Synthesis and Characterisation of Non-Fullerene Electron Acceptors for Organic Photovoltaics

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, Department of Chemistry, Imperial College London.

January 2016
To my beloved husband George
Declaration

The work contained in this thesis was carried out within the Department of Chemistry at Imperial College London, under the supervision of Professor Iain McCulloch, and it is my own work except where otherwise specified.

S. Holliday

January 2016
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Abstract
Recent years have witnessed remarkable advances in the field of organic photovoltaics (OPV). Efficiencies over 10% have now been demonstrated, partly due to the development of new low bandgap donor polymers. The majority of these OPV devices employ a fullerene derivative as the electron-accepting component in the active layer. While fullerenes are excellent acceptors in terms of electron mobility, electron affinity and ability to form suitable bulk heterojunction morphologies, they also have some limitations. These include limited absorption in the visible and near-IR region of the electromagnetic spectrum, poor tunability in terms of energy levels and absorption, and morphological instability. For these reasons, many researchers are seeking to develop alternative acceptors for OPV.

This thesis focuses on the design, synthesis and characterisation of small molecule, non-fullerene acceptors. Initially, C$_3$-symmetric truxenone derivatives were developed, which demonstrated broad absorption and the ability to carefully tune the frontier energy levels of the molecule. However, it appeared that the poor electron mobility, as well as an unfavourable morphology due to large scale crystallisation of the acceptor, limited device performance. The second part of this thesis explores linear small molecules with rhodanine end groups, which also demonstrated an excellent ability to tune the frontier energy levels through changes to the chemical structure. Compared with the truxenones, these acceptors were relatively amorphous and formed a more favourable, intermixed morphology with the donor poly(3-hexylthiophene) (P3HT). Device efficiencies of 4.1% were achieved with this blend, however performance was again limited by microstructure, which in this case was slightly too intermixed, leading to recombination losses. In addition, the lack of complementary absorption of the donor and acceptor reduced the amount of photocurrent that could be generated. The third section of this thesis describes how the molecular structure of this acceptor was modified to overcome both of these issues, by the replacement of an 9,9'-dioctylfluorene core unit with indacenodithiophene, leading to a more planar molecular structure. The increased crystallinity and red-shifted absorption of this acceptor resulted in an improved efficiency of 6.4%, which at the time of writing is the highest efficiency for non-fullerene devices with P3HT. In addition to high efficiency, these devices also had improved air stability compared to P3HT:fullerene devices as well as devices with high-performance donor polymers, demonstrating the real potential application for these materials in commercialisable OPV technology.
Contributions

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (Chapter 3) was synthesised by Mindaugas Kirkus. 2,7-Dibromo-4,9-dihydro-4,4,9,9-octyl-s-indaceno[1,2-b:5,6-b']-dithiophene (Chapter 4) was synthesised by Andrew Wadsworth and the final products EH-IDTBR and O-IDTBR were also synthesised in collaboration with Andrew Wadsworth.

The OFET devices discussed in Chapter 2 were made at BASF, Basel, and the BHJ OPV devices were made by Shahid Ashraf (results not shown). The OPV devices in Chapter 3 were optimised in collaboration with Shahid Ashraf. The OPV devices in Chapter 4 were made by Shahid Ashraf and Amber Yousaf.

The thin film absorption coefficient measurements presented in Chapter 4 were taken by Derya Baran. AFM and powder XRD were carried out by Christian Nielsen. GIXRD was carried out by Zhengrong Shang (Stanford University). SCLC (Chapter 3) was measured by Jason Röhr. Derya Baran and Nicola Gasparini carried out all photo-CELIV and CE measurements (Chapter 4) at the Friedrich-Alexander University Erlangen-Nuremberg. PLQE and TAS experiments were conducted by Ching-Hong Tan, with assistance from Elisa Collado-Fregoso (Chapter 3) and Stoichko Dimitrov (Chapter 4). X-ray crystallography (Chapter 4) was carried out by Andrew White in the Imperial College Chemical Crystallography lab.
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Next I must acknowledge everyone in the NFA team. First of all, Shahid Ashraf for teaching me to make devices and for not giving up on my first rhodanine acceptors, I am ever indebted. Thanks also to Amber Yousaf for working so hard on the project. Derya Baran, for bringing all her great skills and ideas to our group, we are lucky to have you. Thanks to Ching-Hong for the many late nights deconvoluting spectra, and thanks to James for all the insights and inspiration. It has been such a joy and an honour to work with you all.

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Finally, I am grateful to Bob, Christian, George and Jess for taking time to proof read sections of my thesis. Jess must also be thanked for her unfailing support and friendship and for being my shoulder to cry on in the lab. Thanks to my dear family for their reassurance and encouragement throughout my PhD. And thank you George, for being wonderful.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>BFI</td>
<td>tetraazabenzodifluoranthene diimide</td>
</tr>
<tr>
<td>BHJ</td>
<td>bulk heterojunction</td>
</tr>
<tr>
<td>BPO</td>
<td>benzoyl peroxide</td>
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<tr>
<td>BT</td>
<td>2,1,3-benzothiadiazole</td>
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<tr>
<td>CB</td>
<td>chlorobenzene</td>
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<tr>
<td>CE</td>
<td>charge extraction</td>
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<tr>
<td>CELIV</td>
<td>charge extraction by linearly increasing voltage</td>
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<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>D-A</td>
<td>donor-acceptor</td>
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<tr>
<td>DBU</td>
<td>1,8-diazabicyclo[5.4.0]undec-7-ene</td>
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<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
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<tr>
<td>DIO</td>
<td>1,8-diiodooctane</td>
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<td>DFT</td>
<td>density functional theory</td>
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<td>DME</td>
<td>dimethoxyethane</td>
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<td>DPP</td>
<td>diketopyrrolopyrrole</td>
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<tr>
<td>EA</td>
<td>electron affinity</td>
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<td>Eg</td>
<td>bandgap</td>
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<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
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<tr>
<td>eV</td>
<td>electron-volt</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>GIXRD</td>
<td>grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>ICBA</td>
<td>indene-C_{60}-bisadduct</td>
</tr>
<tr>
<td>IDT</td>
<td>indacenodithiophene</td>
</tr>
<tr>
<td>IP</td>
<td>ionisation potential</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>short circuit current</td>
</tr>
<tr>
<td>J_{mp}</td>
<td>current at point of maximum power</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
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NFA  non-fullerene acceptor
NMR  nuclear magnetic resonance spectroscopy
o-DCB  ortho-dichlorobenzene
OPV  organic photovoltaic(s)
P3HT  poly(3-hexylthiophene-2,5-diyl)
PC_{60}BM  phenyl-C_{61}-butyric acid methyl ester
PC_{70}BM  phenyl-C_{71}-butyric acid methyl ester
PCE  power conversion efficiency
PCE-10  poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2,6-diyl)] (a.k.a. PTB7-Th)
PCE-11  poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3''-di(2-octyldodecyl)-2,2'5',2'',5'',2'''-quaterthiophen-5,5'''-diyl)] (a.k.a. PffBT4T-2OD)
PDI  perylene diimide
PEDOT:PSS  poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
P_{in}  incident light power density
PLQ(E)  photoluminescence quenching (efficiency)
PTB7  poly({4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b;4,5-b']dithiophene-2,6-diyl}{3-fluoro-2][(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl})
PV  photovoltaic
SCLC  space charge limited current
T_{50}  time after which PCE falls to 50% of initial value
T_{80}  time after which PCE falls to 80% of initial value
TAS  transient absorption spectroscopy
TBAPF_{6}  tetrabutylammonium hexafluorophosphate
T_{c}  crystallisation temperature
TGA  thermogravimetric analysis
THF  tetrahydrofuran
T_{m}  melting temperature
V_{mp}  voltage at point of maximum power
V_{oc}  open circuit voltage
XRD  X-ray diffraction
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Chapter 1: Introduction
1.1 Why Solar?

It is widely reported that more solar energy strikes the earth in one single hour than the total energy that is consumed globally in one year (2001 data).\textsuperscript{1} This seductive fact has motivated over a century of research and investment into photovoltaic (PV) cells to try to turn this into useful electrical energy in the most efficient and cost-effective manner possible. With the growing international consensus on the need to reduce fossil fuel consumption in order to prevent catastrophic climate change, the interest in solar and other renewable energy sources has become greater than ever. The most common type of photovoltaic cells at present use inorganic semiconductors such as silicon, which can reach power conversion efficiencies (PCEs) of up to up to 13% for amorphous silicon or 26% for crystalline silicon.\textsuperscript{2} However, the brittle and heavy nature of these modules can result in high installation costs and limits the available applications for silicon PV at present. Furthermore, the high embedded energy involved in silicon purification and processing, as well as module manufacture, restricts the overall energy efficiency gain in producing energy from silicon PV. For these reasons, it is paramount to explore other materials systems in order to develop our ability to deploy a versatile range of PV technologies to address any application.

1.2 Organic Photovoltaics

1.2.1 Bulk Heterojunction OPV

One alternative to silicon semiconductors for PV is to use semiconductors made from organic (i.e. carbon-based) materials. Organic photovoltaics (OPV) have the potential to be much more mechanically flexible and lightweight compared to silicon, which broadens the potential for use in different applications and opportunities for product integration. In addition, the low material costs of organic semiconductors and their compatibility with solution processing and high throughput, roll-to-roll printing techniques means that devices have the potential to be produced much more cheaply and with significantly shorter energy payback times. Indeed, while the energy payback time of crystalline silicon PV is in the range of 1-2 years, the energy payback time of organic solar cells can be potentially as short as one day.\textsuperscript{3}
Typically thought of as insulators, organic materials become semiconductors when the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) becomes small enough that an electron can be excited across this gap, for example by the absorption of visible light. This can occur in a system of sp$^2$ hybridised carbon atoms, such as in a highly conjugated polymer or small molecule, whereby this energy gap decreases as the number of alternating double and single bonds is increased. Similar to the band model of inorganic semiconductors, the absorption of a photon can cause an electron to be excited from the HOMO (valence band) to the LUMO (conduction band), whereby charge transport can occur. However, the charges in organic semiconductors remain strongly bound as an electron-hole pair called an exciton, with an exciton binding energy on the order of a few tenths of an eV: much larger than inorganic semiconductors, which have an exciton binding energy of only a few meV. As such, the electron and hole may easily recombine before transport to the electrodes can occur. To overcome this, most organic photovoltaic (OPV) cells employ two semiconductors with offset HOMO and LUMO energies in order to encourage exciton dissociation at the heterojunction between these two materials, as demonstrated in the simplified energy level diagram in Figure 1.1. When an electron is photoexcited on the material with the higher-lying LUMO energy, termed the donor, it is transferred to the material with the lower-lying LUMO, termed the acceptor. Likewise, an electron that is photoexcited on the acceptor leaves behind a hole, which can be transferred to the donor if the HOMO of the donor is higher-lying. The minimum energetic offset $\Delta_{\text{LUMO}}$ required between the donor and acceptor is widely regarded to be around 0.3 eV, although this value depends on the materials in question and it has been found that offsets as small as 0.1 eV can be sufficient for some systems. Likewise, in the case where the acceptor is photoexcited, there must be sufficient offset $\Delta_{\text{HOMO}}$ between the HOMO energies of the materials. The maximum open circuit voltage ($V_{\text{oc}}$) that can be generated by the device is determined by the energy difference between the HOMO of the donor and the LUMO of the acceptor as demonstrated in Figure 1.1. In order to maximize the $V_{\text{oc}}$, therefore, it is preferable to design materials whereby the HOMO of the donor is as deep as possible, and the LUMO of the acceptor as shallow as possible, whilst still
maintaining a large enough $\Delta_{\text{LUMO}}$ (and $\Delta_{\text{HOMO}}$ in the case when the acceptor is photoexcited) to provide a driving force for photoinduced charge transfer.

![Energy level diagram of donor-acceptor interface in an organic solar cell](image)

**Figure 1.1:** Energy level diagram of donor-acceptor interface in an organic solar cell. The maximum $V_{\text{oc}}$ is principally determined by the difference in energy between the HOMO of the donor and LUMO of the acceptor.

