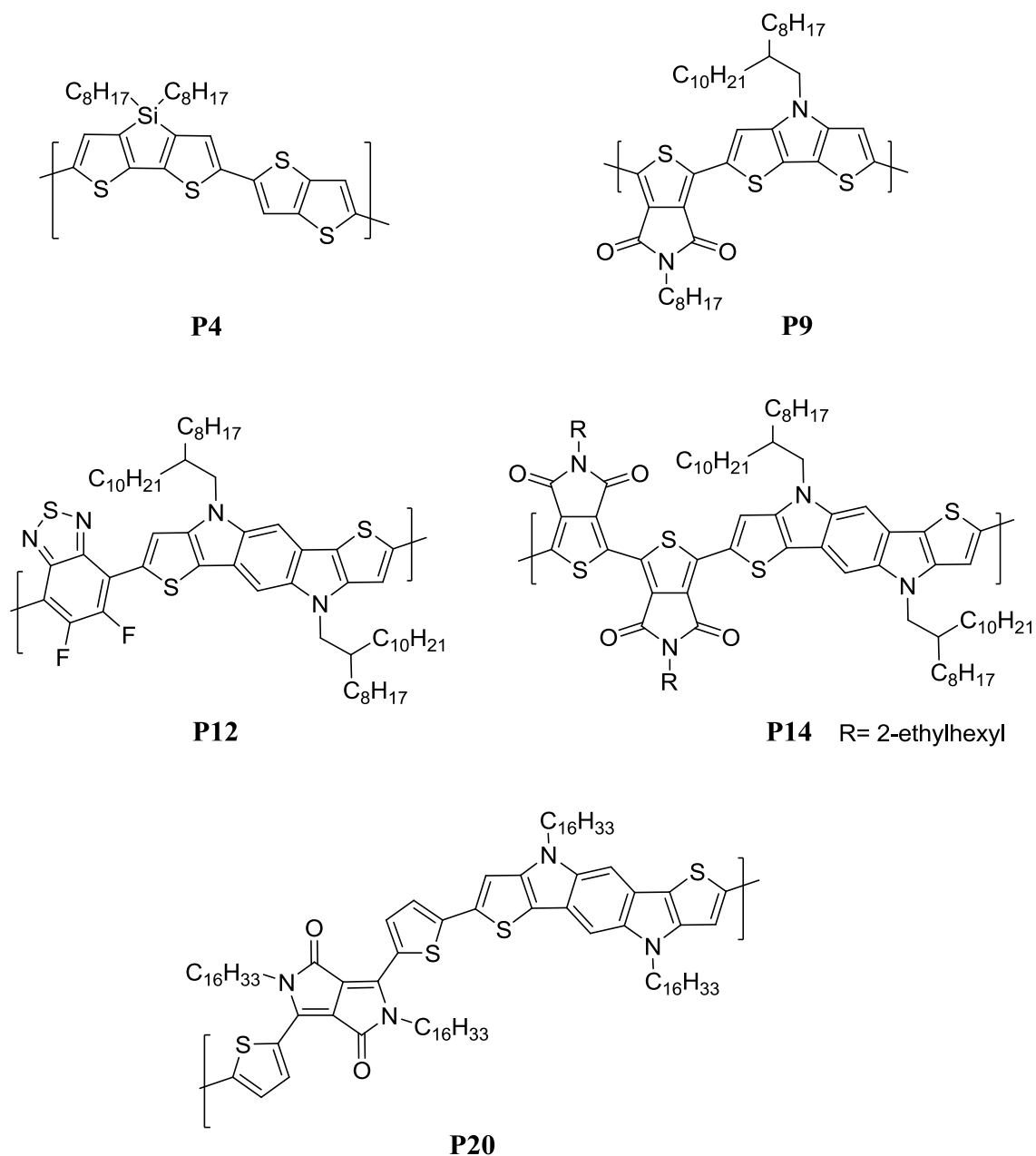
The polymers were then tested as the semiconducting layer in OFET devices and the donor polymer in bulk heterojunction OPVs. It was evident that the polymers based on BT (**P11**

and **P12**) performed best in transistor devices, whereas the TPD containing polymers (**P13** and **P14**) performed best in solar cell devices. If the molecular weight of **P11** and **P12** (Scheme 6.1) could be improved, and the devices optimized, then high hole mobilities could be expected. **P14** (Scheme 6.1) is also of interest due to its exceptionally high fill factor, although J_{sc} would have to be improved in order to reach high PCEs. Unfortunately the intrinsic problem with NIDT containing polymers is the relatively high energy HOMO levels. This means that the V_{oc} of the devices was always limited with PCBM as the electron acceptor.

In **Chapter 4** a novel NIDT monomer with linear hexadecyl substituents was synthesized, along with six novel polymers **P15-P20**. It was found that the solubility of these polymers dictated the molecular weights which could be reached. When the solubility was compromised by the introduction of the TT unit or the hexadecyl NIDT unit, the molecular weight fell significantly. This fall in molecular weight had a detrimental effect on the hole mobility of the polymers.

Polymer **P20** (Scheme 6.1) was the highest performing polymer when tested in OFET devices. Its hole mobility was over one order of magnitude higher than the other polymers. This was due to the introduction of the DPP unit which has excellent hole transport properties. The initial results look promising and work is on-going to optimize this polymers performance.

In terms of OPV performance, the introduction of the hexadecyl NIDT unit in to the polymer led to a decrease in V_{oc} . With the introduction of the linear substituent it is likely that the polymer backbone became more planar, resulting in improved molecular orbital hybridization and a rise in the HOMO level. We can conclude from this that the branched NIDT containing polymers perform better in OPVs.



Scheme 6.1 Polymers which warrant further investigation in order to optimize performance.

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Appendix A

Chapter 1: MOSFET Equations¹¹

L = channel length

W = channel width

C_i = geometric capacitance of the dielectric (17 nF/cm² for 200 nm of SiO₂)

General equation for the thin film transistor model:

$$I_D = \frac{W}{L} \mu C_i \left[(V_G - V_T) V_D - \frac{V_D^2}{2} \right]$$

Linear regime ($V_G - V_T \gg V_D$):

$$I_{D(lin)} = \frac{W}{L} \mu_{lin} C_i (V_G - V_T) V_D$$

$$\therefore \mu_{lin} = \frac{L}{W C_i V_D} \left(\frac{\partial I_{D(lin)}}{\partial V_G} \right)$$

Saturation regime ($V_G - V_T \leq V_D$):

$$I_{D(sat)} = \frac{W}{2L} \mu_{sat} C_i (V_G - V_T)^2$$

$$\therefore \mu_{sat} = \frac{L}{W C_i} \left(\frac{\partial^2 I_{D(sat)}}{\partial V_G^2} \right) = \frac{2L}{W C_i} \left(\frac{\partial \sqrt{I_{D(sat)}}}{\partial V_G} \right)^2$$

GPC traces

Chapter 2

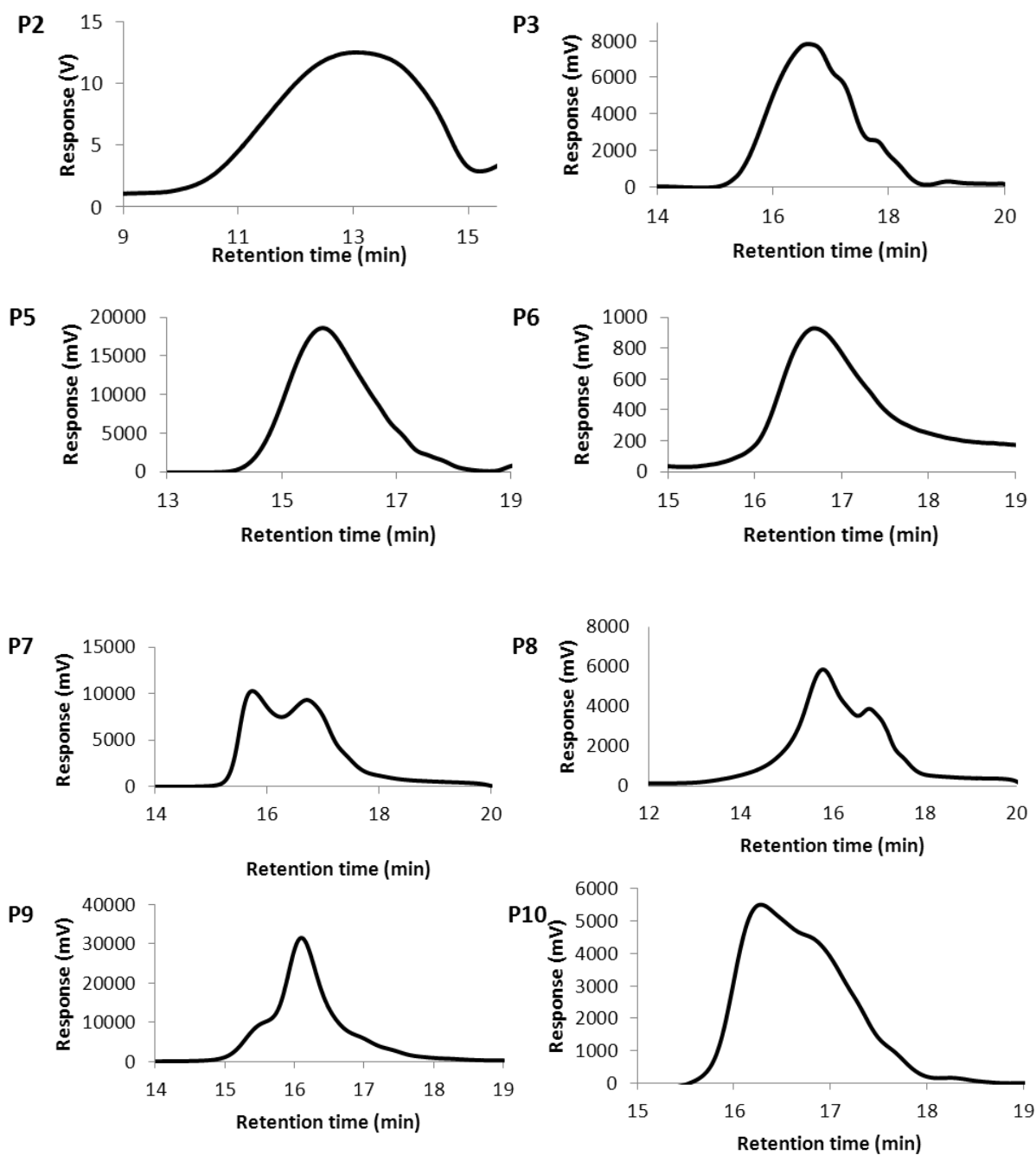


Figure 1 GPC traces of polymers **P2**, **P3**, **P5-P10** at 80 °C, using chlorobenzene as the eluent.

Chapter 3

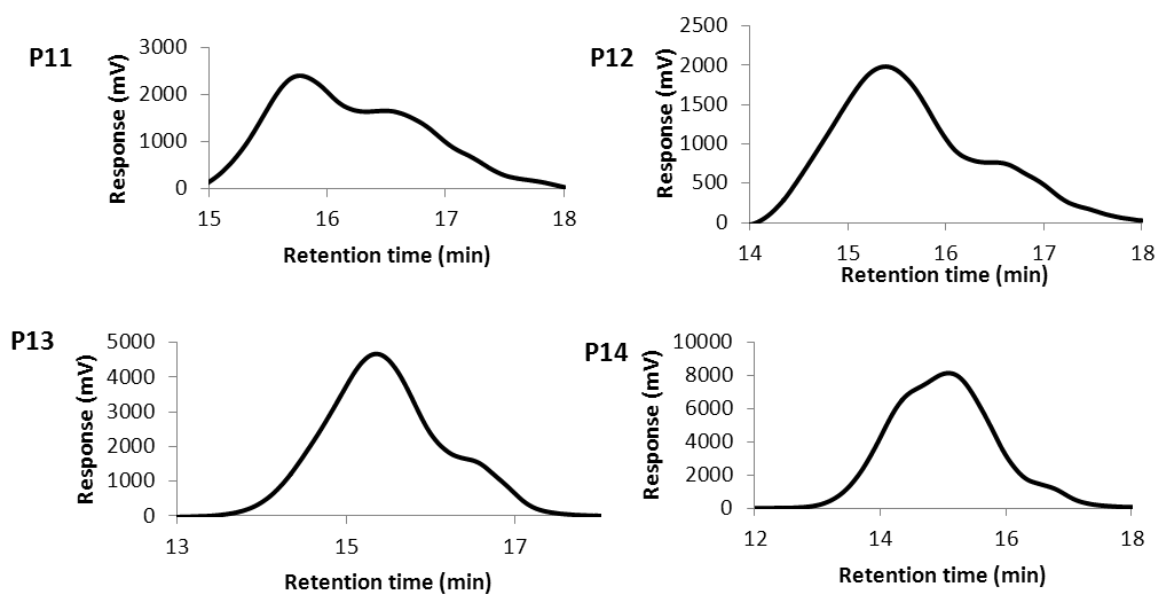


Figure 2 GPC traces of polymers **P11-P14** at 80 °C, using chlorobenzene as the eluent.