In order for excitons to dissociate, they must reach a donor-acceptor interface. However, the diffusion length of excitons in most semiconducting polymers is in the range of 10 nm which means that excitons should be formed within that distance of an interface. This can be achieved by depositing very thin layers (<10 nm) of donor and acceptor on top of each other in a film (bilayer OPV) but this method severely limits light harvesting in the solar cell. One solution is to blend the donor and acceptor on the nanoscale to form a bulk heterojunction film (BHJ OPV), which gives a large number of donor-acceptor interfaces and a percolating pathway for charges to be collected at the electrodes, but without compromising on film thickness as in a bilayer device. This BHJ is usually prepared by co-deposition of the two materials from solution to give a thin film that phase separates into domains of donor and acceptor upon drying. The length scale of phase separation can be controlled by many processing factors such as solvent, temperature and deposition rate in order to achieve finely dispersed blend morphologies. However, if the materials are blended too intimately then
there will be insufficient percolating pathways of donor and acceptor for the charges to reach the electrodes and the rate of charge carrier recombination will be increased, either through geminate pairs that fail to fully dissociate, or non-geminate pairs that are generated from separate absorption events.\textsuperscript{10} Controlling the extent of this phase separation is therefore one of the most important aspects in optimising the performance of BHJ OPV devices, as will be discussed further later in this chapter.

\subsection*{1.2.2 Device Architecture and Characterisation}

Two main architectures are used for OPV devices, as shown in Figure 1.2. In the conventional architecture, the active layer is sandwiched between a transparent conducting anode, typically indium tin oxide (ITO), and a low work function metal cathode such as Ca/Al or LiF/Al. The presence of pinholes in the aluminium layer and the high reactivity of metals such as calcium is one of the principal means of degradation in these devices. In addition, the use of highly acidic PEDOT:PSS as a hole selective interlayer at the anode can lead to further degradation of the device.\textsuperscript{11} By contrast, the inverted architecture uses an electron transport/hole blocking layer of TiO\textsubscript{x} or ZnO in order to selectively collect electrons at the ITO contact, while a high work function metal such as Ag is used as the top electrode. This makes inverted devices inherently more stable to ambient conditions and arguably more scalable in terms of manufacture.\textsuperscript{12}

Figure 1.2: Schematic diagram showing typical conventional and inverted device architectures used in bulk heterojunction organic photovoltaics.
The performance of organic solar cells can be assessed by their current density \((J)\)-voltage \((V)\) characteristics. Figure 1.3 shows an example of a typical \(J-V\) curve with the parameters of short-circuit current \((J_{sc})\), open circuit voltage \((V_{oc})\) and the current and voltage at the point of maximum power, \(J_{mp}\) and \(V_{mp}\), respectively. The power conversion efficiency (PCE) is the product of the \(V_{oc}\), \(J_{sc}\) and fill factor (FF), divided by the incident light power density \(P_{in}\), which for measurement is standardised at 100 mW cm\(^{-2}\) with AM1.5 radiation. The fill factor (FF) is given by the product of the current density and voltage at maximum power divided by the product of the \(J_{sc}\) and \(V_{oc}\). The \(V_{oc}\), as described previously, depends principally on the offset between the HOMO of the donor and LUMO of the acceptor, although it can also be affected by several other factors such as the morphology of the active layer,\(^{13}\) trap-assisted recombination\(^{14}\) and interfacial effects at the electrodes.\(^{15}\) The \(J_{sc}\) also depends on many factors such as the breadth and efficiency of light absorption in the device, charge generation and recombination, charge carrier mobilities, and charge collection efficiency at the electrodes. The FF, meanwhile, is related to the electrical properties of shunt and series resistance in the devices, which are in turn dependent on the mobility, morphology of the active layer and interfacial effects.\(^{16}\)

![Figure 1.3: Profile of a typical \(J-V\) curve for OPV device highlighting \(V_{oc}, J_{sc}\) and the definitions of PCE and FF. \(J_{mp}\) and \(V_{mp}\) are the current density and voltage, respectively, at the point of maximum power.](image-url)
1.2.3 Donor Polymers for OPV

Most BHJ OPV devices employ a semiconducting polymer as the donor and a fullerene derivative as the acceptor. Much research has been focused on the development of the polymer component and as such this field has advanced considerably in recent years.\textsuperscript{5,17-19} In order to maximise the \( J_{sc} \), the polymer should have a broad and strong absorption in the visible and near-IR region where the solar irradiance is highest,\textsuperscript{17} which requires a narrow optical bandgap. This can be achieved in part by increasing the conjugation length of the polymer. Since the band structure of conjugated polymers arises from the interaction of \( \pi \)-orbitals along the chain, every \( \pi \)-conjugated unit added to the system will contribute to further hybridisation of the energy levels and reduction of the bandgap (until the ‘effective conjugation length’ is reached, at which point the addition of further \( \pi \)-conjugated units will have little effect on the bandgap).\textsuperscript{20} As well as the length of the polymer chain, the degree of conjugation is affected by the planarity of the backbone, which should be increased in order to maximise \( \pi \)-orbital overlap. This is in turn controlled through both aromaticity and steric effects between substituents. For example, the bond between two thiophene units has more double bond character relative to the bond between two phenyl units due to the lower aromatic and higher quinoidal character in the former. This sp\(^2\) bond character favours a more co-planar conformation for the thiophene-thiophene linkage, as demonstrated in Figure 1.4. In addition, the bonded thiophenes experience less steric torsion effects from the \( \alpha \)-protons on co-joining rings compared to the coupled phenyl groups, further increasing the planarity.

![Comparison of torsional angle between coupled (a) phenyl-phenyl and (b) thiophene-thiophene molecules. Adapted from McCulloch et al.\textsuperscript{21}](image)

Figure 1.4: Comparison of torsional angle between coupled (a) phenyl-phenyl and (b) thiophene-thiophene molecules. Adapted from McCulloch \textit{et al.}\textsuperscript{21}
As well as resulting in a smaller optical bandgap for the polymer, a co-planar backbone also benefits charge transport in terms of facilitating close intermolecular π-stacking of the chains. For this reason, polythiophenes such as poly(3-hexylthiophene) (P3HT) have been widely used in organic field effect transistors, with their strong intermolecular interactions (π-stacking) between neighbouring chains leading to a closely packed lamellar structure and hole mobilities of up to 0.1-0.3 cm²/Vs. P3HT has also been one of the most widely studied donor polymers for OPV applications for some time, giving modest device efficiencies of 3% on average for P3HT:PC₆₀BM blends and a maximum PCE of 7.4% which was reported with indene-C₆₀-bisadduct (ICBA) as the acceptor. However, the efficiency of P3HT based solar cells is still limited to some extent by the breadth of absorption. With a bandgap of 650 nm (1.9 eV), P3HT is able to harvest 22.4% of available photons from the sun, whereas if this bandgap were extended to 1000 nm then 53% of the available photons could be harvested, which would dramatically improve the J_{sc} that could be achieved.

In order to further reduce the bandgap of donor polymers, chemists now widely employ the technique of molecular orbital hybridisation via alternating electron rich and electron poor moieties along the backbone, to make what are known as donor-acceptor or ‘D-A’ polymers. When these conjugated donor (D) and acceptor (A) segments are combined, a new set of hybridised molecular orbitals is formed (D-A) which has a narrower effective bandgap than either of the components, as illustrated in Figure 1.5. The HOMO of the D-A polymer depends mainly on that of the donor moiety, while the LUMO assumes more of the character of the acceptor, allowing these energy levels to be judiciously tuned in order to optimise the light harvesting properties of the polymer. As such, D-A polymers have demonstrated very high efficiencies in BHJ devices, relative to homopolymers such as P3HT, with up to 10% PCE reported in single junction devices, proving that this technique has been a powerful tool in the progression of OPV.
1.2.4 Fullerene Acceptors

Alongside the donor polymer, BHJ devices require an electron acceptor component as described in 1.2.1. The material used for this has been almost universally some sort of soluble fullerene compound, ever since the introduction of the soluble C₆₀ derivative phenyl-C₆₁-butyric acid-methyl ester (PC₆₀BM) in the mid-1990s. Numerous other C₆₀ and larger (C₇₀, C₈₀) fullerene derivatives have subsequently been developed with slightly modified properties as described elsewhere. Figure 1.6 shows the structure of PC₆₀BM alongside two of the other most commonly used fullerenes phenyl-C₇₁-butyric acid-methyl ester (PC₇₀BM), widely employed for its increased light absorption properties, and indene-C₆₀ bisadduct (ICBA), which is favoured for its reduced electron affinity, and therefore ability to produce a higher $V_{oc}$, compared to PC₆₀BM.
There are several reasons why fullerenes make very effective acceptors and are therefore the materials of choice for testing newly developed donor polymers. One of these is their large electron affinity (low-lying LUMO), reported to be between 3.7 and 4.3 eV for PC$_{60}$BM,$^{30}$ which creates a strong driving force for photoinduced electron transfer from the polymer. Secondly, fullerenes demonstrate high electron mobilities (up to 0.1 cm$^2$/Vs for PC$_{60}$BM by field effect transistor measurements)$^{32}$ and nearly isotropic charge transport properties due to the delocalisation of the LUMO over the whole surface of the molecule. The ability of fullerenes to undergo multiple reversible reduction events is furthermore beneficial in terms of electrochemical stability, and it has been suggested that the presence of low-lying excited states near the LUMO promotes charge separation in polymer-fullerene blends.$^{33}$ Lastly, fullerene acceptors appear to be able to form an suitable BHJ morphology with most polymer donors through solution processing, with aggregation occurring on the appropriate length scale for charge generation and separation, and with a degree of miscibility that results in both mixed and pure domains, which may be beneficial in terms of charge separation.$^{34,35}$ Whatever the particular reasons for their success, it cannot be disputed that large advances in the performance of OPV have been made using fullerene acceptors, with power conversion efficiencies of up to 10% using D-A polymers in single junctions, as mentioned in 1.2.3, and over 11% in tandem devices.$^{36,37}$ However, fullerene acceptors have several shortcomings that limit OPV performance. Foremost, their high degree of molecular symmetry means that fullerenes have severely limited absorption in the visible and near-IR region of the solar spectrum, with a molar

![Figure 1.6: Typical fullerene based acceptors used in BHJ OPV.](Image)
absorption coefficient of only $4.9 \times 10^3$ mol$^{-1}$ cm$^{-1}$ (toluene solution) reported for PC$_{60}$BM at its maximum visible wavelength absorption (400 nm), and $<1.0 \times 10^3$ mol$^{-1}$ cm$^{-1}$ at 650 nm.$^{38}$ The less symmetrical PC$_{70}$BM has an increased absorption in this region of $1.9 \times 10^4$ mol$^{-1}$ cm$^{-1}$ at 400 nm and around $2 \times 10^3$ mol$^{-1}$ cm$^{-1}$ at 650 nm, however the absorption spectrum is essentially still poorly aligned with the incident solar spectrum. This is the reason that most BHJ solar cells rely on the donor polymer as the principal light absorber, with the role of the acceptor being mainly to accept electrons and transport charges, whereas in principle both components could be contributing to the current through absorption. In addition to this limited absorption, fullerene acceptors suffer from issues of morphological instability, with a tendency to diffuse through the blend over time to form large-scale aggregates, disrupting the original optimised BHJ morphology. There is also limited scope to tune the physical properties of fullerenes through chemical modification, as exemplified by the absence of fullerene derivatives with longer wavelength absorption. This is partly because of the types of reactions used to add substituents to C$_{60}$ (e.g. cycloaddition) do not form bonds that allow direct through-bond conjugation between the substituents and the fullerene cage, and the energy levels can therefore only be tuned through weaker inductive effects.$^{8,39}$ This also means that the $V_{oc}$ tends to be limited for fullerene-based solar cells, since it is not easy to raise the energy of the acceptor LUMO. This was partly improved with the introduction of the derivative indeno-C$_{60}$-bisadduct (ICBA), which has an electron affinity 0.17 eV higher than that of PC$_{60}$BM and therefore can produce higher open circuit voltages,$^{39,40}$ however the use of this acceptor is also limited by its high cost. Considering all these shortcomings, there is clearly a need to develop a broader pool of acceptor materials that have the potential to generate higher photocurrents and higher $V_{oc}$ values, ideally with a degree of synthetic flexibility to allow the energy levels and absorption to be matched with those of the donor.

1.3 Non-Fullerene Acceptors

1.3.1 Design Principles

In recent years, the field of research into alternative molecular, non-fullerene acceptor (NFA) materials has expanded rapidly, as exemplified by the large number of review articles that
have been published on this topic between 2014 and 2015.\textsuperscript{41-46} Indeed, prior to 2011 the efficiency of alternative acceptor OPV typically did not rise above 2\%\textsuperscript{47,48} whereas efficiencies of over 8\% have now been reported.\textsuperscript{49,50} While polymeric acceptors are also an area of intense development (polymer-polymer OPV),\textsuperscript{51} small molecules will be discussed here due to their relative ease of purification and well-defined molecular weight that avoids issues around batch-to-batch variation as experienced with polymers.\textsuperscript{52} Typically these small molecule NFAs are designed around an extended \(\pi\)-system of fused rings, to which electron deficient groups are attached in order to lower the LUMO of the molecule to make the material an electron acceptor relative to typical donor polymers. Various structural templates have been explored to this end and these can be broadly classed into fused ring diimides, molecules based on fullerene fragments and calamitic D-A molecules, which are discussed individually in the following sections.

1.3.2 Fused Ring Diimide Acceptors

One of the most widely researched and highly performing classes of NFA to date is based on the perylene diimide (PDI) structure shown in Figure 1.7 (a). With its large, delocalized \(\pi\)-surface and two electron withdrawing imide groups, this unit possesses a large electron affinity (up to 4.6 eV),\textsuperscript{53} excellent electron transport properties, strong visible wavelength absorption and tunable frontier energy levels.\textsuperscript{54} However, the highly planar structure of these molecules also leads to a strong tendency towards \(\pi\)-stacking, with the formation of micron-scale crystallites in some cases, which can be severely detrimental to exciton dissociation in the BHJ blend.\textsuperscript{55} Various attempts to overcome this problem by attaching bulky side-chains resulted in slightly improved microstructure formation and device efficiencies,\textsuperscript{54} however the major development in PDI acceptor design, as well as NFA design in general, was the introduction of twisted PDI dimers. Initially the PDI molecules were linked at the imide position to give the structure shown in Figure 1.7 (b).\textsuperscript{56} Electronic repulsion between the carbonyl groups on this molecule led to an almost perpendicular orientation of the two PDI planes with respect to each other, which significantly reduced the length scale of crystallisation. This resulted in dramatically higher short circuit currents of \textit{ca.} 8 mA cm\(^{-2}\) compared to less than 1 mA cm\(^{-2}\) for the planar PDI, and a subsequent increase in PCE from
Further tailoring of the alkyl chains on the dimer and of the donor polymer gave an improved efficiency of 5.4% PCE. The same principle has been applied to PDI dimerisation through the bay position, with either a single bond linkage as shown in the example in Figure 1.7 (c), a two-carbon bridge, or with a variety of linker groups such as thiophene and spirobifluorene as well as 3D core units such as triphenylamine and tetraphenylethylene, all resulting in highly non-planar structures and efficiencies of 4-7%.

Very recently, the bay-linked twisted PDI dimer illustrated in Figure 1.7 (c) (X = Se) was published giving a PCE of 8.4% with the donor polymer PDBT-T1, which is not far from the 9.7% reported for this polymer with PC70BM. Similar to the sulphur-bridged analogue (X = S) reported previously, the incorporation of the electron-rich selenium atom on the PDI core helps to decrease the electron affinity and increase the $V_{oc}$, while the loose electron cloud of the Se p-orbital was thought to facilitate orbital overlap and electron transport.

Related to PDIs, fused imide structures based on tetraazabenzodifluoranthene diimide (BFI), shown in Figure 1.7 (d), have demonstrated remarkable success as non-fullerene acceptors. This large ladder-type molecule crystallises in a slip-stacked motif with significant $\pi$-overlap between molecules which benefits charge transport, however, analogous to PDIs, the planarity of this molecule leads to strong self-aggregation and therefore large scale phase separation in the blend, limiting device efficiencies to 1.4%. Following from the success of the PDI dimers, the BFI molecules were joined via a bridging thiophene to give a highly twisted dimer ($33^\circ$ between planes), resulting in more favourable phase segregation and significantly higher PCE of 4.9%. It is also noted that the twisted BFI dimer gave higher electron mobility (space charge limited current measurements) in blends due to the more isotropic charge transport relative to the planar BFI, highlighting the importance of a non-planar structure in order to compete with the 3D charge transport properties of fullerenes. It was later shown that the thiophene spacer unit could be replaced with various other aryl groups including thienothiophene, 3,4-dimethylthiophene and selenophene in order to effectively modify the angle between the BFI planes, with the most twisted 3,4-dimethylthiophene bridged molecule ($62^\circ$ between planes) giving an improved PCE of 6.4%. Very recently this was replaced again with an 3,4-ethylenedioxythiophene (EDOT)
spacer, resulting in an even more twisted structure (76° between planes) and the current record non-fullerene device efficiency of 8.5%, which clearly demonstrates a strong correlation between the degree of non-planarity and device performance ($J_{sc}$ and PCE) for these acceptors.

![Chemical structures](image)

Figure 1.7: Chemical structures of (a) perylene diimide (PDI) with functionalisation positions indicated; (c) PDI dimer, where X is S or Se; (c) tetraazabenzodifluoranthene diimide (BFI); (d) BFI dimer, where Ar is thiophene, dimethylthiophene, thienothiophene, selenophene or EDOT.

1.3.3 Acceptors Based on Fullerene Fragments

Relative to the perylene and other fused ring diimides discussed above, small molecules based on fullerene fragments have been explored far less extensively in the field of NFAs. The rather obvious design strategy here is to take polycyclic aromatic hydrocarbon cores
such as corannulene,\textsuperscript{69,70} indenofluorene,\textsuperscript{71,72} emeraldicine\textsuperscript{73,74} and 9,9'-bifluorenylidene\textsuperscript{75-77} as a starting point, in order to try and replicate some of the favourable acceptor properties of fullerenes but with simpler structures that allow more scope for chemical modification. While this is an attractive design route in principle, results so far have not been particularly promising. For example, the C\textsubscript{5}-symmetric corannulene molecule, which is itself a fragment of C\textsubscript{60}, closely resembles C\textsubscript{60} in terms of both electron affinity and molecular curvature.\textsuperscript{78} However, the only application of such molecules in NFAs, with n-hexynaphthalimide and n-hexylphthalimide substituents to increase the electron affinity, resulted in a maximum PCE of only 1.0\%.\textsuperscript{69} Although a reasonably high \textit{V}_{oc} of 0.82 V was achieved with P3HT as the donor, the devices were limited by a low \textit{J}_{sc} and FF, which may again be related to sub-optimal microstructure formation, as a very coarse phase separation was indicated by AFM, indicating that these molecules may over-crystallise in the blend despite the curved geometry and bulky substituents. A similar problem is encountered for the bowl-shaped, C\textsubscript{3}-symmetric truxene molecules discussed further in Chapter 2, further supporting the growing evidence that large, planar surfaces can present a problem for NFA materials unless the strong π-stacking properties can be addressed.

1.3.4 Calamitic Small Molecules

The final class of NFA compounds that will be discussed is based on linear (calamitic) fused ring systems. Frequently these take the same approach as for low-bandgap D-A polymers described in 1.2.3, combining electron-rich and electron-poor segments to induce molecular orbital hybridisation and thereby extend the visible absorption as well as allowing for control over the HOMO and LUMO levels independently via the discrete separation of donor and acceptor units. This resemblance to D-A polymer design is an important advantage, as it means that the vast amount of literature and knowledge, as well as commercially available precursors, in this field can be exploited in the development of these acceptors. Figure 1.8 shows a typical calamitic acceptor design with three structural units. The central \textit{A} moiety is usually chosen to be a relatively electron-rich unit such as fluorene,\textsuperscript{79-81} dibenzosilole,\textsuperscript{82,83} indacenodithiophene,\textsuperscript{84,85} or indacenodithieno[3,2-b]thiophene.\textsuperscript{86} These structures all have positions that can be easily functionalised with solubilising alkyl groups, which allows the
crystallinity and solubility of the material to be controlled without sterically crowding the other electron-poor sections of the molecule. This has been previously suggested to be the preferred case for D-A polymers, wherein the photovoltaic performance of polymer-fullerene blends was shown to be better when the electron-poor monomer was more sterically accessible to facilitate “docking” with the fullerene.\footnote{87} It is not clear whether this theory would also translate to the case of non-fullerene acceptors, but it certainly appears intuitive that charge transfer to the acceptor may be improved if the part of the molecule where the LUMO is located is not crowded with bulky alkyl chains, in order to allow closer intermolecular interactions with the polymer.

![Figure 1.8: Schematic diagram of a typical calamitic acceptor.](image)

In this design, a second $B$ unit is covalently linked to the core, which is often bonded to a terminal $C$ moiety attached through a vinyl linker. Strong electron-withdrawing units tend to be favoured in these peripheral positions, for example diketopyrrolopyrrole (DPP), which has been used as the flanking group with a dithienyl-fluorene core in an small molecule NFA giving 3.2% PCE with P3HT as the donor polymer.\footnote{80} This particular NFA has also subsequently been used in roll-to-roll printed, flexible, ITO-free devices\footnote{88} and ternary blend devices,\footnote{89} demonstrating it to be a versatile acceptor material. It should be noted that in this case, relatively short (n-propyl) groups were used on the electron-rich fluorene core, with relatively bulky (2-ethylhexyl) side-chains on the DPP units, which is in contrast to the hypothesis outlined above. Naphthalimide is another electron-withdrawing group that has been incorporated successfully into the flanking position, in this case using a dicyanodistyrilbenzene core.\footnote{90} This acceptor demonstrated a strong self-assembling tendency, attributed to the cyano substituents, but this was balanced by the non-planar
molecular structure and a favourable morphology was achieved with a small molecule p-DTS(FBTTh$_2$)$_2$ as the donor, with a PCE of 5.4%. Another popular terminal acceptor group is indan-1,3-dione$^{79}$ or the even more electron deficient analogue 1,1-dicyanomethylene-3-indanone. This latter unit has been particularly successful in a series of NFA molecules with indacenodithiophene (IDT) based core units.$^{84-86}$ With their rigid, fused IDT core, the molecular backbone is highly planar for these molecules, which is favourable in terms of increasing the conjugation to reduce the bandgap, plus the push-pull structure afforded by the electron-rich core and electron-deficient flanking groups induces intramolecular charge transfer to further extend the absorption. In order to balance the rigid molecular planarity and prevent the acceptors from over-aggregating in the blend films, bulky 4-hexylphenyl substituents were added to the IDT core. This approach proved very successful, with 6.3% PCE reported for this IDT-based acceptor using the high performance PTB7-Th (PCE-10) donor polymer and a PDI derivative as a cathode interlayer.$^{85}$ Replacing the IDT core with the even more extended analogue indacenodithieno[3,2-b]thiophene, and using the same donor polymer and cathode interlayer, resulted in a further improvement in PCE to 6.8%,$^{86}$ which is the highest efficiency reported for calamitic-type non-fullerene acceptors.

1.4 Important Factors to Consider in NFA Design

1.4.1 Optoelectronic Properties

One of the most important considerations for the design of alternative acceptors is that the material should have an intense and broad absorption in the visible and near-IR part of the spectrum, in order to maximize the light absorbed by the solar cell. Given the very weak absorption of fullerene acceptors at longer wavelengths as discussed in 1.2.4, this is one aspect where NFAs can offer a significant advantage. The absorption coefficient of NFAs can be improved through use of strong dye-based chromophores and may also be improved through increasing the HOMO-LUMO overlap and therefore oscillator strength in the molecule.$^{91-93}$ The optical bandgap of the NFA can also tuned using the same methods outlined in 1.2.3 for donor polymers, via increasing the conjugation, initiating push-pull hybridisation of electron-rich and electron-poor units or by tuning the HOMO and LUMO through electron-withdrawing or electron-donating substituents. The ability to design new
acceptors that absorb light and participate in photocurrent generation is an exciting prospect for the future of OPV, where traditionally all of the photon harvesting has been done by the donor polymer, which must therefore be designed to capture as much of the spectrum as possible. By using a strongly absorbing acceptor, therefore, there is the possibility to harvest light over a broader range of wavelengths by tailoring the materials to have complementary absorption. In addition, it is possible to utilise wider bandgap donors if the NFA can be designed to be the low wavelength absorber.