Chapter 4

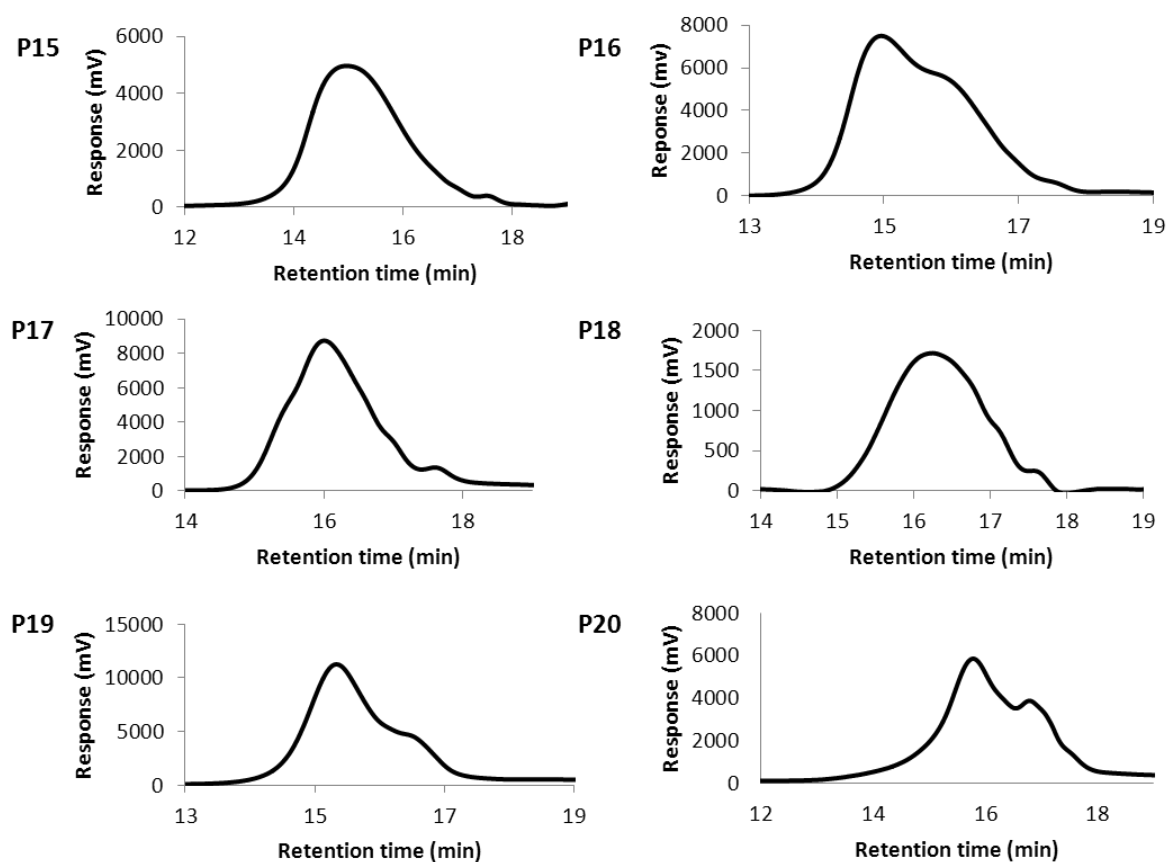
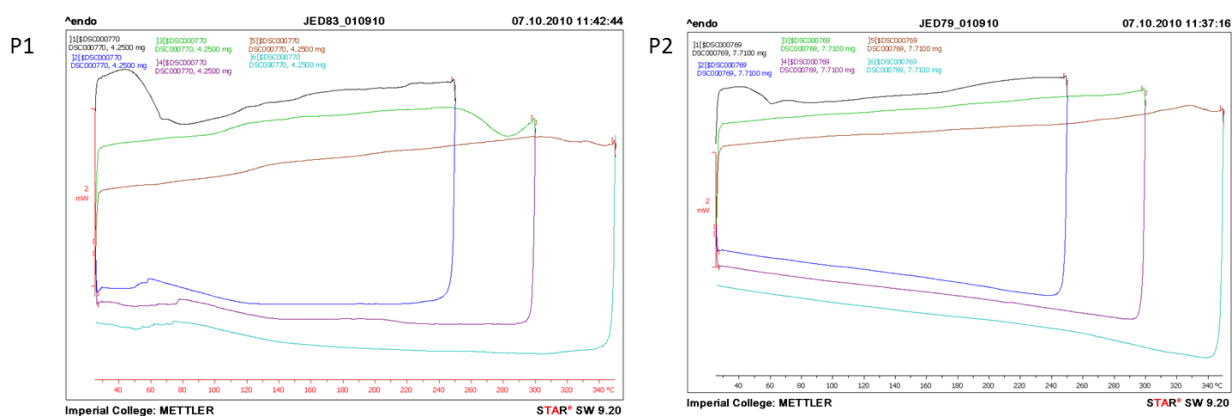


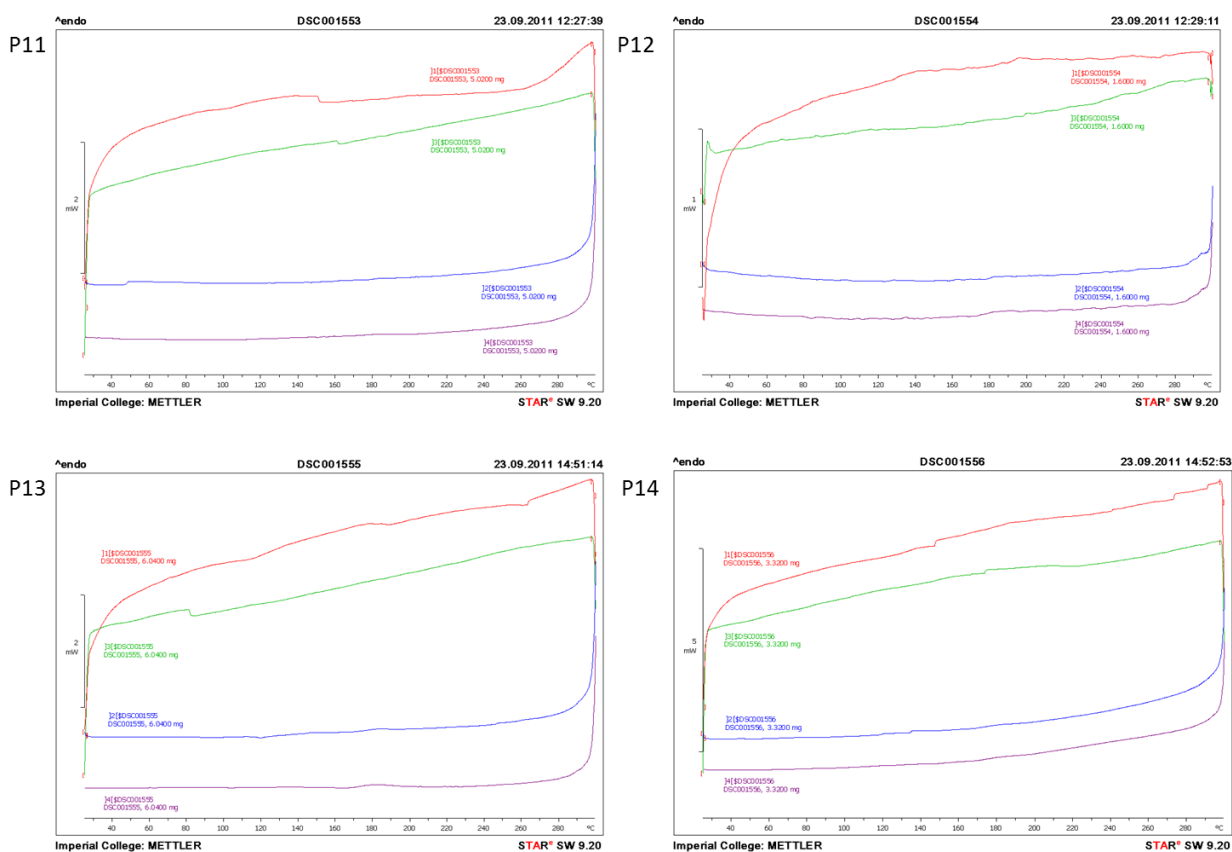
Figure 3 GPC traces of polymers **P16-P20** at 80 °C, using chlorobenzene as the eluent.

DSC

Chapter 2

Figure 4 DSC curves of **P1** and **P2** heated between 40-300 °C.

Chapter 3

Figure 5 DSC curves of **P11-P14** heated between 40-300 °C.

Chapter 4

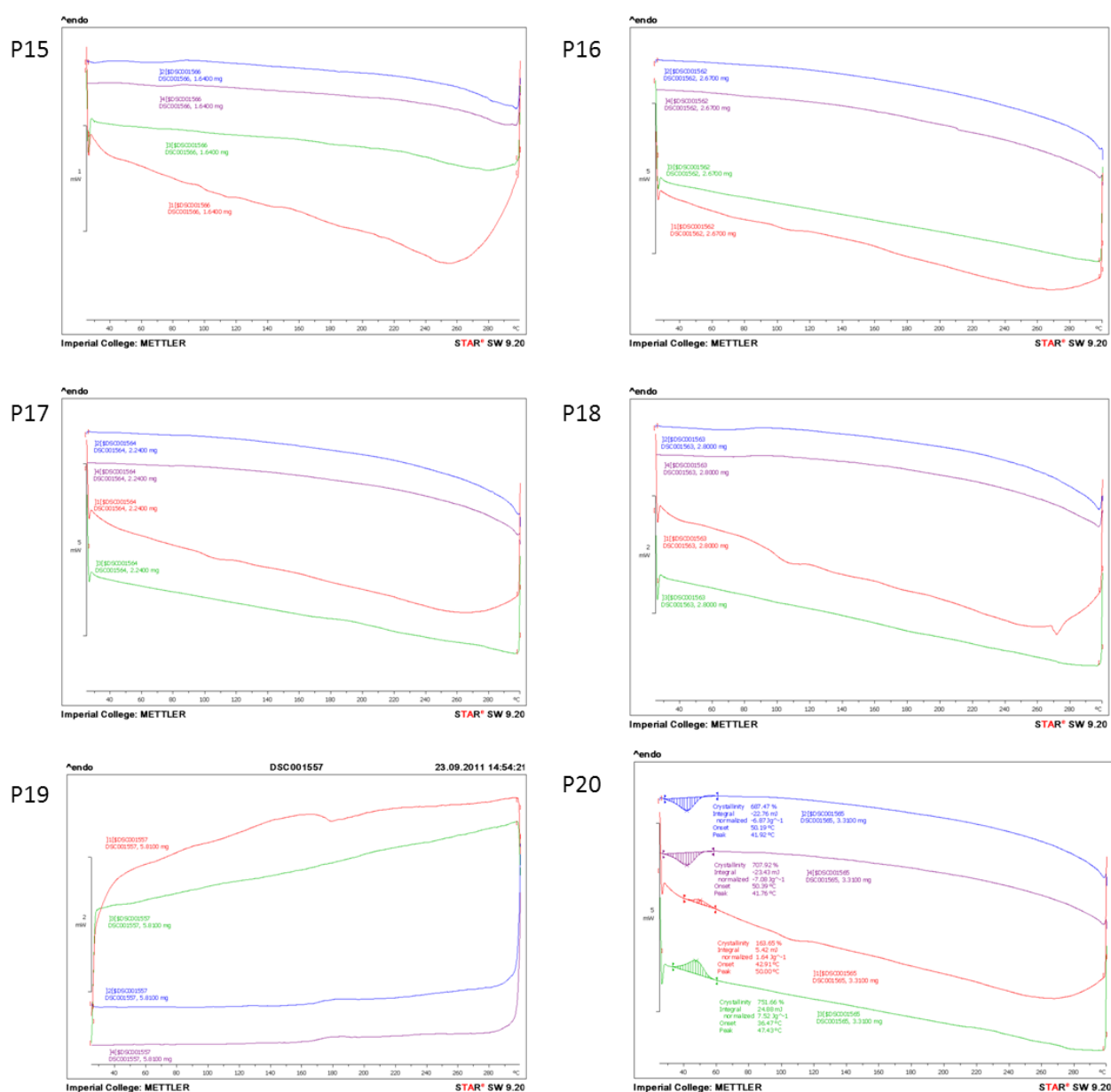


Figure 6 DSC curves of P15-P20 heated between 40-300 °C.

Transistor Output Characteristics

Chapter 2

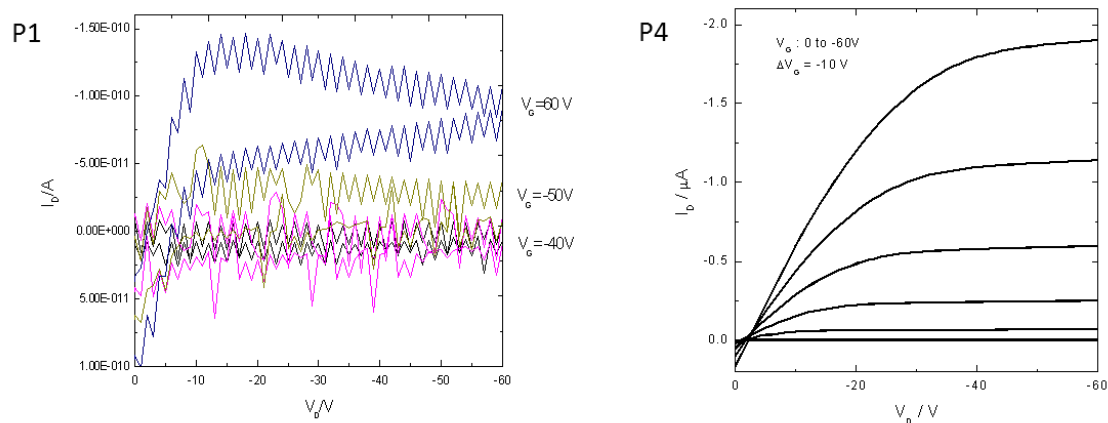


Figure 7 Output curves for **P1** and **P4** using OFETs with Au electrodes.