Another key advantage of NFAs over fullerenes is the ability to tune the LUMO in order to maximise the $V_{oc}$, which is a prohibitive factor with fullerene acceptors due to their deep LUMO energies as outlined in 1.2.4. Indeed, $V_{oc}$ values of 1 V or higher are quite regularly reported for polymer:NFA blends. The amount of LUMO-LUMO offset required for photoinduced charge transfer is still not clearly established and varies from system to system, but the easy tunability of NFAs relative to fullerenes means that the energy levels can be optimised from the side of the acceptor, rather than only the polymer. Also, in a system where the acceptor can also be photoexcited, the HOMO-HOMO offset becomes equally important to optimise in order to facilitate photoinduced hole transfer to the polymer.

1.4.2 Electron Mobility

In contrast to inorganic semiconductors where charges move freely through the conduction band of the material, in organic semiconductors the charges are highly localised and transport occurs through a ‘hopping’ mechanism between the molecules or polymer chains. In order to facilitate this hopping transport between molecules, therefore, it is preferable to have a high degree of molecular order, with short intermolecular contacts between molecules. Designing planar molecules with large π-surfaces can promote self-organisation and interfacial overlap of the molecules to improve the charge carrier mobility, but a very strong tendency to crystallise can lead to large scale phase segregation which can severely reduce the $J_{sc}$, as described for the perylene diimides in 1.3.2. Therefore the strategy of designing non-planar structures, which can retain close intermolecular contacts but limit the length scale of crystallisation, appears to be advantageous. Such non-planar structures may
also increase the dimensionality of charge transport in the films,\textsuperscript{96,97} which can approach the very favourable isotropic electron transport properties of fullerene acceptors.

\subsection*{1.4.3 Microstructure}

In contrast to the “raspberry ripple” model of a BHJ that was once widely presented, with phase pure domains of polymer and fullerene and discrete interfaces between them, there now exists a more sophisticated understanding of the microstructure formed in polymer:fullerene blends. This includes, for example, the formation of both mixed and pure domains in the BHJ, with a significant degree of miscibility found for fullerenes in the amorphous phase of certain polymers.\textsuperscript{98-100} These findings have given rise to a new working model for BHJ blends that comprises at least 3 phases: typically a polymer-rich phase, a fullerene-rich phase, and a mixed disordered phase. The exact relationship between the purity of these domains and properties of charge generation, recombination and transport that affect device performance remains an important question to answer.\textsuperscript{101} It does, however, appear that the ‘energy cascade’ created by the offset in energy between ordered and disordered phases of both the polymer and fullerene, can be beneficial in terms of providing an energetic driving force for charge separation and to sweep charges out of the mixed domains.\textsuperscript{34,102,103} On this basis, it seems that the acceptor should be designed to have some degree of miscibility with the polymer, but still should self-aggregate enough to form some acceptor-rich, ordered domains. This can be controlled in part by the planarity of the NFA structure and the number of bulky or solubilising groups attached to disrupt the packing, as discussed previously.

However, the processing conditions used to deposit the active layer are equally important in determining the morphology. One of the most common methods used to prepare active layers for OPV is spin-coating, which is a relatively inexpensive, straightforward and versatile technique for preparing films reproducibly using a small amount of material.\textsuperscript{104,105} Film formation during spin-coating is a complex process with many factors contributing to the final microstructure, but it can be generally controlled through choice of spin-coating speed, acceleration, solvent system and the temperature of casting solution. The latter is especially important for materials with low solubility or which demonstrate temperature-
dependent pre-aggregation in solution.\textsuperscript{106} Meanwhile, casting from a high boiling point solvent can allow more time for the materials to self-organise during the slow-drying of the film, which can lead to greater phase separation or more crystalline domains being formed. High boiling point solvent additives such as 1,8-diiodooctane (DIO) can also significantly alter the film formation and some of the highest efficiency OPV devices use these solvent additives in the film deposition process,\textsuperscript{107} however, the presence of these high-boiling additives in the film can be a cause of degradation in the active layer.\textsuperscript{108} A similar effect can be achieved using a mixed solvent system such as CHCl$_3$ mixed with the higher boiling o-DCB.\textsuperscript{109} Finally, thermal annealing of the active layer can significantly change the crystallinity, phase separation and orientation of the materials with respect to the substrate.\textsuperscript{110,111}

1.4.4 Donor Choice

Newly developed donor polymers are typically tested (at least initially) with a fullerene acceptor, providing a point of comparison to assess different materials. When a new acceptor is developed, however, there is no such established ‘universal donor’ to evaluate the material with, which can make it difficult to compare the performance of these new materials. Ideally, various donor materials should be screened in order to find the most compatible pairing in terms of complementary absorption, energetic offset and active layer morphology. A few studies have highlighted the importance of optimising this donor-acceptor combination for new NFAs. For example, the blends of 2 different PDI dimers were investigated with 2 different polymer donors and it was shown that a $V_{oc}$ of 0.98 and PCE of 6.3% could be achieved with the best matched combination, while the efficiency was only 3.0% with the less compatible pairing.\textsuperscript{61} Elsewhere, another systematic study of 4 different materials combinations (a polymer and small molecule donor with a polymer and small molecule acceptor) demonstrated a 10-fold difference in PCE in comparing the least compatible materials combination with the best matched combination.\textsuperscript{112}

As well as considering the optoelectronic and morphological compatibility of the 2 materials, it is worth considering the relative merits of the donor polymers in question. It should be emphasised that many of the new NFAs reported in recent years have been tested in devices
with low bandgap polymers based on, for example, benzodithiophene (PTB7 or PTB7-Th (PCE-10)), thiazolothiazole-dithienosilole (PSEHTT) or difluorobenzothiadiazole (PCE-11). With their narrow optical bandgaps and good charge transport properties, these polymers have demonstrated very high efficiencies with fullerene acceptors. It is reasonable to expect, therefore, that their performance with alternative acceptors might also be better compared to, for example, wide bandgap homopolymers such as P3HT, and this should be taken into account when comparing the results of new NFA materials.

Not only should the photovoltaic performance of a donor polymer be considered, but also other aspects such as scalability, reproducibility and stability, if a successful materials combination is to be found. For example, while the PTB7 based polymers demonstrate very high efficiencies, they also present intrinsic difficulties in terms of synthetic scale-up as well as suffering from issues with solubility,\textsuperscript{113} device irreproducibility and photochemical instability,\textsuperscript{114,115} which means that their compatibility with technological scale-up should be questioned. On the other hand, P3HT has already been demonstrated to be easily scalable (being one of the only OPV polymers available in >10 kg quantities)\textsuperscript{26} and is compatible with high-throughput production techniques such as flow-synthesis.\textsuperscript{116} Furthermore, P3HT has already been widely employed in large-area, roll-to-roll printed solar cells\textsuperscript{117} and even in large OPV arrays or ‘solar parks’.\textsuperscript{118} Considering that some of the main advantages envisioned for OPV technology are the low materials and production costs and shorter energy payback times compared to inorganic PV, it would certainly appear that a polymer like P3HT would be a more favourable donor choice than some of the more recent, low bandgap donor polymers in this respect.

1.4.5 Stability

The last design consideration that will be discussed here is that of stability. In order to ensure the commercial development of OPV, it is essential to address issues such as the photochemical and morphological stability of the active layer components, as well as chemical degradation of the electrode and interlayer materials. However, this continues to be a significantly under-reported aspect of OPV research, especially in relation to new
In particular, there are very few stability tests carried out on solar cells of non-fullerene acceptor blends. One important issue with fullerene acceptors such as PC$_{60}$BM is their high diffusion mobility, which causes them to aggregate in the polymer:fullerene blend and form nanocrystalline domains that grow in size over time. This can destroy the active layer morphology that has been carefully optimised in terms of domain size and miscibility, thereby reducing the solar cell performance. In designing alternative acceptors, therefore, the aggregation properties and diffusion mobility is an important aspect to consider in terms of limiting this effect.

The device architecture is another important consideration for stability. As discussed in 1.2.2, inverted devices have been shown to be considerably more stable than conventional structures and therefore it is preferable to develop active layer materials that are compatible with this design, to avoid the inherent degradation caused by the Ca/Al electrode as well as the acidic PEDOT:PSS layer. Finally, the stability of the acceptor and the donor polymer towards ambient conditions as well as under illumination must be considered. Many donor polymers are susceptible to chemical and photochemical instability, and it has been shown in particular that PTB7 derivatives degrade quickly when exposed to light and ambient conditions. On the other hand, the relative stability of P3HT as a donor polymer is a significant advantage of this material in terms of technological deployment. Indeed, P3HT-based solar cells have demonstrated excellent stability to outdoor conditions, with no loss in performance after 1 year of outdoor exposure, and the robustness of P3HT based solar cells has been further demonstrated by their deployment in land, marine and airborne settings.
Chapter 2:

Truxenone Based Electron Acceptors
2.1 Introduction

As discussed in Chapter 1.3.3, one approach to designing fullerene replacements is to take small molecules based on fullerene fragments, with the aim of reproducing the large electron affinity properties and molecular curvature of fullerenes but using simpler and more easily functionalised structures. Various polycyclic aromatic and heteroaromatic hydrocarbon cores have been investigated to this end, including corannulene,\textsuperscript{69,70} indenofluorene,\textsuperscript{71,72} emeraldine\textsuperscript{73,74} and 9,9’-bifluorenylidene.\textsuperscript{75-77} Similarly, the C\textsubscript{3}-symmetric molecule 5H-tribenzo[a,f,k]trindene-5,10,15-trione (truxenone) presented in Figure 2.1 (a) can be considered as a keto-functionalised fullerene partial structure. While truxenone itself is highly planar, substitution at the ketone position for bulkier groups such as 1,3-dithiole,\textsuperscript{128} cyanoacetate\textsuperscript{129,130} or dicyanovinylene\textsuperscript{131,132} forces the molecule to adopt a bowl-like geometry resembling a fullerene partial surface. The ability to modify the electron withdrawing substituents on the core, as well as the possibility to add further substituents to the aryl periphery via carbon-carbon coupling reactions, makes truxenone an excellent starting point candidate for non-fullerene acceptor design. Our research group has previously shown that the electron-deficient truxenone derivative “2a” shown in Figure 2.1 (b), which has dicyanovinylene functionalities on the core and 5-hexylthienyl substituents on the periphery, could be implemented as an electron acceptor in bilayer organic photovoltaics with an evaporated donor (SubPc) and solution-processed acceptor with encouraging results.\textsuperscript{132} As well as being highly soluble in both halogenated and non-halogenated solvents and exhibiting good thermal stability, the material demonstrated strong absorption in the UV and visible region of the spectrum, complementary to the absorption of many low bandgap donor polymers. In addition, this truxenone derivative was a strong electron accepting properties, with an electron affinity even larger than that of PC\textsubscript{60}BM. Efficiencies of 1.0% PCE were achieved with subphthalocyanine (SubPc) as the donor layer, which was higher than the PC\textsubscript{60}BM reference device with 0.8% PCE.
Based on these promising bilayer OPV results, truxenone “2a” was employed in bulk heterojunction devices with P3HT as the donor. These results were much less encouraging, however, with a maximum PCE of 0.17% achieved from these blends. It was revealed by atomic force microscopy (AFM) that micron-scale crystallites of the acceptor were formed in the blend, and that this crystallisation was further exacerbated by thermal annealing (Figure 2.2), which may be responsible for the very large leakage currents demonstrated by these blends. Based on these observations, an opportunity was apparent to design truxenone derivatives that would have a reduced tendency to crystallise in the blend in order to improve the bulk heterojunction active layer microstructure, whilst retaining the favourable electron accepting and absorption properties of these materials.

Figure 2.1: Chemical structures of (a) unsubstituted truxenone core; (b) truxenone derivative “2a” published by Nielsen et al.\textsuperscript{132}

Figure 2.2: AFM (height) images of P3HT:truxenone “2a” (1:2) blend films (a) as-cast and (b) annealed at 130 °C for 10 min.
2.2 Phenyl- and Fluorene-flanked Truxenone Derivatives

2.2.1 New Truxenone Acceptor Design

Considering the strong tendency of the thienyl-flanked truxenones to self-aggregate in blends with P3HT, a new series of truxenone derivatives was designed with modified flanking groups to try to reduce the degree of crystallinity and improve mixing with the donor polymer, whilst retaining the strong UV-vis absorption and electron acceptor properties of the initial derivatives. 4-Hexylphenyl and 9,9'-dioctylfluorenyl were chosen as flanking groups, with the core unit bearing either ketone or dicyanovinylene functionalities, giving the four acceptor molecules PHTr, CN-PHTTr, FFTr and CN-FFTr as shown in Figure 2.3. Due to the reduced quinoidal character of the phenyl-phenyl bond relative to thienyl-phenyl bond as described in Chapter 1.2.3, the phenyl-flanked derivatives are expected to exhibit reduced planarity compared to truxenone “2a”. Indeed, calculations using Density Functional Theory (DFT) predict a torsional angle of 34° for the phenyl-phenyl bond in PHTr, compared to 26° for the thienyl-phenyl bond in truxenone “2a”\textsuperscript{132}. Introduction of the bulkier 9,9'-dioctylfluorene flanking group was designed to further disrupt the packing due to its greater steric bulk as well as the presence of long n-octyl chains which are oriented in the perpendicular plane to the fluorene aromatic system.

Figure 2.3: Chemical structure of new 4-hexylphenyl and 9,9'-dioctylfluorenyl flanked truxenones PHTr, CN-PHTTr, FFTr and CN-FFTr.
2.2.2 Truxenone Acceptor Synthesis

The synthesis of the new truxenone–based acceptors is outlined in Scheme 2.1. The starting material 4,9,14-tribromotruxenone was prepared via a simple 2-step synthesis involving bromination of 5-bromo-indan-1-one followed by thermal trimerisation (see Chapter 5.2). The very low solubility of this compound in most organic solvents meant that NMR could not evaluate the purity of this precursor, however Suzuki coupling of this compound with either the 4-hexylphenyl or 9,9'-dioctylfluorene boronic ester produced a highly soluble compound that could be purified by column chromatography to give the products PHTr and FFTr in 45% and 53% yield, respectively. The 9,9'-dioctylfluorene in this instance was
purchased commercially, while the 4-hexylphenyl boronic ester was synthesized via lithiation and borylation of 1-bromo-4-hexylbenzene as described in Chapter 5.2. Knoevenagel condensation of the purified Suzuki products PHTr and FFTr was then carried out with malononitrile, followed by further purification by column chromatography, to afford the dicyanovinylene derivatives CN-PHTr and CN-FFTr in moderate yields (15% and 42%, respectively). Even with a large excess of both the boronic ester and the malononitrile reagents, the inherent difficulty of forming 3 new carbon-carbon bonds on each molecule can be considered part of the reason for the rather low yields in each of the Suzuki and Knoevenagel steps.

2.2.3 DFT Modelling of Truxenone Acceptors

Figure 2.4 shows the molecular conformation of the truxenone acceptors calculated by DFT using Gaussian and the B3LYP/6-31G* level of theory. Even with the n-octyl groups on FFTr substituted for ethyl groups, the distorted planarity of the bulkier fluorene substituents can be easily compared with the phenyl substituents. It can also be seen how the planarity of the truxenone core is disrupted upon formation of the Knoevenagel adduct in order to accommodate the larger dicyanovinyl groups, resulting in a twisted, bowl-like geometry similar to that previously reported for the thienyl-flanked truxenones. DFT modelling was also used to calculate the spatial distribution of the frontier molecular orbitals, as visualised in Figure 2.5. It can be seen that the LUMO is localised in each case on the electron-deficient truxenone core, while the HOMO is located on the relatively electron rich aryl periphery. This property can be useful in terms of molecular design, as it means that HOMO and LUMO energies may be modified independently of each other and therefore the energy levels of the material can be tuned to match with different donor materials in terms of absorption and energetic offset. The frontier molecular orbitals for these truxenones are doubly degenerate due to the three-fold symmetry of the molecules, as exemplified in Figure 2.6 for PHTr by the equivalency of the HOMO/HOMO-1 and LUMO/LUMO+1 distributions. This degeneracy may also be beneficial in terms of charge transfer, as it has previously been suggested that the triply degenerate LUMOs of fullerenes are responsible for the high rates of charge transfer in polymer-fullerene blends.
Figure 2.4: Energy-minimised side-view conformations of PHTtr, CN-PHTtr (methyl in place of hexyl groups), FFTr and CN-FFTr (ethyl in place of octyl groups) as calculated by (DFT B3LYP/6-31G*).

Figure 2.5: Calculated energies and distribution of HOMO (bottom) and LUMO (top) for truxenone acceptors as calculated using DFT (B3LYP/6-31G*).
2.2.3 Optoelectronic Properties of Truxenone Acceptors

Measurement of the ionization potentials (IP) and electron affinities (EA) was carried out using cyclic voltammetry of the acceptors in dichloromethane solution, as detailed in the Chapter 5.6, and these results are summarized in Table 2.1. It is evident that substitution of the ketone groups on the core for the more strongly electron withdrawing dicyanovinyl groups has a significant effect on the EA, with an increase of around 0.5 eV in both cases. However, this substitution has minimal effect on the IP of the materials, with an increase of only 0.04-0.06 eV upon formation of the dicyanovinyl adduct. Changing the aryl flanking group, however, has a stronger effect on the IP. The more electron-rich fluorene substituent results in a smaller IP (5.89 eV and 5.95 eV for FFTr and CN-FFTr, respectively) compared to the phenyl substituent (6.09 eV and 6.13 for PHTr and CN-PHTr). The EA, meanwhile, is largely unaffected by changing the aryl flanking group: PHTr and FFTr have EA values of 3.53 eV and 3.52 eV, respectively, and likewise CN-PHTr and CN-FFTr have EA values of 4.04 eV and 4.05 eV, respectively.

These results can be understood in the context of the DFT calculations presented in Figure 2.5, where it was shown that the HOMO is localised on the aryl peripheral group while the
LUMO is localised on the electron-deficient core. Therefore, it would be expected that modification of the aryl peripheral groups would only affect the IP, and likewise that modification of the central ketone groups would affect only the EA of the material. This ability to modify the IP and EA of the molecules independently of the other, via modification of either the core or peripheral substituents, is a great advantage in terms of tuning the energy levels of the acceptor to match those of donor materials. As discussed in Chapter 1.2.4, this is a property that fullerene acceptors are considerably lacking in.

Table 2.1: Optoelectronic Properties of Truxenone Acceptors.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{max}} \text{ soln (nm)})</th>
<th>(\varepsilon \text{ (}10^4 \text{ M}^{-1} \text{ cm}^{-1}))</th>
<th>(\text{EA (eV)})</th>
<th>(\text{IP (eV)})</th>
<th>(E_{\text{g}}^{\text{elec}} \text{ (eV)})</th>
<th>(E_{\text{g}}^{\text{opt}} \text{ (eV)})</th>
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<tbody>
<tr>
<td>PC_{60}BM</td>
<td>328</td>
<td>0.39 (400 nm)</td>
<td>3.75</td>
<td>5.89</td>
<td>2.14</td>
<td>1.75</td>
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<tr>
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<td>6.09</td>
<td>2.56</td>
<td>2.73</td>
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<tr>
<td>CN-PHTr</td>
<td>282, 402</td>
<td>8.60 (402 nm)</td>
<td>4.04</td>
<td>6.13</td>
<td>2.09</td>
<td>2.29</td>
</tr>
<tr>
<td>FFTr</td>
<td>351</td>
<td>-</td>
<td>3.52</td>
<td>5.89</td>
<td>2.37</td>
<td>2.48</td>
</tr>
<tr>
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<td>-</td>
<td>4.05</td>
<td>5.95</td>
<td>1.90</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Measured by \(a\) UV-vis spectroscopy of acceptors \((10^{-5} \text{ M})\) in CH\(_2\)Cl\(_2\) solution; \(b\) cyclic voltammetry of acceptors \((3 \times 10^{-4} \text{ M})\) in CH\(_2\)Cl\(_2\) solution with TBA PF\(_6\) (0.3 M) electrolyte.

The UV-vis absorption spectra of the truxenone acceptors measured in dichloromethane solution \((10^{-5} \text{ mol l}^{-1})\) are shown in Fig. 2.7. The acceptors demonstrate strong absorption in the 300-600 nm region, which provides improved overlap with the incident solar spectrum compared to PC\(_{60}\)BM, for which the visible wavelength absorption is significantly lower. Molar extinction coefficients of \(1.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}\) and \(8.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\) were measured for PHTr and CN-PHTr, respectively, at their absorption maxima, compared to only \(3.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\) measured for PC\(_{60}\)BM at its maximum absorption wavelength in the visible region (400 nm). For both the phenyl- and fluorenyl-flanked derivatives, formation of the Knoevenagel adduct results in a significant reduction in optical bandgap (as estimated from solution data), which can be correlated with their larger electron affinities upon addition of the stronger dicyanovinyl electron withdrawing group. In comparing PHTr and FFTr, a broader absorption profile is observed for the fluorene analogue, with a pronounced shoulder.
occurring between 400 and 480 nm. Likewise, in comparing CN-PHTr and CN-FFTr, the absorption onset is significantly red-shifted, with the appearance of a broad shoulder between 480-600 nm. The smaller optical bandgap of the fluorene, compared to the phenyl analogues, again correlates with the smaller ionisation potentials measured for these materials (with equivalent electron affinities).

Figure 2.7: Normalised UV-vis absorption spectra for (a) PHTr and CN-PHTr and (b) FFTr and CN-FFTr acceptors in CH₂Cl₂ solution (10⁻⁵ M).

2.2.4 Bulk Heterojunction OPV Devices with Truxenone Acceptors

Bulk heterojunction solar cells were fabricated (by Shahid Ashraf) with the CN-PHTr and CN-FFTr acceptors using P3HT as the donor polymer in order to provide a comparison with the thienyl-flanked truxenone BHJ devices prepared previously. As shown in Figure 2.8, both acceptors have thin film UV-vis absorption maxima between 300-450 nm, which suitably complements the absorption of P3HT, making these materials well matched in terms of the potential to generate photocurrent broadly across the spectrum. In addition, with electron affinities that are even larger than that of PC₆₀BM, there should be more than sufficient energetic offset between the LUMO of these acceptor derivatives and the LUMO of P3HT in order to facilitate electron transfer upon donor photoexcitation, and likewise there is a large enough offset between the HOMO energies to facilitate hole transfer when the acceptor is photoexcited. BHJ OPV devices were fabricated in an inverted architecture (ITO/ZnO/P3HT:truxenone (1:1)/MoO₃/Ag) with active layers spin-coated from 20 mg ml⁻¹
chlorobenzene solutions and then annealed at 110 °C for 10 min. However, it was not possible to achieve effective photodiode behavior from these materials, with less than 0.05% PCE achieved from either blend.

Figure 2.8: (a) Normalised UV-vis absorption spectra for CN-PHTr and CN-FFTr acceptor thin films compared to P3HT, spin-coated from CHCl₃.

Atomic force microscopy (AFM) was carried out on the P3HT:truxenone (1:1) films in order to investigate the morphology of both blends, in particular, whether the incorporation of bulky flanking groups had effectively reduced the large-scale crystallisation of the acceptor within the blend as observed for the thienyl-flanked analogues presented in Chapter 2.1. Figure 2.8 shows AFM height images measured by Christian Nielsen for the as-cast and annealed (10 min at 100 °C) films. The as-cast blends in both cases have rather small feature sizes, with a slightly coarser topology for the CN-PHTr blend compared to the CN-FFTr blend, but with none of the micron-scale crystallites that were observed for the thienyl-flanked derivative (Figure 2.2 (a)). After annealing, CN-PHTr does appear to form elongated features 1-4 μm in length similar to those observed for the thienyl-flanked derivative, although with a slightly reduced aspect ratio in this case. The CN-FFTr blends, meanwhile, appear equally smooth and featureless before and after annealing. These results suggest that both new acceptor derivatives have been successful to some degree in terms of their reduced the tendency to crystallise and phase segregate within the blend, given that there is no large-scale crystallisation observed in the as-cast films as for the thienyl-flanked truxenone. With
the bulkier fluorenyl-flanked truxenone, such aggregation does not even occur with annealing. However, crystallisation of the phenyl-flanked truxenone does still occur (at least on the surface of the film) after annealing on a length-scale that is still clearly larger than typical exciton diffusion lengths. Since the P3HT:truxenone OPV devices in this case were measured after annealing, as is typically required for P3HT based solar cells to improve the microstructural order and hole mobility in the polymer,\textsuperscript{26,133-135} this could be one explanation for the negligible photodiode behavior. However, if this were the only factor then it might be expected that the P3HT:CN-FFTr blend would demonstrate improved photovoltaic performance, which was not the case.