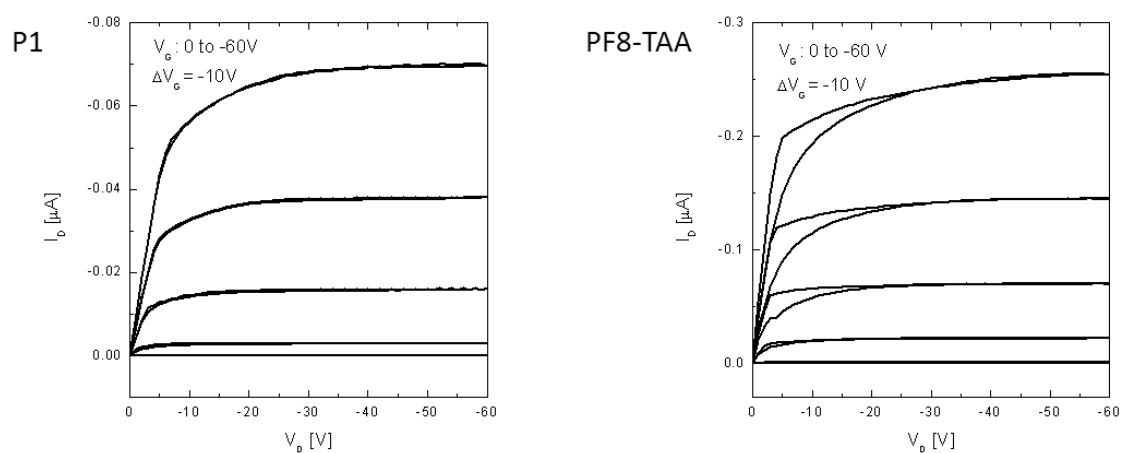


Figure 8 Output curves for **P1** and **PF8-TAA** using OFETs with Au/MoO₃ electrodes.

Chapter 3

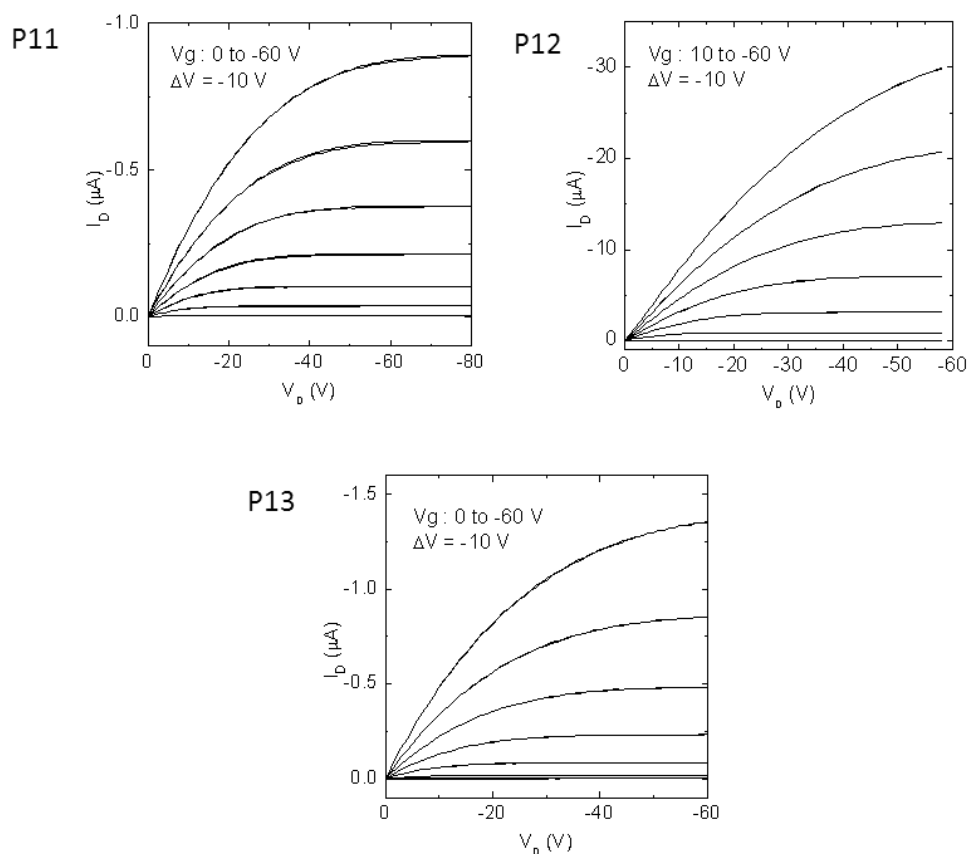


Figure 9 Output curves for **P11-P13** using Au electrodes

Chapter 4

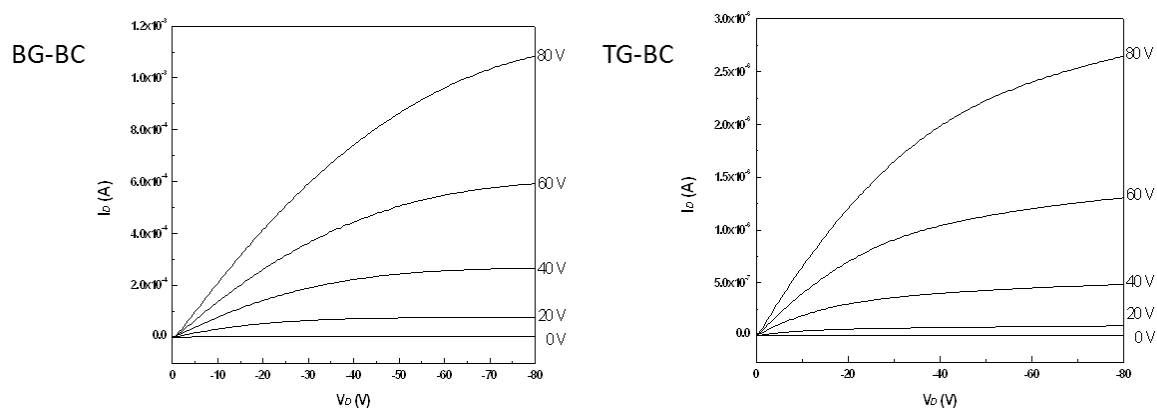


Figure 10 Output curves for **P20** in BG-BC and TG-BC architecture devices.

Appendix B

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PAPER

Pyrroloindacenodithiophene containing polymers for organic field effect transistors and organic photovoltaics†

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The synthesis of the novel electron-rich pyrroloindacenodithiophene (NIDT) unit is reported. Stille copolymerization of the distannylated NIDT unit, with the electron-deficient dibrominated benzothiadiazole (BT), difluorobenzothiadiazole (ffBT), thienopyrrolodione (TPD) and 1,1'-bithienopyrrolodione (biTPD) units afforded a series of low band gap semiconducting polymers. Initial testing shows promise for the use of these materials as p-type semiconductors in organic field effect transistors (OFETs) with mobilities as high as $0.07 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ being measured. These materials have also been tested as the donor polymer in polymer/fullerene bulk heterojunction organic photovoltaics (OPVs) giving maximum efficiencies of 2.5%.

Introduction

Over the past few decades π -conjugated polymer semiconductors have attracted a lot of attention for use in electronic applications, as a low cost alternative to inorganic semiconducting materials. They enable the fabrication of lightweight, flexible organic field effect transistor (OFET) and organic photovoltaic (OPV) devices by solution processing techniques. Recent advances in polymer synthesis and device fabrication have led to mobilities as high as $\sim 3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and power conversion efficiencies (PCE) above 7% for OFET and OPV devices, respectively.^{1–5}

Recently, we have demonstrated that indacenodithiophene is a versatile conjugated unit when copolymerized with appropriate monomers, enabling high performing field effect transistors and solar cells.^{6,7} With its rigid, planar, conjugated structure, conformational disorder is minimized, which contributes to high charge carrier mobility, whereas the electron rich nature of the peripheral thiophene units facilitates molecular orbital hybridization with electron poor co-monomers, leading to low band gap absorbers. The thiophene links along the backbone promote coplanarity of adjacent aromatic units, enhancing π -conjugation and intermolecular π -stacking, whereas the bridging heteroatoms both offer a centre for solubilizing functionality, and

a versatile position to fine-tune the molecular orbital energy levels. For example, polymers employing the carbon bridged unit poly(indacenodithiophene-*co*-benzothiadiazole) (PIDT-BT) exhibited very high hole mobilities ($\sim 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) when tested in OFET devices.⁷ The silicon bridging analogue poly(silaindacenodithiophene-*co*-benzothiadiazole) (PSiIDT-BT) showed reduced mobility in OFETs but a high power conversion efficiency (PCE) of $\sim 4\%$ in solar cell devices, with a larger open circuit voltage (V_{oc}) than the carbon bridged polymer, due to the contribution of the silicon to lower the HOMO energy level.⁶ Replacing the bridging heteroatom with the more electron donating nitrogen atom would further promote molecular orbital hybridization leading to lower bandgaps, whereas the electron rich nature of the backbone should promote good hole transport. For these reasons, the synthesis of the novel pyrroloindacenodithiophene (NIDT) unit was realized.

High charge carrier mobility is important not only in organic transistors, but can be beneficial in OPVs as this should increase both the fill factor, and also the J_{sc} . Unfortunately, the V_{oc} would be expected to be slightly reduced as the introduction of a more electron rich donor unit would be likely to raise the HOMO level of the donor polymer.⁸

Results and discussion

Synthesis and characterization

The structure and synthesis of the novel NIDT unit is shown in Scheme 1. Ogawa *et al.* report on the structure of dithienopyrrole.⁹ X-ray data indicates that the nitrogen in the pyrrole moiety is sp^2 hybridized, with the first carbon of the alkyl

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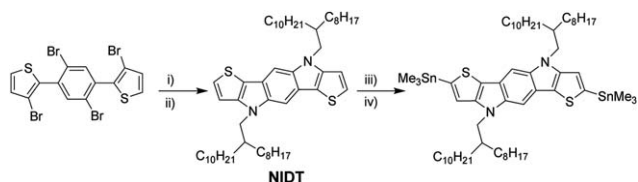
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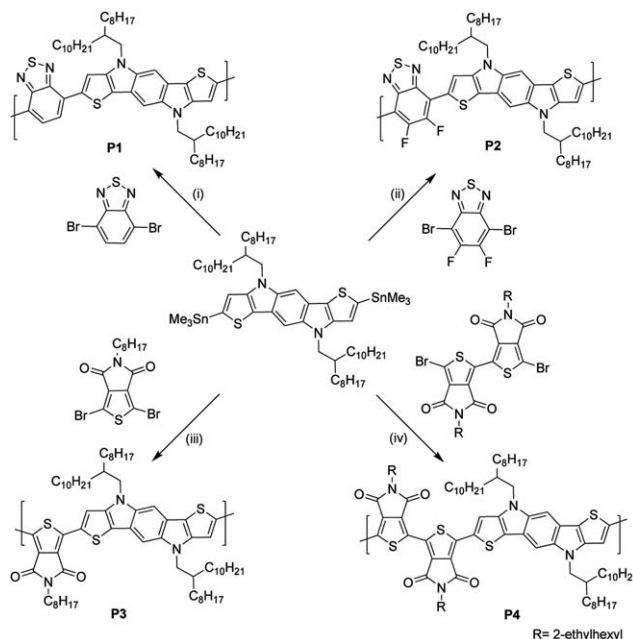
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1jm13428k



Scheme 1 Reagents and conditions: i) 5 mol % Pd_2dba_3 , 20 mol% BINAP, NaOtBu , 2-octyldodecylamine, toluene, 120 °C, 24 h; ii) 4 mol% Pd_2dba_3 , 16 mol% BINAP, NaOtBu , 2-octyldodecylamine, toluene, 120 °C, 24 h; iii) 3 eq. $n\text{BuLi}$, THF, -40 °C, 2 h; iv) 3.5 eq. Me_3SnCl , -40 to 25 °C, 24 h.

substituent in the plane of the molecule. The lone pair of the nitrogen donates into the conjugated π -system, thus contributing to the electron density of the ring.⁹ It is expected that the pyrrole moieties of the NIDT unit will exhibit sp^2 hybridized bridging nitrogens leading to a fully aromatic molecule, unlike the C and Si analogues. To support this, the structure was modelled and compared to the carbon analogue (IDT) using Gaussian at the B3LYP/6-31G* level. The calculated energy-minimised conformations of NIDT and IDT are shown in Fig. 1 and it is clear that the bridging atoms are sp^2 hybridised for NIDT, with a resultant in-plane bond between the ring nitrogen and the aliphatic carbon, and sp^3 hybridised for IDT. The difference in aromaticity is further evidenced by the HOMO distributions of the two structures (Fig. 1). Whereas the lone pair of the nitrogen in NIDT is clearly delocalised over the entire planar backbone, the HOMO of IDT has nodal planes that intersect the bridging carbon atoms, limiting the delocalisation. The first carbon in the alkyl chain is therefore likely to be in the plane of the molecule, rather than out of the plane as observed in the case of IDT and SiIDT. The rest of the alkyl chain is free to rotate but strong π -interactions could force it in to the plane reducing the π - π stacking distance between chains, therefore increasing interchain charge transfer and promoting molecular order. The alkyl functionality on the bridging nitrogen was required to be long and branched to enable the resulting polymer to be soluble at higher molecular weights. It has been shown in a number of studies that an increase in molecular weight will lead to an improvement in the polymers performance in both OFET and OPV devices.^{1,10–13}

The structures of the polymers are shown in Scheme 2. Four acceptor units were chosen for copolymerization. The electron poor benzothiadiazole (BT) unit facilitates molecular orbital



Scheme 2 Reagents and conditions: i) 4 mol% $\text{Pd}(\text{PPh}_3)_4$, xylene, 180 °C, 40 min, μW ; ii) 2 mol% Pd_2dba_3 , 8 mol% $\text{P}(o\text{-tolyl})_3$, chlorobenzene, 200 °C, 30 min, μW ; iii) 2 mol% Pd_2dba_3 , 8 mol% $\text{P}(o\text{-tolyl})_3$, chlorobenzene, 200 °C, 30 min, μW ; iv) 2 mol% Pd_2dba_3 , 8 mol% $\text{P}(o\text{-tolyl})_3$, chlorobenzene, 200 °C, 30 min, μW .

hybridization with the electron rich NIDT unit, leading to a low band gap polymer which is desirable for efficient solar light harvesting. The orthogonal dipole from the benzothiadiazole unit, in combination with electron rich co-repeat units have also been shown to enhance π -stacking, leading to materials with very high hole mobilities in OFET devices.⁷ The difluorobenzothiadiazole (ffBT) unit with the addition of electron withdrawing fluorine groups attached to the phenyl ring makes this monomer even more electron deficient than BT, whereas the fluorine-sulphur short contacts have been shown to enhance coplanarity between coupled units, thus improving π -delocalization.^{4,14} This was expected to improve hole mobility in OFET devices.

The thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit has been chosen because of its solubilizing influence on the polymer, due to the alkyl functionality on the nitrogen, and the relatively strong electron withdrawing effect due to the presence of the imide group.⁸ This will encourage electronic orbital hybridisation, leading to a low band gap polymer. A linear alkyl chain on the pyrrolidione was required in this case to promote crystallinity and therefore good charge transport. These units have also previously shown promise in OPVs.^{3,8,15–17} The 1,1'-bithienopyrrolodione (biTPD) unit has previously been shown to lower the LUMO level of a polymer significantly in comparison to TPD. The HOMO level of the polymer is also slightly lowered which is expected to lead to an increase in V_{oc} , while the reduced band gap would improve photon absorption. This monomer was therefore attractive in order to lower the HOMO and improve V_{oc} of photovoltaic devices.¹⁸

The unsubstituted NIDT monomer was synthesized using the same conditions for the synthesis of dithieno[3,2-*b*:2',3'-*d'*]

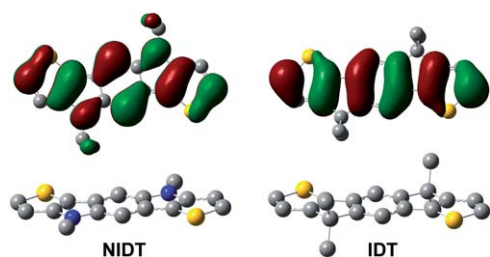


Fig. 1 Minimum-energy conformations (bottom) and HOMO distributions (top) of the NIDT (left) and IDT (right) monomers optimized using Gaussian at the B3LYP/6-31G* level; all hydrogen atoms are omitted for clarity.

pyrrole.¹⁹ The double Buchwald–Hartwig amination reaction was carried out on the 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) as shown in Scheme 1. The product was isolated with a 40% overall yield. Lithiation of NIDT followed by the addition of trimethylstannyl chloride afforded the distannylated monomer in high yield (Scheme 1). Polymers **P1**, **P2**, **P3** and **P4** were all synthesized *via* microwave assisted Stille cross-coupling (Scheme 2) of the distannylated NIDT with the appropriate dibrominated acceptor unit. The polymers were purified by Soxhlet extraction using acetone, hexane and, finally, chloroform. Each chloroform fraction was concentrated and washed with aqueous sodium diethyldithiocarbamate tetrahydrate to remove any palladium catalyst, then the chloroform fraction was separated and the polymer reprecipitated into methanol. Polymerizations proceeded in high yield producing materials with moderate number-average molecular weights (M_n) for **P2**, **P3** and **P4** (Table 1), as measured using Gel Permeation Chromatography (GPC), at 80 °C in chlorobenzene. **P1** had low M_n due to its poor solubility which led to the polymer precipitating from solution before higher molecular weights could be reached. For **P3** the presence of the linear solubilizing side chain on the pyrrolidone unit did not improve the degree of polymerization (DP) as much as expected. This could be due to steric effects from the imide group which may inhibit the coupling reaction and counteract the increase in solubility. All four polymers are soluble in organic solvents such as chloroform and chlorobenzene.

Optical properties and energy levels

All four polymers showed long wavelength absorption maxima both in solution and thin film UV-Vis measurements (Fig. 2 and Table 1). **P1** developed a pronounced shoulder on the long wavelength side of the absorption maximum, on going from solution to thin film, at around 830 nm which could be indicative of planarization of the backbone and increased π -stacking. For **P2** and **P3** we did not observe a shoulder suggesting there is little order gained when going from solution to solid state. **P4** showed a red shift of 15 nm in its absorption maximum, which could be attributed to solid state packing effects. The correspondingly low band gaps of these polymers (Table 1), estimated from the absorption onset, suggests that these polymers should perform well in organic photovoltaic (OPV) devices.

As predicted the HOMO level of **P1** (Table 1) was raised significantly in comparison to the C and Si analogues which have HOMO levels of -5.4 eV and -5.5 eV respectively,^{6,7} despite the

low molecular weight of **P1**. Also, the band gap of **P1** (1.4 eV) is lower than that observed for the C (1.7 eV) and Si (1.9 eV) analogues.^{6,7} This confirms our hypothesis that the addition of the electron donating nitrogen group increases molecular orbital hybridization, raising the HOMO and reducing the band gap.

It is evident that the molecular orbital energy levels are also influenced by the acceptor co-monomer present. In order to further understand the electronic properties of the materials, their trimers were modelled using Gaussian at the B3LYP/6-31G* level. The side-chain substituents were replaced with methyl groups in order to simplify the calculations, with minimum effect on electronic properties. The HOMO and LUMO wave functions of the trimer model are shown in Fig. 3. **P1** and **P2** show a similar density of states distribution for both the HOMO and LUMO wave functions. The HOMO calculation showed a broad distribution along the backbone, but the LUMO is mainly located on the acceptor part of the molecule for **P1** and **P2**. The fluorine substituents on the co-monomer in **P2** should further withdraw electron density from the conjugated system in comparison to **P1**, and reduce both the HOMO and LUMO levels.⁴ However, this lowering of the HOMO may be partially counteracted by the planarizing effect caused by the short contact interactions between fluorine and the neighbouring sulphur atom, raising the HOMO and leading to a minimal overall effect on the energy level as seen from the experimental data (Table 1).²⁰ In fact the experimental data shows a 0.1 eV increase in the LUMO level of **P2**, but this is expected to be a result of standard experimental error associated with the measurement of the HOMO level and band gap from which the LUMO is calculated, and it is likely that the energy levels are very similar. **P3** and **P4** show the same HOMO distribution across the backbone as observed for **P1** and **P2**, but they differ significantly in terms of the LUMO wave functions. The experimental and calculated data (Table 1) show that the HOMO of **P3** is lower than **P1**. This could be due to the strong electron withdrawing effect of the imide unit. The LUMO of **P1** is localized on the BT unit, whereas the LUMO of **P3** is delocalized across the backbone. Fig. 3 shows that there is less contribution from the electron withdrawing imide group of the TPD unit into the LUMO, than the thiazole unit of BT. The TPD unit therefore has less of an electron withdrawing influence than BT, leading to a higher lying LUMO (Table 1). For **P4**, the LUMO shows a high density of states around the acceptor unit (Fig. 3), similar to that observed for **P1** and **P2**, leading to a larger stabilization of the LUMO level with respect to **P3**. This is due to the higher density of electron withdrawing groups in biTPD and a larger contribution from them to stabilize the LUMO compared to **P3**. The biTPD

Table 1 Properties of polymers **P1**, **P2**, **P3** and **P4**

Polymer	M_n (kDa) ^a	M_w (kDa) ^a	DP	$\lambda_{\max}$ (nm)		E_g (eV) ^d	HOMO (eV)		LUMO (eV)	
				soln. ^b	film ^c		Exp. ^e	Calc. ^g	Exp. ^f	Calc. ^g
P1	7	12	7–12	770	774, 830	1.4	–4.9	–4.4	–3.5	–3.0
P2	11	25	11–25	780	785	1.5	–4.9	–4.5	–3.4	–3.1
P3	12	28	11–26	635	634	1.7	–5.1	–4.6	–3.4	–2.8
P4	22	57	16–42	680	650, 695	1.6	–5.1	–4.8	–3.5	–3.0

^a Determined by GPC using polystyrene standards and chlorobenzene as the eluent. ^b Measured in chloroform solution. ^c Spin cast from 5 mg mL^{–1} chlorobenzene solution. ^d Estimated from the absorption onset of thin film UV-vis spectra. ^e Measured by ambient photoelectron spectroscopy (PESA). ^f Estimated by addition of E_g to the HOMO. ^g Calculated from the trimer model using Gaussian at the B3LYP/6-31G* level.

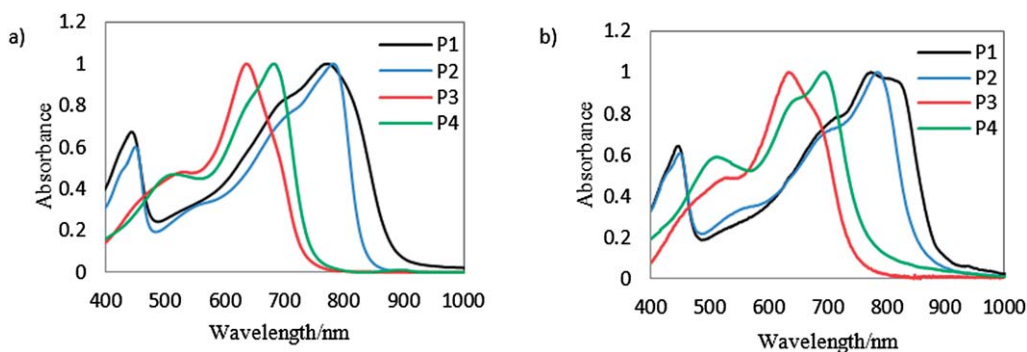


Fig. 2 a) Solution (in chloroform) UV-Vis spectra of polymers **P1**, **P2**, **P3** and **P4**. b) Thin film (from chlorobenzene) UV-Vis spectra of polymers **P1**, **P2**, **P3** and **P4**.

unit therefore has the effect of stabilizing the HOMO but at the same time reducing the band gap.¹⁸ This is optimal for solar cells as the reduced band gap will increase the solar light harvesting potential and the lower HOMO level will improve the V_{oc} . This effect can be observed from the calculated HOMO and LUMO values but the experimental data shows little effect on the HOMO (Table 1). This could be due to the molecular weight of **P4** being much larger than **P3**, which results in the HOMO being raised, reducing the difference between the HOMO energy levels of **P3** and **P4**,¹¹ or simply due to the experimental error associated with the energy level measurements. It must also be noted that comparison and analysis of the experimental energy levels for **P1**–**P3** is somewhat complicated due to the fact that at low molecular weights the band gap can be molecular weight dependent.¹¹

OFET properties

To measure the p-type charge carrier mobility bottom-gate, top-contact (BG-TC) architecture OFET devices were fabricated on

highly doped p-type Si substrates with SiO_2 as the dielectric and n-doped silicon as the common gate. The gold source and drain electrodes were deposited by thermal evaporation and the semiconducting polymer was spin-coated from a hot 1,2-dichlorobenzene solution at 1000 rpm, then annealed at 150 °C or 200 °C for 10 min. The annealing temperature had minimal effect on performance as all four polymers are amorphous. Differential Scanning Calorimetry (DSC) showed no transitions or decomposition between 25–300 °C (see Electronic Supplementary Information (ESI)).

The charge carrier mobility was calculated from the transfer characteristics of the device, in the saturation regime, using previously reported procedures.²¹ The results are summarized in Table 2. Fig. 4 displays a typical transfer curve and the output characteristics obtained from an OFET (channel length (L)/width (W) of 20/1000 μm) at a drain voltage (V_D) of -5 V and -60 V, using **P2** as the semiconducting layer. This material showed the best transfer and output characteristics with a maximum recorded hole mobility of $0.07 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and

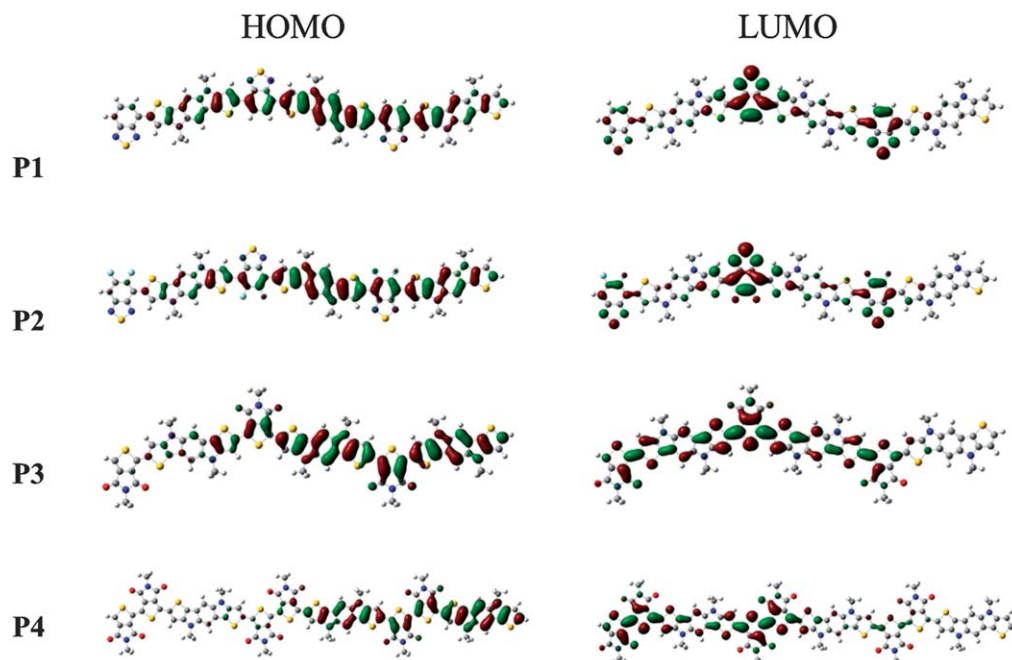
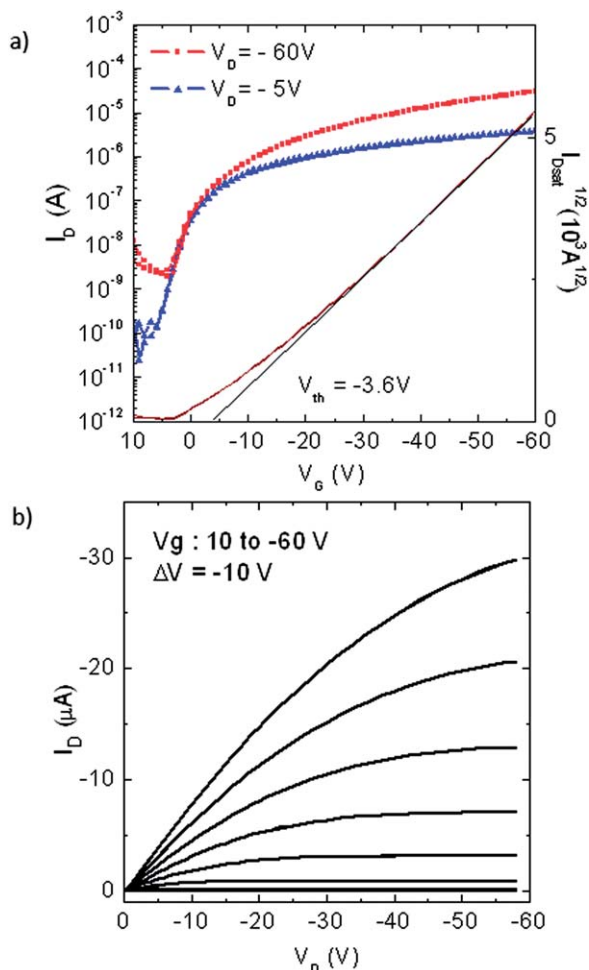


Fig. 3 The HOMO and LUMO wavefunctions of the trimer model of polymers **P1**, **P2**, **P3** and **P4**.