![AFM height images](image)

**Figure 2.9:** AFM height images of (a) P3HT:CN-PHTr as-cast and (b) P3HT:CN-PHTr annealed (100 °C for 10 min) blends; (c) P3HT:CN-FFTr and (d) P3HT:CN-FFTr annealed (100 °C for 10 min) blends.

Field effect transistors were fabricated (by BASF) with 6CN-PHTr in order to ascertain whether charge transport was a limiting factor in the OPV device performance. Bottom gate bottom contact transistor devices were prepared by spin-coating the small molecule from CHCl\textsubscript{3} solution at 1000 rpm. Smooth, homogeneous films were formed but the n-type
mobility measured was only 1.2 x 10^{-6} \text{cm}^2/\text{Vs}. When the small molecule was blended with poly(\(\alpha\)-methylstyrene) in a 1:1 ratio, the n-type mobility increased slightly to 7.8 x 10^{-6} \text{cm}^2/\text{Vs}. No p-type mobility was observed in either case. Electron mobility is an important factor in determining solar cell performance for both fullerene and non-fullerene acceptors as discussed in Chapter 1.4.2. This could therefore help explain the poor device performance of these truxenone derivatives. One hypothesis for the low electron mobility could be that the localisation of the LUMO on the central part of the molecule, shielded by the bulky flanking groups and side-chains, prevents effective charge transport within the acceptor. Therefore, the transport properties could be improved by either reducing the steric bulk in general, or by perhaps redesigning the structure so that the LUMO is located on the outside of the molecule, with the HOMO on the inside.

### 2.3 Conclusions

A new series of four truxenone derivatives was synthesised for application in organic solar cells as fullerene replacement electron acceptors. The molecules were produced via a relatively short synthesis route, although reaction yields were low, which may be partly due to the C_3-symmetry of the molecule and the need to form three new bonds at each step. The materials all demonstrated strong absorption between 300-500 nm where fullerenes have relatively low absorption, making them well matched with a variety of donor polymers in terms of generating photocurrent more broadly across the incident solar spectrum. The electron affinities could be tailored to be either higher than that of PC_{60}BM (PHTr, FFTr) or significantly lower (CN-PHTr, CN-FFTr), depending on whether ketone or dicyanovinyl functionalities were used on the core. Meanwhile, the ionisation potentials measured were either equivalent to those of PC_{60}BM or lower, depending on whether phenyl or fluorene substituents were employed on the periphery. This demonstrates the powerful tunability of these molecular systems, in comparison to fullerenes, with the ability to modify the HOMO and LUMO energies independently of each other in order to control the bandgap, for example, or to properly match the frontier energy levels with that of a particular donor. BHJ solar cells were fabricated in the inverted architecture with CN-PHTr or CN-FFTr as the acceptor and P3HT as the donor polymer, however these did not produce working
photodiodes. In terms of morphology, these truxenone derivatives did appear to have a slightly reduced tendency to crystallise in the blend compared to the previous thienyl-flanked truxenones, as hypothesised. However, the phenyl-flanked derivative still crystallised upon thermal annealing into domains far exceeding typical exciton diffusion lengths. While this is evidently not favourable in terms of achieving an ideal nanoscale morphology in BHJ blends, it is unlikely that this is the only factor in the poor device performance, considering that the fluorene-flanked truxenone did not exhibit any improved performance despite the absence of such micron-scale acceptor crystallisation in this blend. Field effect transistor measurements of electron transport in CN-PHTr revealed very low mobility values of $10^{-6}$ cm$^2$/Vs, which could offer another explanation for the poor OPV device characteristics measured. The reason for this low mobility has not been established, but it could be related to the bulky, twisted molecular structure, which prevents effective close contacts. Alternatively, it could be related to the localisation of the LUMO on the interior of the molecule, where it is to some degree shielded by the peripheral substituents and efficient electron transport is therefore prevented.
Chapter 3:
A Simple Linear Acceptor with Dye-Based Flanking Groups
3.1 Introduction

When designing a material to replace fullerenes, one of the most important considerations is that the structure should be easily modified to facilitate materials optimisation and rapid advancement in this field, as well as allowing for the properties of the acceptor to be tuned with respect to a particular donor material or a preferred set of processing conditions. In addition, the synthesis should ideally be straightforward and scalable in the interest of technological scale-up.

As outlined in Chapter 1.3.4, linear or calamitic small molecules, consisting of extended π-conjugated frameworks with electron-deficient functionalities, are excellent candidates in this respect. Because the design of these linear molecules is so similar to that of donor-acceptor semiconducting polymer repeat units, it is possible to take advantage of the decades of literature and experience in this field to accelerate the development of new acceptors. In addition, the structural template outlined in Figure 1.8 is easily modified by the use of interchangeable building blocks with a convergent synthesis route, making this a versatile route in terms of tuning the material properties for optimisation with different donor materials.

The small molecules presented in this chapter are based on the $A/B/C$ motif proposed in Chapter 1.3.4. Here we employ 9,9-dialkylfluorene as the central unit ($A$), with either an electron poor benzothiadiazole or electron rich thiophene in the $B$ position. The effects of changing benzothiadiazole for thiophene on the molecular energy levels and planarity are presented in Chapter 3.3. Rhodanine dye derivatives are employed in the flanking $C$ position, and the electron accepting properties of this unit can be tailored with the introduction of dicyanovinyl groups (Chapter 3.3). The performance of these new acceptor materials in BHJ OPV devices is assessed with P3HT as the donor polymer. P3HT is chosen in this case as a benchmark polymer for testing, since it is one of the most established, thoroughly studied and widely available polymers in the field as well as being one of the best candidates for large scale, commercialisable OPV as discussed in Chapter 1.4.4, making it an excellent choice for non-fullerene acceptor devices.
3.2 Calamitic Acceptor with Rhodanine Flanking Groups

3.2.1 FBR Design

Figure 3.1 shows the structure of the calamitic acceptor that will be discussed in this chapter, named FBR for its inclusion of fluorene, benzothiadiazole and rhodanine units. Fluorene was chosen for the central $A$ position, being a unit that is relatively electron-rich as well as being easy to synthesise and therefore inexpensive and widely available, making it an excellent candidate for the design of a simple, scalable small molecule acceptor. Fluorene is easily functionalised at the 2,7-position (via bromination and subsequent borylation) to enable coupling reactions with other units. Furthermore, the acidity of the protons on the bridging (C9) carbon allows for straightforward alkylation at this position (using base and an alkyl halide) in order to tune the solubility of this unit.

![Figure 3.1: Chemical structure of small molecule acceptor FBR.](image)

Benzothiadiazole (BT) was chosen here for the $B$ position. As well as being a strong acceptor group used very successfully in donor-acceptor polymers,$^{17,136}$ BT is important here for control of the molecular conformation. In OPV polymers, phenyl-phenyl linkages are typically avoided due to the relatively large torsional angle of this bond in comparison to the more quinoidal, less sterically hindered and therefore more planar thienyl-thienyl or thienyl-phenyl linkages, as discussed in Chapter 1.2.3. However, here we exploit this large torsional angle between fluorene and BT in order to purposefully disrupt the planarity of the molecule. As discussed in Chapter 1.3, a common problem with small molecule non-fullerene acceptors designed hitherto (such as PDI and the truxenone derivatives presented in Chapter 2) is their strong tendency to crystallise into large domains that exceed the exciton diffusion length. To avoid this problem, FBR was designed with an inherently twisted structure in
order to control the degree of crystallisation and prevent the self-trapping of excitons that can lead to poor device performance in highly phase-separated blends. This approach is similar to the twisted PDI dimers discussed in Chapter 1.3.2, but here we utilise the intrinsic dihedral angle between phenyl groups and apply this to simple linear molecules.

Aldehyde functionalisation of the BT unit allows for facile Knoevenagel condensation reactions to be carried out with a variety of electron accepting moieties bearing acidic methylene carbons. In this case, 3-ethylrhodanine was chosen as the flanking (C) unit. Derivatives of the 5-membered heterocycle rhodanine are widely used as electron deficient units in dye chemistry for the creation of strong push-pull chromophores\textsuperscript{137-139} and recently there have been several reports of rhodanine end groups used for small molecule donor materials,\textsuperscript{140-142} however there are very few instances of rhodanine derivatives being integrated into acceptor materials.\textsuperscript{81} As well as giving additional electron withdrawing character to the outside of the molecule via its ketone and thio-ketone groups, rhodanine offers the capacity for further functionalisation via the addition of dicyanovinyl groups, as will be discussed in Chapter 3.3, as well as by variation of the alkyl group on the imide (studies not presented herein). For FBR, an ethyl group was chosen in this position in order to inhibit the strong hydrogen bonding usually associated with N-H rhodanine. In addition, it was anticipated that the incorporation of an ethyl group would ensure solubility of the material in common organic solvents, without adding excessive steric bulk to the electron accepting part of the molecule. By locating the main solubilising (n-octyl) groups on the electron rich core rather than the periphery, it was considered that the electron deficient part of the molecule could be made more sterically available for electron transfer. This theory is based partly on studies of polymer-fullerene systems showing that the electron-deficient moieties of the polymer should be sterically accessible in order to facilitate registry or “docking” with the fullerene.\textsuperscript{87} Similarly, it was conjectured that charge transfer from the polymer to the small molecule acceptor could be improved by minimising the alkyl chain density on the most electron-poor parts of the molecule.
3.2.2 FBR Synthesis

In order to attach aldehyde groups to the benzothiadiazole unit to allow for facile condensation reaction with the terminal rhodanine units, the 7-bromo-2,1,3-benzothiadiazole-4-carboxaldehyde unit 3.5 was prepared. Due to the synthetic difficulties in brominating the benzothiadiazole unit asymmetrically, a route was instead developed using 2,3-diaminotoluene as the starting material as outlined in Scheme 3.1. Initially, condensation of 2,3-diaminotoluene with thionyl chloride was used to obtain the 4-methyl-2,1,3-benzothiadiazole 3.2, but this method involved purification by lengthy steam distillation and yields of only 57%. Instead, the use of N-thionylaniline gave 3.2 in 81% yield with more straightforward purification by column chromatography. Subsequent bromination using 1 equivalent of bromine in aqueous HBr gave 3.3 in 59% yield without any further purification. This was then subjected to free-radical bromination on the methyl group using N-bromosuccinimide and benzoyl peroxide as the initiator, giving 3.4 in 57% yield after purification by column chromatography and recrystallisation. Subsequent conversion to the aldehyde using refluxing formic acid gave 3.5 in 95% yield. It should be noted that this product was prepared relatively easily on a 6 g scale and it could be expected that further scale-up would be equally straightforward.

Scheme 3.1: Synthesis of 7-bromo-2,1,3-benzothiadiazole-4-carboxaldehyde.

The boronic ester of 9,9-dioctylfluorene 3.6 was prepared by M. Kirkus using previously published methods.143,144 This was reacted with 3.5 via palladium-catalysed Suzuki coupling to afford the intermediate 3.7 in 60-90% yields after purification by column chromatography. Finally, Knoevenagel condensation of 3.7 with 3-ethylrhodanine in the presence of piperidine yielded the final product FBR (78% yield) which could be easily purified by column chromatography and precipitation into methanol. The product is stable.
up to 300 °C as shown by thermogravimetric analysis (see Appendix) and highly soluble in common organic solvents such as chloroform and toluene. Given the small number of synthetic steps (including those involved in the synthesis of the precursors 3.5 and 3.6) and relatively high yields, it may be considered that larger scale production of FBR should be easily possible. This demonstrates an important advantage over fullerene based acceptors, which are well-known for their difficult synthesis and purification routes.\(^{145}\)

![Scheme 3.2: Synthesis of small molecule acceptor FBR.](image)

### 3.2.3 DFT Modelling of FBR

Density functional theory (DFT) at the B3LYP/6-31G* level of theory was used to calculate the energy-minimised structure of FBR in the gas phase, shown in Figure 3.2. A relatively large dihedral angle of 35° was calculated between the fluorene and benzothiadiazole groups, leading to a non-planar 3-dimensional structure overall which is favoured for preventing excessive crystallisation as discussed in 3.2.1. In addition, it may be expected that this twisted molecular structure could give potential for charge transport in more than one direction, making it more similar to the relatively isotropic transport of fullerenes.

From visualisation of the frontier molecular orbitals (Figure 3.2 (b), (c)) it can be seen that the HOMO is delocalised over the whole molecule, whereas the LUMO is more localised onto the electron-poor periphery. This large, electron-accepting area on the outer, sterically exposed portion of the molecule is anticipated to benefit electron transfer to the acceptor, as discussed in 3.2.1.
3.2.4 Physical Properties of FBR

UV-vis absorption spectroscopy of FBR reveals a maximum absorption ($\lambda_{\text{max}}$) at 489 nm in solution and 509 nm in the thin film as shown in Figure 3.3. This offers a significant advantage over PC$_{60}$BM (thin film $\lambda_{\text{max}}$ ca. 300 nm) as it absorbs in a region of the electromagnetic spectrum with much higher solar flux$^{146}$ and therefore has potential to make a bigger contribution to the photocurrent via absorption. The extinction coefficient of FBR, measured at its $\lambda_{\text{max}}$ in chloroform solution, is also an order of magnitude larger than that of PC$_{60}$BM at its maximum absorption wavelength in the visible region, as shown in Table 3.1. As discussed previously, the visible wavelength absorption of PC$_{60}$BM is severely limited due to the high degree of symmetry which makes many of the low-energy transitions forbidden, so the increased absorption coefficient of FBR further demonstrates the potential of this small molecule to contribute to photocurrent through absorption.
Figure 3.3: (a) Normalised UV-vis absorption spectra of FBR in CHCl₃ solution (10⁻⁵ M) alongside thin film absorption of FBR and PC₆₀BM spin-cast from CHCl₃ (5 mg ml⁻¹); (b) First reduction cycles by CV of FBR and PC₆₀BM (3 x 10⁻⁴ M) in CH₂Cl₂ solution with 0.3 M TBAPF₆ electrolyte.

The electrochemical behavior of FBR was studied by cyclic voltammetry (CV) alongside that of PC₆₀BM for comparison. Figure 3.3 (b) shows the first reduction cycles of the acceptors which were initially measured in solution to allow the electrochemical reversibility to be evaluated. Within the reduction limits of the solvent, FBR demonstrates two reversible reductions, while three reversible reductions are observed for PC₆₀BM as has frequently been reported elsewhere. The reversibility demonstrates that the reduced species are electrochemically stable, which is an important consideration for the operational stability of devices. Meanwhile, the presence of multiple reduction events indicates that there are several low-lying excited states in the acceptor, a property that has previously been observed to facilitate charge separation for polymer:fullerene systems. The ionisation potential (IP) and electron affinity (EA) of the acceptors was calculated from the onset of oxidation and reduction, respectively, according to the methods described in Chapter 5, and these results are presented in Table 3.1. The electron affinity of FBR is 0.27 eV smaller than that of PC₆₀BM according to these solution CV measurements, which should be beneficial in terms of maximising the open circuit voltage. Cyclic voltammetry was also carried out in the solid state by spin-coating the materials from solution onto the working electrode surface, which in this case was ITO on glass, with a slightly larger EA measured in the thin film for both acceptors. The value of 3.73 eV for FBR suggests that it will have adequate LUMO-LUMO offset with many common donor polymers for efficient electron transfer. The larger EA
obtained for PC_{60}BM is also more similar to the values typically reported,\textsuperscript{148} although it should be noted that a wide range of EA values (3.8-4.2 eV) are found in the literature.\textsuperscript{147,149}

### Table 3.1: Optoelectronic Properties of FBR Compared with PC_{60}BM.

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<th>$E_g^{\text{opt}}$ (eV)\textsuperscript{b}</th>
<th>$E_g^{\text{elec}}$ (eV)\textsuperscript{c}</th>
<th>IP (eV)\textsuperscript{c}</th>
<th>EA (eV)\textsuperscript{c}</th>
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<td>5.47 (489 nm)</td>
<td>509</td>
<td>2.14</td>
<td>2.13</td>
<td>5.70</td>
<td>3.57</td>
<td>3.73</td>
</tr>
</tbody>
</table>

\textsuperscript{a) measured in CHCl$_3$ solution (at maximum visible wavelength absorption); \textsuperscript{b) measured in thin-film, spin-cast from CHCl$_3$ solution (5 mg ml$^{-1}$); \textsuperscript{c) measured by cyclic voltammetry of acceptors (3 x 10$^{-4}$ M) in CH$_2$Cl$_2$ solution with 0.3 M TBAPF$_6$ electrolyte; \textsuperscript{d) measured by cyclic voltammetry on the thin film with 0.1 M TBAPF$_6$ electrolyte in acetonitrile.}

Specular X-ray diffraction (XRD) was carried out on FBR films drop-cast from solution. The absence of any reflections consistent with crystallinity in the drop-cast films (Figure 3.4 (a)), even after annealing, indicates that FBR is essentially amorphous, at least within the length scale of the measurement’s accuracy. Differential scanning calorimetry (DSC) of FBR was also carried out, as shown in Figure 3.4 (b). A sharp melting endothermic transition is observed at around 200 °C on the first heating cycle, signifying that there is at least some degree of structural order within the bulk material. The broad shoulder visible in the onset of the melt could indicate the presence of conformational polymorphs here. On cooling from the melt, however, it was not possible to recrystallise FBR. The second heating and cooling cycle were also featureless, suggesting that the material becomes kinetically trapped in the amorphous phase. It should be noted that repeated attempts have been made to recrystallise FBR from the melt, either by cooling very slowly at 1 °C/min or by using isothermal steps on cooling, but no sign of recrystallisation has as yet been observed. The amorphous nature of FBR can be related to its twisted molecular structure as discussed in 3.2.3, which appears to very effectively prevent the molecule from closely packing in the solid state as anticipated from the design of the fluorene-benzothiadiazole linker.
3.2.5 Photovoltaic Performance of FBR with P3HT

In order to evaluate the potential of FBR as a non-fullerene acceptor, bulk heterojunction OPV devices were prepared using P3HT as the donor. P3HT was chosen both for its widespread availability and suitability as a benchmark polymer for comparison of device data, and because of its potential for industrial scale-up, as discussed previously. Devices were fabricated in an inverted architecture (glass/ITO/ZnO/P3HT:FBR/MoO$_3$/Ag) due to the enhanced stability over conventional architectures, as discussed in Chapter 1.2.2. This allowed devices to be fabricated and tested under ambient conditions (excluding thermal annealing and evaporation of MoO$_3$/Ag layers, which was carried out under an inert atmosphere). P3HT:PC$_{60}$BM devices were also prepared for comparison using the same device configuration. Various blend ratios, solvent systems, spin-coating conditions and annealing temperatures were tested for P3HT:FBR to optimise the blend, and the best results were found by spin coating at 4000-5000 rpm from a 1:1 P3HT:FBR solution (total concentration 16 mg ml$^{-1}$) in CHCl$_3$:o-DCB (4:1), followed by annealing at 110 °C for 15 min. It should be noted that as-cast blends performed very poorly, as is typically the case with P3HT-based devices which require at least some degree of thermal annealing to induce microstructural order in the polymer (for increased hole mobility) and crystallisation-induced phase segregation,$^{26,133-135}$ and this aspect is arguably one drawback to using P3HT as a
donor polymer in terms of technological scale-up. The P3HT:PC$_{60}$BM blends were prepared using a previously optimised procedure of 1:1 donor:acceptor in o-DCB (total concentration 40 mg ml$^{-1}$), spin-coated at 1500 rpm and annealed at 130 °C for 20 min. This higher concentration and slower spin speed gave thicker active layers of 148 nm for P3HT:PC$_{60}$BM, compared to an optimised thickness of only 80 nm for P3HT:FBR as measured by profilometry. This might be expected to limit the photocurrent produced by FBR devices in comparison to the PC$_{60}$BM reference devices. Figure 3.5 shows the $J$-$V$ characteristics and EQE spectra of both optimised devices, measured under simulated AM1.5G illumination at 100 mW cm$^{-2}$, and their photovoltaic performance is summarised in Table 3.2.

Figure 3.5: (a) $J$-$V$ curves and (b) EQE spectra of optimised P3HT:FBR and P3HT:PC$_{60}$BM devices (AM1.5G illumination at 100 mW cm$^{-2}$).

Table 3.2: Photovoltaic Performance of Optimised P3HT:Acceptor (1:1) Devices measured under AM1.5G illumination at 100 mW cm$^{-2}$.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PC$_{60}$BM</td>
<td>9.07</td>
<td>0.59</td>
<td>0.66</td>
<td>3.53</td>
</tr>
<tr>
<td>P3HT:FBR</td>
<td>7.95</td>
<td>0.82</td>
<td>0.63</td>
<td>4.11</td>
</tr>
</tbody>
</table>
It can be seen from the $J-V$ curve in Figure 3.5 (a) and Table 3.2 that a slightly lower short-circuit current is produced by the FBR device (7.95 mA cm$^{-2}$) compared to the fullerene reference device (9.07 mA cm$^{-2}$), which may be partially accounted for by the reduced thickness and more modest annealing of the FBR devices as described above. However, the non-fullerene devices produce a significantly higher open circuit voltage of 0.82 V compared to 0.59 V for the fullerene device, which can be attributed to the smaller electron affinity of FBR relative to PC$_{60}$BM. This results in a power conversion efficiency of 4.11% for the FBR devices, which is higher than that of the PC$_{60}$BM device (3.53%) as well as being among the highest reported efficiencies for non-fullerene acceptors with P3HT as the donor.\(^{42}\)

From Figure 3.5 (b) it can be seen that the maximum EQE intensity is lower for P3HT:FBR (65%) despite both the donor and acceptor absorbing strongly at this wavelength (ca. 500 nm). This can likely be explained by the smaller thickness of these active layers compared to the P3HT:PC$_{60}$BM blends, as described above, as well as their reduced annealing time and temperature. It is also evident from this EQE spectrum that the amount of photocurrent harvested across the spectrum for P3HT:FBR is limited due to the largely overlapping absorption profiles of the donor and acceptor. This leads to the speculation that higher efficiencies could be achieved with FBR blended with a lower bandgap donor material to generate photocurrent across a broader part of the spectrum. Alternatively, it may be possible to improve the performance with P3HT if the acceptor could be modified to give a more complementary absorption profile and this is the approach that will be explored in Chapter 4.

### 3.2.6 Charge Separation and Recombination Dynamics

Photoluminescence quenching (PLQ) studies were carried out by Ching-Hong Tan on the P3HT:FBR and P3HT:PC$_{60}$BM blends and neat films as shown in Figure 3.6. For the P3HT:FBR blend (excited at 600 nm in order to selectively excite the P3HT), photoluminescence of the donor is quenched with 96% efficiency as shown in Figure 3.6 (b). Likewise, the acceptor emission is 99% quenched (Figure 3.6 (c)) upon excitation at 532 nm. This indicates that exciton separation is highly efficient upon excitation of either donor or
acceptor, which is consistent with the formation of a favourable Type-II heterojunction for this blend. A minimal effect is seen upon thermal annealing of the P3HT:FBR device, with PLQ reduced to 93% and 95% for donor and acceptor, respectively, indicating that only a modest increase in phase segregation occurs with annealing. By contrast, in the case of P3HT:PC_{60}BM only 80% quenching efficiency of the polymer photoluminescence is observed (Figure 3.6 (b)). This has been previously correlated with strong phase segregation in such blends, with pure domains of P3HT formed on the 5-10 nm length scale.\textsuperscript{34} These studies strongly indicate, therefore, that FBR and P3HT form a more intimately mixed blend compared to P3HT with PC_{60}BM.