Table 2 Summary of OFET device results

Polymer	μ_{sat} mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$I_{\text{on/off}}$
P1	0.02	10^4
P2	0.07	10^4
P3	0.01	10^3
P4	0.001	10^3

**Fig. 4** a) Transfer curve and b) output characteristics of an OFET device (channel length (L)/width (W) of 20/1000 μm) at a drain voltage (V_D) of -5 V and -60 V , using **P2** as the semiconducting layer.

a current on/off ratio ($I_{\text{on/off}}$) of 10^4 . **P1** exhibited reasonable mobilities ($0.02\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) for a device with channel length 200 μm , annealed at $200\text{ }^\circ\text{C}$ and displayed an $I_{\text{on/off}}$ of 10^4 . The mobility of **P1** is slightly better than that obtained for the Si analogue ($8 \times 10^{-3}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$),⁶ but much less than that obtained for the C bridging version, which had a mobility of $\sim 1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.⁷ A reason for the lower mobility of **P1** compared to **P2** could be due to the improved interchain charge transport of **P2** caused by the planarization of the backbone by S-F short contact interactions, thus promoting shorter interchain π -stacking distances, or it could be as a result of the low molecular weight of **P1**. A higher molecular weight polymer should have a higher mobility.¹ **P3** gave a lower mobility than **P1** and **P2** ($0.01\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) with an on/off ratio of 10^3 . The lower mobility is

likely to be due to the weaker π -stacking interactions of the TPD units, which reduce molecular order. **P4** gave the lowest mobility ($0.001\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) which was expected as the biTPD unit possesses branched 2-ethylhexyl units which are bulky and suppress π -stacking. The reader is referred to the ESI for the transfer and output characteristics of **P1**, **P3** and **P4**. All four polymers exhibit hole mobilities which are state of the art for bottom gate architecture and within the desirable range for OPV applications.

Photovoltaic properties

Solar cells with device structure ITO/PEDOT:PSS/Polymer(**P1–P4**):PC₇₁BM/Ca/Al were fabricated; the J - V characteristics are illustrated in Fig. 5a and the properties are summarized in Table 3. The active layers were spin-coated from dichlorobenzene (DCB), with a blend ratio of Polymer (**P1–P4**):PC₇₁BM of 1 : 3 (w/w).

The morphology of the blended films (Polymer (**P1–P4**):PC₇₁BM (1: 3 w/w)) was also studied by tapping-mode atomic force microscopy (AFM). Fig. 6 shows the AFM images of the blended films, cast from the polymer solutions in *o*-dichlorobenzene.

The device with **P2**:PC₇₁BM blend demonstrated a higher V_{oc} value compared to **P1**:PC₇₁BM, but the overall performance of both materials remains similar. The AFM images of the blend of **P1** and **P2** with PC₇₁BM feature large domains. The greater phase segregation and rougher surfaces of the **P1** and **P2** blends presumably arose because of poor miscibility with PC₇₁BM.

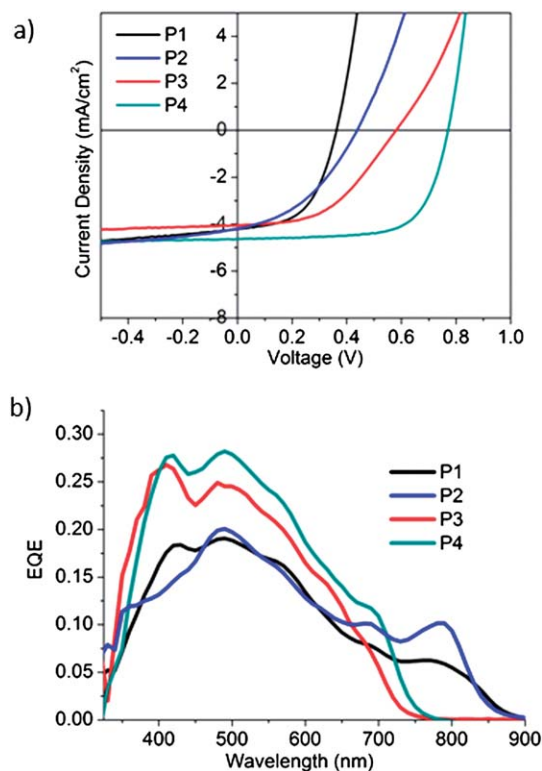
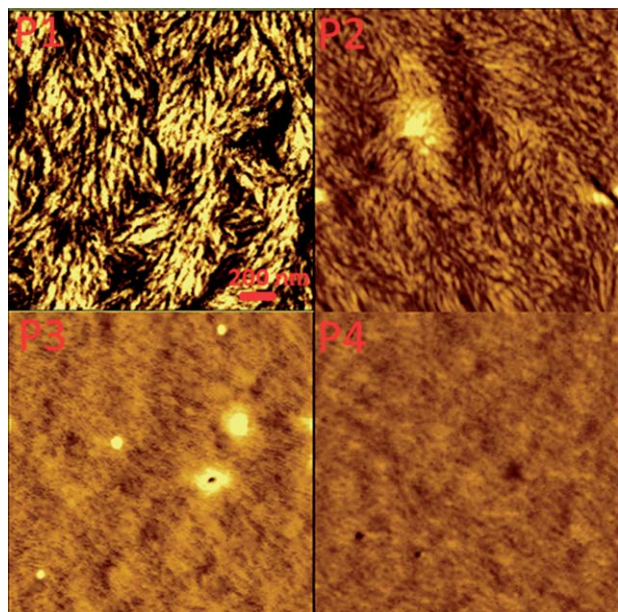
**Fig. 5** a) J - V characteristics of polymer (**P1–P4**):PC₇₁BM blends prepared at a blend ratio of 1 : 3 (w/w); b) EQE curves of polymer (**P1–P4**):PC₇₁BM blends, each prepared at a blend ratio of 1 : 3 (w/w).

Table 3 Photovoltaic properties of polymer solar cells incorporating **P1–P4**:PC₇₁BM blends

Polymer:PC ₇₁ BM (1 : 3)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
P1	4.20	0.36	53.6	0.8
P2	3.69	0.44	40.0	0.7
P3	4.04	0.58	47.8	1.1
P4	4.62	0.77	68.8	2.5

**Fig. 6** AFM topography images ($2 \times 2 \mu\text{m}$) of polymer (**P1–P4**):PC₇₁BM (1 : 3 w/w) blend films from *o*-DCB.

These large domain sizes hinder exciton dissociation and charge transport in these devices. **P3** and **P4** performed better than **P1** and **P2**, attributed to the larger V_{oc} originating from the lower HOMO energy levels of the polymers. The J_{sc} values of **P3** and **P4** based devices were almost similar. **P4** exhibited higher V_{oc} and FF value than that of **P3**, resulting in the improved power conversion efficiency of 2.5%. Although the experimental HOMO levels are the same for **P3** and **P4**, possibly due to experimental error, the calculated values are in agreement with the increase in V_{oc} observed for **P4**. It has also been shown, in the case of P3HT, that an increase in molecular weight can have a positive impact on J_{sc} , V_{oc} , FF and therefore PCE.^{11,13} These reasons can help explain why we observe this increase in V_{oc} . The performance of the polymers in the OPV devices can be molecular weight dependent. Thus, the better performance of **P4** can also be attributed to its high molecular weight compared to **P1–P3**. Also, the AFM images clearly reveal that the **P4** blend was more homogeneous and smoother than the other three polymers, with the lowest root mean square (RMS) roughness of 0.44 nm. This improved blend morphology can help explain why **P4** has a much improved PCE.^{8,22–24}

As expected, the replacement of acceptor units from BT (or ffBT) to TPD (or biTPD) led to higher V_{oc} in these devices, which significantly improved device performance.

Fig. 5b shows the external quantum efficiency (EQE) of the best device as a function of wavelength, which is consistent with the copolymers UV–Vis absorption spectra, indicating that all the absorption of the polymers contributed to the photovoltaic conversion. These devices exhibited significantly broad EQE responses extending from the visible to the NIR, with a maximum intensity ranging between 400 and 500 nm. We attribute the higher EQE responses in the visible region to the corresponding higher absorbance of the blend, resulting from both the intrinsic absorption of the polymer and the presence of a high content of PC₇₁BM, which also absorbs significantly at 400–500 nm. In contrast, these devices displayed relatively lower EQE responses at wavelengths above 650 nm because of the moderate absorbance of the polymer. The device of **P4** blend exhibited a higher EQE response than that of other polymer blends, with a maximum of 28% at 490 nm, corresponding to its higher photocurrent.

We speculate that the lower power conversion efficiencies of these polymers in bulk heterojunction devices are most likely due to the limited molecular weights and sub-optimal phase separation within the blends, as demonstrated by the large polymer/PC₇₁BM aggregates in the **P1** and **P2** blends.

Further experiments to improve the device performance of these polymers are under way. The use of additives or co-solvents also is known to impact the blend morphology which can result in better performance.^{3,17,22}

Conclusions

Four novel semiconducting polymers have been synthesized *via* Stille coupling polymerization, in high yields but with moderate-low molecular weights. All four polymers exhibited long wavelength absorptions, with corresponding low band gaps. They have been employed, as the hole conducting layer, in solution processed OFET devices. **P2** exhibited the highest hole mobility ($0.07 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). The photovoltaic properties of these polymers were investigated using the device configuration of ITO/PEDOT: PSS/Polymer(**P1–P4**):PC₇₁BM/Ca/Al. **P4** performed best, achieving a PCE of 2.5%, with the highest J_{sc} , V_{oc} and FF. The performances of **P1** and **P2** were limited by the high HOMO levels of the polymers leading to low V_{oc} . The efficiency of the devices were also affected by the blend morphologies, with the most homogeneous blend giving the best results (**P4**:PC₇₁BM). We have also shown that replacing the bridging atom of the IDT unit with nitrogen has a significant effect on the molecular orbitals, leading to a more planar, fully aromatic molecule.

Experimental section

OFET device fabrication

Bottom-gate, top-contact devices were fabricated on highly doped p-type Si with 400 nm SiO₂ dielectric layer. Si/SiO₂ was treated with OTS or HMDS depending on the wettability of each polymer. For source and drain electrodes, 60 nm Au electrodes were deposited by thermal evaporation. Polymer films were spin cast from hot 1,2-dichlorobenzene solution (5 mg mL^{-1}) at 1000 rpm and annealed at 150 °C or 200 °C for 10 min. All procedures/measurements were carried out in a dry nitrogen filled glove box.

OPV device fabrication

ITO-coated glass substrates were cleaned with acetone and isopropyl alcohol, followed by drying and oxygen plasma treatment. A 30 nm layer of PEDOT:PSS (AI4083) was spin-coated onto the plasma-treated ITO substrate and annealed at 150 °C for 30 min. An active layer consisting of 1 : 3 blend of polymer (10 mg mL⁻¹) and PC₇₁BM (30 mg mL⁻¹, Solenne) dissolved in *o*-dichlorobenzene (*o*-DCB) was spin-coated on the PEDOT:PSS layer and then Ca (30 nm)/Al (100 nm) cathode was finally deposited by thermal evaporation under high vacuum (10⁻⁶ mbar) through a shadow mask. The pixel size, defined by the spatial overlap of the ITO anode and Ca/Al cathode, was 0.045 cm². The device characteristics were obtained using a xenon lamp at AM1.5 solar illumination (Oriel Instruments). AFM was carried out using an Agilent 5500 Atomic Force Microscope and post-processing Pico Image software.

Synthesis

2-Octyl-1-dodecylamine,²⁵ 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene),⁶ 4,7-dibromobenzo-5,6-difluoro[*c*][1,2,5]-thiadiazole (ffBT),⁴ 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione (TPD)^{8,16,26,27} and 3,3'-dibromo-5,5'-di-2-ethylhexyl-1,4,4'*H* 1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(5*H*, 5'*H*)-tetrone (biTPD)¹⁸ were prepared according to literature procedures. Unless otherwise stated, all reactions were conducted under nitrogen, using a nitrogen filled dual manifold and standard Schlenk line techniques. All solvents and reagents were obtained from commercial sources and used as received, unless otherwise stated. Where required, toluene and THF were dried by distillation from Na-benzophenone. ¹H NMR spectra were measured on a Bruker Av-400 (400 MHz) instrument and ¹³C NMR were measured on a Bruker Av-400 (100 MHz). Chemical shifts are reported in ppm, relative to the residual protons in the deuterated solvents. All spectra were analysed using MestreNova software, from *MestreLab*. UV-Vis spectra were recorded on a UV-1601 Shimadzu UV-Vis spectrometer. Electrospray mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. Electron Ionization (EI) mass spectrometry was performed on a Micromass Autospec Premier instrument. Photoelectron spectroscopy in air (PESA) measurements were made using a Riken Keiki AC-II at CSIRO Materials Science and Engineering. Elemental Analyses were determined by Mr. Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7 8BD. GPC data was collected using an Agilent Technologies 1200 series instrument, with two mixed B columns, in series, and using chlorobenzene as the eluent, at a flow rate of 1 mL min⁻¹. The instrument was calibrated using narrow polydispersity polystyrene standards. Flash column chromatography was performed on Merck Kieselgel 60 (230–400 mesh) silica. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick Merck 5715 Kieselgel 60 F₂₅₄ silica gel plates and observed under 254 nm or 366 nm ultraviolet light.

Benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b*]thiophene) (NIDT)

A dry Schlenk tube was charged with 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) (1.10 g, 1.97 mmol),

Pd₂dba₃ (90 mg, 98.5 μmol), BINAP (245 mg, 0.39 mmol) and NaO^tBu (1.01 g, 10.48 mmol). Three consecutive vacuum/nitrogen cycles were carried out on the contents of the Schlenk tube, before adding 2-octyl-1-dodecylamine (1.29 g, 4.33 mmol) and dry toluene (40 mL). The reaction mixture was heated to 120 °C for 24 h. The reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 × 100 mL). The combined organic fractions were washed with brine (200 mL) and dried (MgSO₄). The volatiles were removed *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, 0–5% CH₂Cl₂/Hexane) yielded a mixture of monoring-closed and mono-aminated product as a colourless oil (915 mg).

This mixture (910 mg) was placed in a Schlenk tube, along with Pd₂dba₃ (45 mg, 0.05 mmol), BINAP (122 mg, 0.20 mmol) and NaO^tBu (586 mg, 6.1 mmol). Three consecutive vacuum/nitrogen cycles were carried out on the contents of the Schlenk tube, before adding 2-octyl-1-dodecylamine (361 mg, 1.22 mmol) and dry toluene (40 mL). The reaction mixture was heated to 120 °C and monitored using TLC. Once the reaction had reached completion (20 h) the reaction mixture was allowed to cool, then water (20 mL) was added and the product was extracted with ethyl acetate (3 × 100 mL). The combined organics were washed with brine (200 mL) and dried (MgSO₄). The volatiles were removed *in vacuo* to give a crude brown solid. Purification by column chromatography (silica gel, 0–5% CH₂Cl₂/hexane) yielded the title compound (638 mg, 40% overall yield) as a pale yellow solid; (found: C, 78.28; H, 10.78; N, 3.28. C₅₄H₈₈N₂S₂ requires: C, 78.20; H, 10.70; N, 3.38%); δ_H (400 MHz, CDCl₃) 7.59 (2H, s, Ar*H*), 7.34 (2H, d, ²J_{HH} = 5.2 Hz, Ar*H*), 7.05 (2H, d, ²J_{HH} = 5.2 Hz, Ar*H*), 4.16 (4H, d, ³J_{HH} = 7.2 Hz, –NCH₂–), 2.23–2.10 (2H, m, –NCH₂CH–), 1.44–1.18 (64 H, m, –CH₂–), 0.90–0.84 (12H, m, –CH₃); δ_C (100 MHz, CDCl₃); 146.7, 138.1, 125.7, 119.3, 114.9, 110.8, 98.3, 50.1, 38.2, 31.9, 31.9, 31.8, 30.0, 29.6, 29.6, 29.4, 29.3, 26.5, 22.7, 22.7, 14.2; *m/z* (EI) 828.6 [M⁺], 829.6, 830.6.

Benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b*]thiophene)

A dry Schlenk tube was charged with benzo[1,2-*b*:4,5-*b'*]bis(4-(2-octyl-1-dodecyl)-4*H*-amino[3,2-*b*]thiophene) (630 mg, 0.75 mmol) and dissolved in dry THF (10 mL). The solution was cooled to –40 °C with an acetonitrile/dry ice bath, then *n*BuLi (1.6 mL, 2.56 mmol, 1.6 M solution in hexanes) was added, dropwise, to the flask. Once the addition was complete, the solution was left to stir for a further 2 h at 0 °C. The reaction mixture was cooled back to –40 °C and trimethyltin chloride (3 mL, 3 mmol, 1 M solution in THF) was added in one portion. The reaction was allowed to warm to room temperature, overnight. The reaction was quenched with water (10 mL) and hexane (20 mL) was added. The organic layer was separated from the aqueous layer and washed with water (4 × 20 mL). The organic layer was then dried (MgSO₄) and the volatiles were removed *in vacuo*. The yellow oil was dried under high vacuum for 8 h, then placed in the freezer to give a yellow solid (950 mg, 97%). The product was used in the next step without further purification. δ_H (400 MHz, CDCl₃): 7.62 (2H, s, Ar*H*), 7.10 (2H, s, Ar*H*), 4.19 (4H, d, ³J_{HH} = 7.2 Hz, –NCH₂–), 2.15–2.10 (2H, m,

–NCH₂CH–), 1.51–1.24 (64 H, m, –CH₂–), 0.96–0.88 (12H, m, CH₃), 0.48 (18H, s, SnMe₃); δ_{C} (100 MHz, CDCl₃) 149.2, 139.2, 138.6, 121.0, 119.1, 117.7, 98.5, 49.9, 38.2, 31.9, 30.1, 29.7, 29.4, 26.4, 22.7, 14.2; m/z (EI) 1154.6 [M⁺].

Synthesis of P1

An oven-dried 5 mL microwave vial was charged with benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino [3,2-*b*]thiophene) (250 mg, 0.216 mmol), 4,7-dibromobenzo[*c*] [1,2,5]thiadiazole (64 mg, 0.216 mmol) and Pd(PPh₃)₄ (10 mg, 8.58 μ mol). The cap was placed on the vial and dry *o*-xylene (0.8 mL) was added. The reaction mixture was purged with argon for 20 min, before being placed in the microwave and subjected to the following conditions: 100 °C for 2 min, 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min and 180 °C for 40 min. Once the reaction had cooled, the viscous green liquid was precipitated in acidified methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate, at 50 °C for 1 h, then the organic layer was separated and washed with water, then dried (MgSO₄). The chloroform was concentrated and reprecipitated in methanol. The dark green precipitate (140 mg, 79%) was collected by filtration. GPC (chlorobenzene 80 °C): M_n 7000 g mol^{–1}, M_w 12 000 g mol^{–1}; δ_{H} (400 MHz, CDCl₃) 7.90 (4H, bs, ArH), 6.30 (2H, bs, ArH), 4.40–3.50 (4H, m, –NCH₂–), 2.40–0.30 (78H, m, CH₂ and CH₃); λ_{max} (film) 774, 830 nm.

Synthesis of P2

An oven dried 5 mL microwave vial was charged with benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino [3,2-*b*]thiophene) (200 mg, 0.173 mmol), 4,7-dibromobenzo-5,6-difluoro[*c*] [1,2,5]thiadiazole (55 mg, 0.168 mmol), Pd₂dba₃ (2.3 mg, 2.52 μ mol) and tri-*o*-tolylphosphine (3.1 mg, 0.01 mmol). The cap was placed on the vial and dry chlorobenzene (1.2 mL) was added. The reaction mixture was then purged with argon for 20 min before being placed in the microwave and subjected to the following conditions: 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, 180 °C for 2 min and 200 °C for 30 min. Once the reaction had cooled the viscous green liquid was precipitated in acidic methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate at 50 °C for 1 h then the organic layer was separated and washed with water, then dried (MgSO₄). The chloroform was concentrated and reprecipitated in methanol. The dark green precipitate (160 mg, 89%) was collected by filtration. GPC (chlorobenzene 80 °C): M_n 11 000 g mol^{–1}, M_w 25 000 g mol^{–1}; δ_{H} (400 MHz, CDCl₃) 8.25 (2H, bs, ArH), 6.70 (2H, bs, ArH), 4.50–3.60 (4H, m, –NCH₂–), 2.90–0.5 (78H, m, CH₂ and CH₃); λ_{max} (film) 785 nm.

Synthesis of P3

An oven dried 5 mL microwave vial was charged with benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino

[3,2-*b*]thiophene) (200 mg, 0.173 mmol), 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione (71 mg, 0.168 mmol), Pd₂dba₃ (2.3 mg, 2.52 μ mol) and tri-*o*-tolylphosphine (3.1 mg, 0.01 vial and dry chlorobenzene (1 mL) was added to the vial. The reaction mixture was then purged with argon for 20 min before being placed in the microwave and subjected to the following conditions: 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, 180 °C for 2 min and 200 °C for 30 min. Once the reaction had cooled, the viscous blue liquid was precipitated in acidic methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate, at 50 °C for 1 h, then the organic layer was separated and washed with water, then dried (MgSO₄). The chloroform was concentrated and reprecipitated in methanol. The dark blue precipitate (150 mg, 79%) was collected by filtration. GPC (chlorobenzene 80 °C): M_n 12 000 g mol^{–1}, M_w 28 000 g mol^{–1}; δ_{H} (400 MHz, CDCl₃) 8.18 (2H, bs, ArH), 6.26 (2H, bs, ArH), 4.65–3.20 (4H, m, –NCH₂–), 2.40–0.75 (95H, m, CH₂ and CH₃); λ_{max} (film) 634 nm.

Synthesis of P4

An oven dried 5 mL microwave vial was charged with benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4-(2-octyl-1-dodecyl)-4*H*-amino [3,2-*b*]thiophene) (210 mg, 0.182 mmol), 3,3'-dibromo-5,5'-di-2-ethylhexyl 1-4*H*,4'*H* 1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6' (5*H*, 5'*H*)-tetrone (125 mg, 0.182 mmol), Pd₂dba₃ (2.5 mg, 2.73 μ mol) and tri-*o*-tolylphosphine (3.3 mg, 0.01 mmol). The cap was placed on the vial and dry chlorobenzene (1 mL) was added to the vial. The reaction mixture was then purged with argon for 20 min before being placed in the microwave and subjected to the following conditions: 120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, 180 °C for 2 min and 200 °C for 30 min. Once the reaction had cooled the viscous blue liquid was precipitated in acidic methanol and filtered through a Soxhlet thimble. The precipitates were purified by Soxhlet extraction with acetone, methanol and chloroform. The chloroform fraction was stirred with aqueous sodium diethyldithiocarbamate tetrahydrate at 50 °C for 1 h then the organic layer was separated and washed with water, then dried (MgSO₄). The chloroform was concentrated and reprecipitated in methanol. The dark blue precipitate (190 mg, 77%) was collected by filtration. GPC (chlorobenzene 80 °C): M_n 22 000 g mol^{–1}, M_w 57 000 g mol^{–1}; δ_{H} (400 MHz, CDCl₃) 8.40 (2H, bs, ArH), 6.50 (2H, bs, ArH), 4.50–3.25 (8H, m, –NCH₂–), 2.40–0.50 (108H, m, CH₂ and CH₃); λ_{max} (film) 650, 695 nm.

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Appendix C

Design of Semiconducting Indacenodithiophene Polymers for High Performance Transistors and Solar Cells

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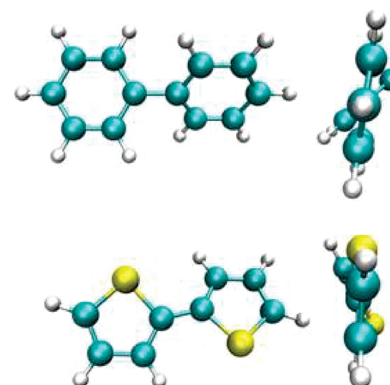
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CONSPECTUS

The prospect of using low cost, high throughput material deposition processes to fabricate organic circuitry and solar cells continues to drive research towards improving the performance of the semiconducting materials utilized in these devices. Conjugated aromatic polymers have emerged as a leading candidate semiconductor material class, due to their combination of their amenability to processing and reasonable electrical and optical performance. Challenges remain, however, to further improve the charge carrier mobility of the polymers for transistor applications and the power conversion efficiency for solar cells. This optimization requires a clear understanding of the relationship between molecular structure and both electronic properties and thin film morphology.

In this Account, we describe an optimization process for a series of semiconducting polymers based on an electron rich indacenodithiophene aromatic backbone skeleton. We demonstrate the effect of bridging atoms, alkyl chain functionalization, and co-repeating units on the morphology, molecular orbital energy levels, charge carrier mobility, and solar cell efficiencies. This conjugated unit is extremely versatile with a coplanar aromatic ring structure, and the electron density can be manipulated by the choice of bridging group between the rings. The functionality of the bridging group also plays an important role in the polymer solubility, and out of plane aliphatic chains present in both the carbon and silicon bridge promote solubility. This particular polymer conformation, however, typically suppresses long range organization and crystallinity, which had been shown to strongly influence charge transport. In many cases, polymers exhibited both high solubility and excellent charge transport properties, even where there was no observable evidence of polymer crystallinity. The optical bandgap of the polymers can be tuned by the combination of the donating power of the bridging unit and the electron withdrawing nature of co-repeat units, alternating along the polymer backbone. Using strong donors and acceptors, we could shift the absorption into the near infrared.



Introduction

The device performance of organic semiconducting polymers continues to improve.^{1–3} Central to these improvements has been the elucidation of fundamental relationships between molecular structure, morphology, molecular orbital energy levels, and their subsequent impact on electrical performance.^{4,5} Optimization of both solar cell and transistor devices requires judicious compromises and trade-offs

between such factors as solubility, crystallinity, and molecular orbital energy levels.

The design of the delocalized π conjugated aromatic backbone dictates the energy of the frontier molecular orbitals, which has significant impact on polymer optical absorption and charge transport. Control of these energy levels through molecular design is therefore a crucial aspect in the development of new semiconducting polymers, and

depends on several factors. A high electron density increases the energy level of the HOMO. This is a consequence of electron donation into the π orbital system, either inductively or by donation of unpaired electrons, that is, mesomeric donation. For example, silicon atoms, with low electronegativity, when directly bonded to the π electron system can donate inductively, whereas oxygen, nitrogen, and sulfur have unpaired electrons which can directly conjugate into π orbital systems when directly bonded, overcoming their higher electronegativity than carbon. When the lone pair of these heteroatoms is unable to conjugate into the π electron system, for example, as is the case of nitrogen in either a pyridine or thiazole ring, the electronegativity of the heteroatom dominates, and reduces the overall electron density in comparison to carbon. The electron density can be further reduced by the incorporation of electron withdrawing groups which, again, can either inductively or resonantly withdraw electrons. For example, the cyano group can resonantly accept electrons, stabilizing the LUMO, with the additional lowering of both the HOMO and LUMO energy levels through a contributing inductive effect. The silicon atom, when part of a silole unit, has also been shown to confer additional stability to the LUMO, arising from the in-phase mixing of σ^* and π^* orbitals from the silylene and conjugated moieties.⁶ Another factor in the energy levels of both the HOMO and the LUMO is the length and extent of the conjugated system. Simply increasing the number of delocalized electrons which contribute to the HOMO and LUMO, through adding additional conjugated units, will initially reduce the bandgap through both increasing the energy of the HOMO, while reducing the energy of the LUMO. This occurs when the polymer is of oligomeric length and up to the maximum size where the “effective conjugation length” of the polymer is reached. Beyond this length, the energy levels remain quite constant. In the case where the polymer has a relatively localized electronic orbital distribution, then the values of the energy levels are not so affected by increasing conjugation. The π orbital overlap between rings linked by a single bond is maximized when the rings are coplanar. This manifests as an increased conjugation, and hence reduced bandgap through a lowering of the LUMO energy and raising of the HOMO energy. The planarity can be optimized by ensuring that there is minimal steric overlap between substituents on the carbon adjacent to the linked carbon. This is illustrated in Figure 1 where steric effects from the two alpha hydrogen atoms promote a larger out of plane twist between the two coupled phenyl rings than between the two thiophenes. As a result,

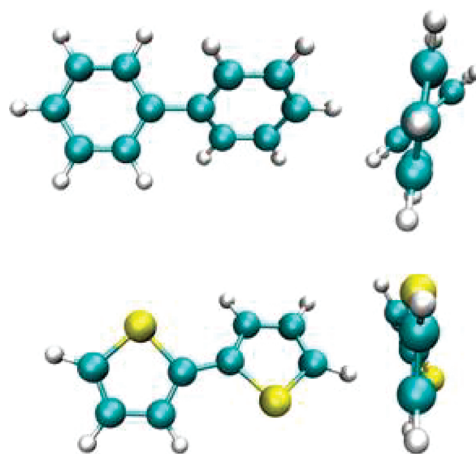


FIGURE 1. Overhead (left) and cross-section (right) view of both a phenyl–phenyl (top) and thiophene–thiophene (bottom) coupled dimer molecule.

not only is a corresponding blue shift in the absorption spectra typically observed, but intermolecular π stacking is also suppressed, leading to a more amorphous morphology. The bond character linking two adjacent conjugated units also plays a role in coplanarity. The more aromatically stable the ring, the more single bond character the linking bond takes, whereas more quinoidal units promote more double bond character, with the sp^2 nature of the bond favoring a coplanar conformation. The reduced coplanarity of the more aromatic units, in combination with additional aromatic stabilization, results in a blue shift. The most common method of designing a low bandgap is to facilitate molecular orbital hybridization between adjacent conjugated electron rich and electron poor units along the polymer backbone. In this case, the HOMO of the hybridized π orbital system assumes the character of the electron rich component, while the LUMO resembles the electron poor component, as shown in Figure 2. This donor–acceptor class of polymers have proven to be successful light absorbers in bulk heterojunction solar cells, leading to high efficiency devices.^{7,8}

The performance of a bulk heterojunction solar cell device is often expressed as its power conversion efficiency. This figure of merit is the product of the device short circuit current, open circuit voltage, and the fill factor. Both the voltage and current extracted from the device are strongly influenced by the molecular orbital energy level values of both the light absorbing donor polymer and the electron acceptor. The basic heterojunction energy diagram is shown in Figure 3. Previous work has established a correlation between the open circuit voltage of the cell, and the donor polymer HOMO energy level.⁹ As lower lying HOMO energies promote larger open circuit voltages, it is therefore

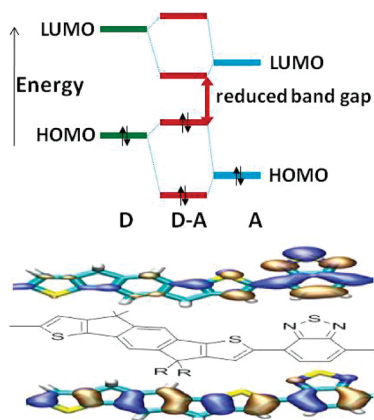


FIGURE 2. Molecular orbital hybridization of a conjugated donor–acceptor motif, illustrated below with the LUMO (above) and HOMO (below) distributions of a model indacenodithiophene-co-benzothiadiazole copolymer. Here the LUMO is strongly localized on the benzothiadiazole unit, whereas the HOMO, although predominantly on the thiophene units, is more delocalized.

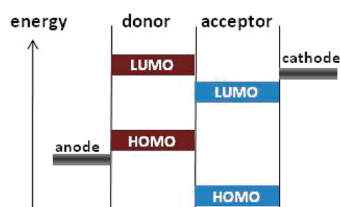


FIGURE 3. Bulk heterojunction energy diagram.

desirable to ensure that the donor polymer HOMO is of low energy. A compromising caveat to this statement is that independently lowering the HOMO level without correspondingly stabilizing the LUMO will result in an increase in the donor bandgap. In order to maximize the exciton formation within the device (and subsequently the charge generation), it is however necessary to overlap the spectral absorption of the donor to the solar spectrum as much as possible. This requires the donor polymer to have a small bandgap, and therefore, lowering the HOMO level is counterintuitive to this objective. It is therefore preferred to stabilize the LUMO energy level of the donor, rather than raise the HOMO energy level, in order to achieve a lower bandgap. However, there is a limit to the extent that the LUMO of the donor can be stabilized. Efficient electron transfer between the donor polymer and the acceptor requires that there is an exothermic energy offset between the two energy levels. The precise value of this energy offset appears to be sensitive to the class of polymer, but is typically 0.3 eV or more.¹⁰ Clearly, knowledge of the LUMO energy level of the acceptor is required for this optimization. The device fill factor provides a measure of the rectification

of the device, and is attributed to a variety of factors including active layer carrier mobility, charge recombination, and extraction. The morphology of the donor–acceptor layer blend is critical in this regard. Phase separation into domains of length scales corresponding to the exciton diffusion length are required to maximize transfer of the excited donor electron to the acceptor. It is also necessary that the phases optimize charge percolation to the electrodes as well as minimizing recombination. A molecular blend of donor and acceptor is clearly suboptimal; however, it is not yet clear whether some level of intermixing at the heterojunction interface is preferential. Polymer crystallization or acceptor aggregation can help to drive phase separation, and has been shown to be assisted by choice of solvent, additive, and fabrication temperature. Minimizing the solubility or partitioning of the fullerene within the polymer domains helps to ensure effective phase separation. Polymer–fullerene intercalation has been particularly observed with the donor polymer pBTTT¹¹ where the fullerene has the appropriate size to occupy the free volume between adjacent alkyl side chains along the polymer backbone, resulting in a bimolecular crystal. At fullerene concentrations which allow full intercalation, no electron transport can be observed, and device PCEs are low. Increasing the fullerene concentration beyond the saturation solubility promotes additional clusters of fullerene in addition to the bimolecular crystal, with a resultant improvement in electron transport¹¹ and device PCE. It is not advantageous to require high ratios of the fullerene, however, as they dilute the film absorbance, thus requiring thicker films which often have poorer currents and fill factors.

Optimal synthetic protocols and polymer purification procedures are required to ensure that the polymer has sufficient molecular weight¹² and appropriate end groups,^{13,14} and does not contain traces of catalytic or other impurities¹⁵ which can have a detrimental effect on the intrinsic performance of the polymer. In particular, removal of oligomeric species by either chromatographic or reprecipitation/extraction techniques often has a significant beneficial effect.¹⁶ As a rough rule of thumb, number average molecular weights of above 25 kDa/mol are optimal. Very high molecular weights, however, often result in solubility problems, with small gel particles forming, which can disrupt thin film coherence and quality. The high viscosity of such polymers can also impede thin film crystallization processes, leading to more amorphous film properties.

For a p-type transistor device, the energy level of the HOMO is critical for ensuring a good match with the work

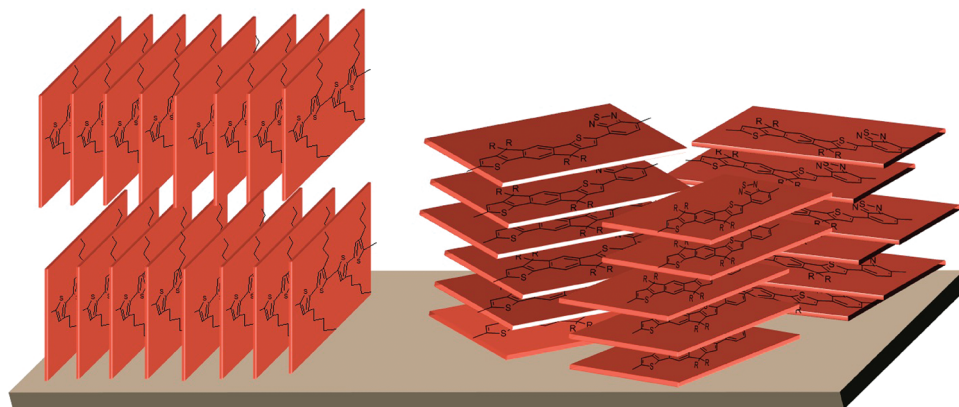


FIGURE 4. Schematic depiction of the preferred orientation of P3HT p-stacked lamella (left) with an out of plane polymer backbone orientation and (right) the in-plane orientation of a CIDT-BT copolymer domain; both have been experimentally observed by two dimensional high resolution grazing incidence X-ray diffraction.^{2,33}

function of the source and drain electrodes. Any large endothermic energy offset manifests as device contact resistance, which particularly impedes current through the channel at small source drain voltages. An additional consideration is that more trap site energy levels are accessible for holes when the HOMO is low lying, which often reduces the carrier mobility. The energy level of the HOMO also plays an important role in the ambient stability of the semiconductor. It has been shown¹⁷ that the electrochemical oxidative stability of a conjugated molecule to the combination of oxygen and moisture depends on the energy of electrons in the HOMO. When this energy is greater than -4.9 eV (i.e., closer to vacuum energy level) then the oxidation of π electrons is thermodynamically favorable in the presence of oxygen and saturated water environment. Therefore, it is important to ensure in the molecular design that the HOMO energy level does not exceed -4.9 eV. Polymers with HOMO energy levels higher than this threshold value will require either dry conditions or the additional exclusion of oxygen. Thin film morphology plays a critical role in charge transport. There are many reports from the literature that demonstrate the benefits of a close packed, crystalline microstructure, where the conjugated polymer backbones, particularly polythiophenes, have a coplanar conformation and can orient in π stacked lamella.¹⁸ Short intermolecular distances of less than 3.8 Å were also reported to facilitate optimal charge hopping, with a preferred orientation of the backbones orthogonal to the substrate, and thus also orthogonal to the direction of charge transport, as shown on the left side of Figure 4. More recently, high mobility polymers have been developed, where the degree of crystallinity appears to be much lower, and the orientation of the backbone does not require to be

orthogonal to the substrate^{1,19,20} and in fact the plane of the backbone lies in the plane of the substrate, as can be seen in the right side of Figure 4. These polymers, often containing electron withdrawing groups such as benzothiadiazole, imide, or diketopyrrolopyrrole units, have donor–acceptor character, with dipoles oriented normal to the backbone axis and it is believed that these dipole–dipole interactions may drive local aggregation, and orient adjacent backbones in an optimal configuration for charge hopping. Additionally, the possibility arises from this motif that a more three-dimensional transport can arise from the in-plane backbone orientation; that is, transport can now also occur out of plane in the π stacked direction. It is clear that good charge transport requires optimal alignment at the grain boundaries to increase the correlation length.^{21,22} Alignment of polymer backbones between grains significantly assists in intergrain transport.²³ Control, optimization, and even identification of this effect in polymer films are still currently a long way from being well understood.

Indacenodithiophene Copolymers

The indacenodithiophene (IDT) unit^{19,24,25} shown in Figure 5, possesses many desirable features for incorporation into semiconducting polymers. The three aromatic rings are in conjugation, and a bridging atom fixes coplanarity between the rings, thus maximizing π orbital overlap as well as reducing conformational energetic disorder. The bridging position also offers the opportunity to attach side groups, typically aliphatic hydrocarbon chains, which can aid solubility and impact polymer thin film morphology, depending on their length and shape. In bulk heterojunction thin film blends, the length and degree of branching of the chains

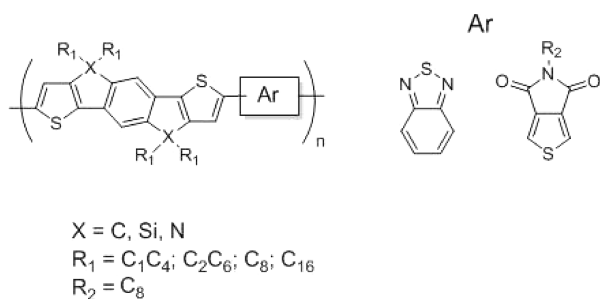


FIGURE 5. Molecular structure of indacenodithiophene conjugated copolymers.

also significantly influences the extent of partitioning of fullerene molecules within the polymer, which in turn influences charge recombination and solar cell device current. The choice of bridging atom influences the degree of aromaticity of the repeat unit, the planarity of the substituents projecting from the bridge, and through electron donation or inductive effects, can influence the electron density of the unit. These effects strongly influence the frontier molecular orbital energy levels and distribution. In this Account, we describe the properties of the carbon (CIDT), nitrogen (NIDT), and silicon (SiIDT) analogues, copolymerized with benzothiadiazole (BT) and thienopyrrolodione (TPD) comonomer. Of the three bridging atoms considered in this series, both the carbon and silicon project their two substituents out of the backbone plane, whereas the nitrogen projects its single substituent within the plane of the backbone. This significantly influences microstructure and solubility. Whereas both the carbon and silicon can to some extent inductively donate electrons into the π conjugated system, the lone electron pair of the nitrogen can donate, thus increasing electron density and rendering the unit fully aromatic (and subsequently fully planar), with 22 electrons in the π system. The full extent to which the lone pair increases the π orbital electron density is however in part mitigated by the aromatic stabilization. The ring arrangement of the indacenodithiophene, with a central phenyl ring coupled in both the 1 and 4 positions with thiophene, has several consequences. The conjugated system is preserved along the length of the unit, with an optimal balance in electron density achieved by the combination of the relatively electron poor phenyl ring, with more electron rich thiophene units. In the donor–acceptor polymer architecture, the HOMO energy level is mainly distributed over the indacenodithiophene unit; therefore, the electron density dictates this energy, with obvious consequences for optical absorption, stability, transport, and solar cell voltage. The peripheral thiophene rings are polymerized in the 2 and 2'

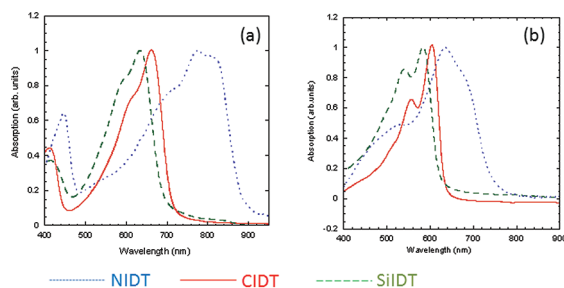
positions, with resultant minimal steric twisting effects, thus preserving a planar backbone conformation with most comonomer. Molecular modeling of the CIDT-BT copolymer suggests that the rotamer of lower energy is when the hydrogen of the CIDT is pointing toward the nitrogen of the BT. There is less steric strain and also the possibility of a degree of hydrogen bonding. The difference in energy is minimal, however, so both rotamers are likely to coexist. It was anticipated that the polymer morphology could be manipulated by the functionality of the bridging unit. For example, linear alkyl chains would be expected to facilitate optimal intermolecular packing, leading to improved order. This has yet to be fully established, and in fact even the linear alkyl chain analogues of the CIDT copolymer series do not exhibit a high degree of crystallinity. The NIDT unit, being fully aromatic, projects its alkyl chain in the plane of the aromatic unit, potentially allowing close π stacked intermolecular distances. In contrast, the sp_3 hybridized carbon and silicon atoms project their alkyl substituents out of the plane of the aromatic unit, thus potentially inhibiting π stacking.

Polymer Characterization

Synthesis of both the nitrogen (NIDT) and silicon (SiIDT) bridged indacenodithiophene copolymers was carried out using Stille coupling of the trimethyltin IDT monomers with the corresponding dibromide of the comonomers, as previously published. The carbon (CIDT) bridged indacenodithiophene polymer was typically synthesized by Suzuki coupling from the dibromide IDT monomer, coupled with the boronates of the comonomers. In part, this was necessary as the CIDT tin monomer was typically an oil, and lacked the necessary thermal stability. The C_1C_4 CIDT-TPD was however prepared by Stille coupling, as the trimethyl tin monomer in this case was a crystalline solid which could be readily purified. Both the SiIDT and CIDT units are highly soluble when C_2C_6 , C_8 , and C_{16} chains are attached, and impart this solubility into their respective copolymers. The C_1C_4 CIDT unit has typically poor solubility. Polymer molecular weight has a strong influence on solubility; for example, high molecular weight batches of the C_8 CIDT-BT polymer are only sparingly soluble. One consequence of a highly soluble polymer is that polymerizations can proceed to high molecular weight without precipitation. This was not the case for the CIDT-TPD copolymer, where the molecular weight appeared to be limited by the lack of solubility provided by the short branched C_1C_4 chain. The NIDT unit, with its planar structure and reduced alkyl chain density, suffers from a lower solubility, and so most

TABLE 1. Physical and Optical Properties of IDT Copolymers

repeat unit	alkyl chain	comonomer	M_n (kDa)	M_w (kDa)	$\lambda_{\max}$ (nm) soln	$\lambda_{\max}$ (nm) film	HOMO (eV)	LUMO (eV)
NIDT	C8C10	BT	7	10	770	774, 830	−4.90	−3.39
NIDT	C8C10	TPD	12	28	635	634	−5.05	−3.40
SiIDT	C8	BT	30	56	620	634	−5.45	−3.65
SiIDT	C8	TPD	17	35	578	589	−5.47	−3.49
CIDT	C1C4	BT	9	13	645	655	−5.30	−3.60
CIDT	C1C4	TPD	16	25	603	608	−5.49	−3.53



Thin Film UV spectra of (a) IDT-BT and (b) IDT-TPD copolymers

FIGURE 6. Thin film UV spectra of (a) IDT-BT and (b) IDT-TPD copolymers.

copolymers without a high degree of compensating solubility from the corepeat unit have lower molecular weight.

The copolymers listed in Table 1 comprise an indacenodithiophene unit coupled in an alternating A–B sequence with two electron poor comonomers, benzothiadiazole (BT) and a linear alkylated (octyl) thienopyrrolodione²⁶ (C₈TPD). Polymers with the NIDT unit have the highest energy HOMO, due to the greatest electron density, and subsequently have the lowest bandgap, as illustrated in Figure 6. The silicon bridged SiIDT polymers have the lowest energy HOMO levels. One explanation for this is that the larger Si–C bond length imparts a compensating increase in the bond length of the C–C bond linking the two phenyl groups in the SiIDT unit. Molecular modeling has shown that there is significant antibonding character between these carbons and so increasing the distance of this interaction will lower the antibonding energy and hence lower the HOMO. Modeling also reveals that the LUMO distribution of the BT polymers is localized on the BT unit, whereas the LUMO of the TPD polymers is more delocalized along the conjugated backbone. There is therefore less contribution to the LUMO from the electron withdrawing imide group of the TPD unit than the thiadiazole unit of BT. The TPD unit therefore has less of an electron withdrawing influence than BT on the conjugated system, which should lead to a higher lying LUMO. This is observed in the case of both the silicon and carbon bridged polymers; however, the low molecular weight of the NIDT-BT polymer is likely to be responsible for its unexpectedly high energy LUMO. The TPD unit was also observed to

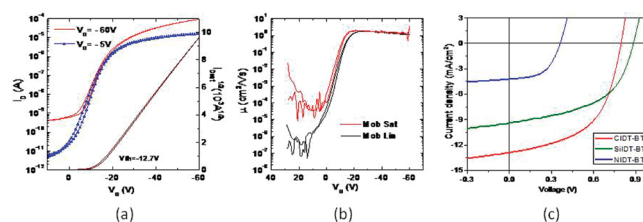


FIGURE 7. (a). Transfer characteristics of a top-gate, bottom-contact transistor device fabricated on glass with CIDT-BT semiconducting polymer, pentafluorobenzene thiol treated Au electrodes, CYTOP dielectric, and aluminum gate. The polymer film was spin-casted at 2000 rpm from hot chlorobenzene solution (5 mg/mL) and annealed at 150 °C for 10 min. $L = 50 \mu\text{m}$, $W = 1000 \mu\text{m}$, $\mu_{\text{lin}} = 1.77 \text{ cm}^2/(\text{V s})$, $\mu_{\text{sat}} = 2.0 \text{ cm}^2/(\text{V s})$. (b) Plot of extracted linear and saturation mobility of the same device as a function of gate voltage (c) I – V characteristics of IDT-BT: PC71BM solar cells under AM1.5 solar illumination. The device area for both the NIDT and SiIDT devices was 0.045 cm^2 , and the CIDT device area was 0.06 cm^2 . Device architecture is ITO/PEDOT (30 nm)/polymer:PC71BM (1:3.5) (80–90 nm)/Ca (30 nm)/Al (100 nm). Solvent was *o*-DCB. PCEs of polymers are CIDT-BT (5.49%), SiIDT-BT (4.3%), and NIDT-BT (0.81%).

lower the HOMO energy of the polymers, in comparison to the BT unit. This can be attributed to the strong contribution of the imide group on the HOMO of the TPD unit. Consequently, the bandgaps of the TPD polymers are comparatively larger than the BT copolymers. Although it has been demonstrated²⁷ that the alkyl side chains can play a significant role in the solid state energy levels of donor–acceptor semiconducting polymers, (presumably the differing packing behavior influences backbone planarity), we did not observe any significant effect in the IDT polymer series when the alkyl chains were varied.²⁸

IDT based polymers have been employed in both solar cell and transistor applications, with considerable success.^{19,25,28,29,30} Transistor devices with CIDT copolymers, and in particular with benzothiadiazole as a comonomer have shown extremely high hole mobilities in top gate device architectures, as shown in Figure 7a, where a saturation mobility value of $2 \text{ cm}^2/(\text{V s})$ was achieved. These high mobilities are also essentially field independent, as shown in Figure 7b. The thin film morphology, however, does not exhibit the high degree of order or optimal molecular orientation previously demonstrated to be a prerequisite for high carrier mobility in other thiophene based polymer thin films.³¹ In fact, an in-plane orientation of the

TABLE 2. Device Properties of IDT Copolymers

repeat unit	alky chain	comonomer	hole mobility ($\text{cm}^2/(\text{V s})$)	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF
NIDT	C8C10	BT	0.03	0.81	0.36	4.20	0.54
NIDT	C8C10	TPD	0.01	1.16	0.58	4.04	0.48
SiIDT	C8	BT	0.008	4.3	0.88	9.39	0.52
SiIDT	C8	TPD	0.03	2.59	1.00	6.31	0.41
CIDT	C1C4	BT	0.003	3.79	0.78	9.75	0.49
CIDT	C2C6	BT	0.57	5.5	0.79	11.45	0.49
CIDT	C8	BT	0.15	3.39	0.74	10.05	0.46
CIDT	C16	BT	1.2	0.66	0.75	2.02	0.44
CIDT	C1C4	TPD		3.59	0.92	8.41	0.46

polymer backbone appears to persist in the film, with an absence of higher order lamellar reflections in grazing incidence 2D XRD and no observable thermal transitions measured by differential scanning calorimetry indicating a lack of large scale crystallinity. Remarkably, the branched C_2C_6 chain polymer also exhibits high carrier mobility, despite an apparent lack of any order. The NIDT polymers did not exhibit high mobility with either the BT or TPD comonomers, perhaps limited by the low molecular weight of these polymers (Table 2). Mobilities of almost $0.1 \text{ cm}^2/(\text{V s})$ were achieved with a difluorobenzothiadiazole comonomer, reported elsewhere,³² where the molecular weight was a little higher, and the F–S short contacts may act to planarize the backbone, leading to shorter π – π intermolecular distances and enhanced transport. The silicon containing polymers also exhibited low carrier mobilities. This is attributed, in part, to the low lying HOMO energy levels, which may induce contact resistance at the electrode interface, unless very high work function electrodes, such as platinum, are employed. There did not appear to be a strong correlation between the comonomer and charge carrier mobility, although a more systematic study over a consistent molecular weight range and optimized conditions may yet yield more information. It is clear however that the very high mobility devices were only obtained with the BT unit.

Both of the indacenodithiophene polymer series described in this Account possess attractive features for their application in organic bulk heterojunction solar cells. The hybridized nature of the molecular orbital energy levels results in relatively low bandgaps, the charge carrier mobility of many of the polymers is very high, and the HOMO energy levels are sufficiently deep to ensure good cell voltages. On optimization of the device performance, it was found that the optimum weight ratio of fullerene/polymer blends was at least 3:1. We have speculated²⁸ that the relatively open conformation of the IDT unit allows significant fullerene partitioning within the backbone, and when the fullerene loading exceeds the solubility limit in the polymer, it then phase separates into aggregates,

generating the optimal bulk heterojunction morphology. There is considerable room for further optimization of the heterojunction morphology, as fill factors seldom exceed 0.5, even for the highest performing devices. Having such high fullerene weight requirements also necessitates the use of PC_{71}BM as electron acceptor, in order to increase the optical absorption of the blend film. The silicon containing polymers, with the lowest energy HOMOs, generate the largest open circuit voltages, whereas the NIDT polymers, with the highest energy HOMOs, have the smallest open circuit voltages. We also note that the BT-containing copolymers generally perform better in solar cells than the TPD-containing analogues (except for NIDT, where the performance of the BT polymer is most likely limited by the rather low molecular weight). The lower lying HOMOs of the TPD polymers ensure a higher V_{oc} , but more significantly the increased bandgaps as compared to the corresponding BT polymers give rise to a poorer overlap with the solar spectrum and consequently a reduced J_{sc} . A maximum power conversion efficiency of 5.5% was achieved with the ethylhexyl branched CIDT-BT copolymer.

Conclusions

A range of indacenodithiophene copolymers were synthesized with differing bridging atoms and comonomers, focused on optimizing the frontier molecular orbital energy levels, and thin film microstructure for light absorption, electron transfer, and charge transport. The microstructure of pristine thin films of all polymers studied had a lack of observable crystallinity; however, high performance transistors and solar cells were able to be fabricated.

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AC-2 measurements, and James Kirkpatrick for molecular modeling.

BIOGRAPHICAL INFORMATION

Iain McCulloch is Professor of Polymer Materials in the Department of Chemistry at Imperial College London, with research interests in organic semiconducting materials synthesis, characterization, and devices. He was previously the Organic Electronics Research Manager at Merck Chemicals. His achievements have been recognized with several awards including the Royal Society of Chemistry Creativity in Industry Prize.

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FOOTNOTES

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