![Figure 3.6](image)

Figure 3.6: (a) UV-vis absorption spectra of P3HT, FBR and P3HT:FBR blends (as-cast and annealed at 100 °C for 15 min); PLQE of (b) P3HT in P3HT:FBR blends (as-cast and annealed at 100 °C for 15 min) excited at 600 nm; (c) P3HT in P3HT:PC_{60}BM as-cast blend excited at 532 nm; (d) FBR in P3HT:FBR blends (as-cast and annealed at 100 °C for 15 min) excited at 532 nm.
The charge generation processes in the P3HT:FBR and P3HT:PC$_{60}$BM blends was studied by ultrafast transient absorption spectroscopy (TAS) by Ching-Hong Tan and Elisa Collado-Fregoso. Figure 3.7 (a) shows the transient data at a probe wavelength of 725 nm (transient spectra shown in the Appendix) which corresponds to the maximum PL wavelength of P3HT. The polymer is selectively excited at 600 nm in this case. Initially, the P3HT excitons show a negative signal which can be assigned to stimulated emission, while the polarons yield a positive signal. It appears from the transient data that the rise time of the P3HT:PC$_{60}$BM blend is biphasic, with an initial fast (instrument response-limited) phase which corresponds to P3HT excitons that are formed close to the donor:acceptor interface, followed by a slower phase that is limited by exciton diffusion to the interface, corresponding to excitons generated within “pure” polymer domains. On the other hand, P3HT:FBR demonstrates significantly faster rise kinetics which are limited only by the instrument response and do not fit with a biphasic model. This indicates a more intimately mixed morphology for this blend, resulting in faster exciton quenching and polaron formation relative to the P3HT:PC$_{60}$BM reference. From the decay phase at ca. 200 ps and beyond, it is apparent that the FBR blend also exhibits faster recombination, which was confirmed by laser intensity studies (not shown herein) to correspond to geminate recombination processes. The microsecond transient data shown in Figure 3.7 (b) also demonstrates faster decay dynamics for the P3HT:FBR blend, this time corresponding to non-geminate recombination, which is again consistent with a more intermixed morphology for this blend.

Considering the faster recombination losses of P3HT:FBR observed by transient absorption studies, it is possible to understand the difference in optimal active layer thickness of these blends compared to the reference fullerene devices, given the losses occurring during charge transport through the active layer. Increased recombination for these blends may also be a reason why the $V_{oc}$ of P3HT:FBR devices is not as large as expected, considering the smaller electron affinity compared to PC$_{60}$BM, as it been shown elsewhere that faster recombination losses lead to reduced $V_{oc}$.\textsuperscript{151}
3.2.7 Morphology of P3HT:FBR Blends

The results of photoluminescence quenching and transient absorption experiments indicated a higher degree of intermixing in the P3HT:FBR blend compared to P3HT:PC_{60}BM. 2D grazing incidence x-ray diffraction (GIXRD) studies were carried out by Zhengrong Shang on the P3HT:FBR films in order to better characterise the crystalline structure and extent of long-range order in this blend. The GIXRD pattern of neat FBR (Figure 3.8 (a)) shows only a weak amorphous halo, consistent with the lack of crystalline reflections in the specular XRD shown in Figure 3.4. The P3HT:FBR blend film (Figure 3.8 (b)) shows intense \((h00)\) and \((010)\) plane reflections in the \(q_x\) and \(q_{xy}\) axes, respectively, corresponding to the crystallisation of P3HT with a predominantly edge-on orientation of the thiophene units, as is typically seen for P3HT:PC_{60}BM blend films\(^{152,153}\) as well as for pure P3HT films.\(^{104,154,155}\) However, no reflections are observed relating to the acceptor in the blend, supporting the theory that the highly amorphous, twisted FBR molecule is not able to crystallise in the blend, which hinders it from forming domains of an appropriate length scale for charge separation as supported by the PL and TAS results discussed above.
Differential scanning calorimetry (DSC) studies add further evidence for the lack of acceptor crystallisation in the blend. Figure 3.9 (a) shows the first heating cycles of the neat and blended samples, which were drop-cast from chloroform solution. In the blend sample, one endothermic transition is observed corresponding to the melting transition of P3HT, which has been significantly broadened and depressed (by 20 °C) relative to the pure sample due to disruption of polymer crystallisation in the presence of the acceptor, as has been previously reported for P3HT:PC$_{60}$BM blends.\textsuperscript{34,156,157} Unlike typical P3HT:PC$_{60}$BM blends, however, there is no melting endotherm corresponding to FBR, further illustrating the lack of acceptor crystallisation in this blend. Likewise, the cooling curves in Figure 3.9 (b) show recrystallisation of the polymer but no exotherm corresponding to FBR. This supports the GIXRD data in evidencing the inability of FBR to crystallise in this particular blend, and the highly intermixed morphology that results from this appears to contribute to increased recombination in P3HT:FBR devices, as shown by PL and transient absorption studies.
3.2.8 Charge Transport of P3HT:FBR Blends

Space-charge-limited current (SCLC) measurements\textsuperscript{158} were carried out by Jason Röhr to determine the electron mobility of FBR in the blend in comparison with PC\textsubscript{60}BM. Devices were prepared with ITO/TiO\textsubscript{2} and Ca/Al as electron selective contacts, and blend thicknesses were measured using a profilometer. The \textit{J-V} curves shown in Figure 3.10, measured between -5 and 5 V in steps of 0.05 V, were fitted using a numerical solver.\textsuperscript{159} Typically the Mott-Gurney square law is used to fit SCLC data, but the assumptions used in this case are generally not applicable to thin devices or systems which contain trap states,\textsuperscript{160} therefore a different numerical fitting approach was used\textsuperscript{161} and these numerical fits are shown in Figure 3.10 as black lines. It was found that the electron mobility for P3HT:FBR was very similar to that of P3HT:PC\textsubscript{60}BM, with values of $2.6 \times 10^{-6}$ cm\textsuperscript{2}/Vs and $2.3 \times 10^{-5}$ cm\textsuperscript{2}/Vs, respectively. However, it was also found that the P3HT:FBR demonstrated trap behaviour, so that exponential tails were needed to fit this data and this may explain the lower current density measured for these devices, despite their similar electron mobilities.
3.2.9 Morphological Stability of P3HT:FBR Blends

As discussed in Chapter 1.4.5, device stability is an important aspect in terms of technological scale-up of OPV, and fullerene-based devices notoriously suffer from problems with morphological stability, with large-scale aggregation and crystallisation of the acceptor leading to a reduction in solar cell performance over time.\textsuperscript{125} Optical microscopy can be used to monitor this process, using thermal annealing to accelerate the aging process in the thin film. In order to compare the morphological stability of the P3HT:FBR blend with that of P3HT:PC\textsubscript{60}BM, thin films were prepared on glass using the same conditions as for the active layers used in devices. These films were heated at 140 °C for a period of several hours and monitored using optical microscopy, as shown in Figure 3.11. After annealing for 1 h, large fullerene aggregates are visible in the P3HT:PC\textsubscript{60}BM films, as has been widely shown elsewhere.\textsuperscript{157,162,163} By contrast, the FBR blend films appear smooth and featureless after annealing for 1 h and even after 12 h, demonstrating that this new, highly amorphous acceptor offers some advantage over PC\textsubscript{60}BM in terms of morphological stability, at least with respect to vertical phase segregation as observed by these methods.
3.3 Linear Acceptors with Finely Tuned Energy Levels

As discussed in Chapter 3.1, one advantage of this simple, calamitic acceptor design is the ability to tune the electronic and material properties by interchanging the molecular building blocks used. The acceptor FBR presented in 3.2 consisted of a relatively electron donating 9,9-dioctylfluorene core with the strong electron accepting groups 2,1,3-benzothiadiazole and 3-ethylrhodanine on the periphery. It was also shown in Chapter 2 that dicyanovinyl groups can be used to further increase the electron accepting character of a molecule, as has also been widely demonstrated elsewhere.\(^{83,132,164}\) The same principle is applied here with the rhodanine flanked acceptors by substitution of dicyanovinyl at the thioketone position of the rhodanine heterocycle. Further tuning of the energy levels is achieved by switching the flanking benzothiadiazole moieties in FBR for electron rich thiophenes, which has the effect of raising the HOMO and LUMO levels of the molecule. Using this toolkit of building blocks: rhodanine, dicyanovinyl-rhodanine, benzothiadiazole and thiophene, alongside the same 9,9-dioctylfluorene core, a series of four different acceptors were synthesised with incrementally
adjusted frontier energy levels via the same straightforward synthesis route. Furthermore, the effect of the thiophene unit on the planarity of the structure and therefore the extent of crystallisation of this compared to FBR, is herein demonstrated. This acceptor series demonstrates the ability to finely tune the electronic and structural properties with this particular calamitic acceptor design, which can facilitate the proper matching of acceptors with donor materials in terms of their energy levels or extent of crystallinity.

3.3.1 Synthesis of Dicyanovinyl Rhodanine Acceptor Derivatives

In order to prepare the dicyanovinyl-substituted rhodanine, malononitrile was reacted with ethyl isothiocyanate and 2-bromoacetate in the presence of DBU\textsuperscript{52,165} to give the product 3.8 in reasonable yields (61\%) as shown in Scheme 3.4. This compound was then reacted with the dialdehyde intermediate 3.7 using the same approach described in Chapter 3.2 for FBR, this time giving the target molecule CN-FBR in 83\% yield as shown in Scheme 3.4.

For replacement of the benzothiadiazole unit of FBR with thiophene, commercially available 5-bromo-2-thiophenecarboxaldehyde was coupled with 9,9\'-dioctylfluorene as shown in Scheme 3.5 to give the intermediate 3.9 (76\% yield), followed by condensation with 3-ethylrhodanine (71\% yield) to give the target molecule FTR. It should be noted that the synthesis of FTR has since been reported elsewhere, and its application in solar cell devices with P3HT has been demonstrated.\textsuperscript{81}
Scheme 3.5: Synthesis of FTR small molecule acceptor.

The synthesis of CN-FTR was carried out by the same method but using the dicyanovinyl rhodanine derivative 3.8 as the flanking group, as demonstrated in Scheme 3.6. This demonstrates the great versatility of the devised synthesis route for these calamitic acceptors, whereby the same Suzuki coupling and Knoevenagel condensation reactions can proceed successfully with a variety of different structural units.

Scheme 3.6: Synthesis of CN-FTR small molecule acceptor.

3.3.2 DFT Modelling of Dicyanovinyl Rhodanine Acceptor Derivatives

The energy minimized structures of the four small acceptors were calculated using density functional theory (DFT) at the B3LYP/6-31G* level of theory with methyl groups replacing the n-octyl chains in each case, to simplify the calculations. As discussed in Chapter 3.1, a relatively large dihedral angle of 35° was calculated for FBR between the fluorene core and adjacent benzothiadiazole units, as demonstrated again in Figure 3.12. By contrast, FTR was calculated to be effectively planar (dihedral angle of 2°) due to the increased quinoidal character of the thiienyl-phenyl versus the phenyl-phenyl bond, as well as the reduced steric
effect from the adjacent alpha protons on the coupled phenyl rings. One result of this increased planarity for FTR and CN-FTR is that both the HOMO and LUMO are relatively well distributed across the whole molecule, in contrast with FBR and CN-FBR where the LUMO is localised onto the electron-withdrawing periphery as presented in Figure 3.13.

Figure 3.12: Energy minimised structures of FBR and FTR (calculated by DFT using Gaussian B3LYP/6-31G* with methyl groups replacing the n-octyl groups) with visualisation of their respective dihedral planes.

Figure 3.13: Energy minimised structures of FTR, CN-FTR, FBR and CN-FBR (with methyl replacing the n-octyl groups) as calculated by DFT (Gaussian B3LYP/6-31G*) with visualisation of HOMO (bottom) and LUMO (top).

3.3.3 Optoelectronic Properties of Dicyanovinyl Rhodanine Derivatives

The UV-vis absorption spectra of the four acceptors are compared in Figure 3.14, with the data summarised in Table 3.3. The absorption maxima in solution of all four acceptor derivatives are very similar (Figure 3.14 (a)), although the absorption of CN-FTR is slightly red-shifted relative to the other acceptors. The thin film spectra (Figure 3.14 (b)) are equally
similar, but in this case both dicyanovinyl adducts have slightly red-shifted absorption onsets, with optical bandgaps calculated as 2.07 eV and 2.08 eV for CN-FTR and CN-FBR, respectively, compared to the unsubstituted rhodanine analogues which have optical bandgaps of 2.15 eV and 2.14 eV for FTR and FBR, respectively.

![Normalized UV-vis absorption spectra of acceptors](image)

**Figure 3.14:** Normalised UV-vis absorption spectra of acceptors in (a) CHCl₃ solution (10⁻⁵ M) and (b) thin film spin-cast from CHCl₃ (10 ml ml⁻¹).

**Table 3.3: Optoelectronic Properties of Dicyanovinyl Rhodanine Acceptors**

<table>
<thead>
<tr>
<th></th>
<th>ε (10⁴ M⁻¹ cm⁻¹)ᵃ</th>
<th>λ_max (nm)ᵇ</th>
<th>λ_max (nm)ᵇ</th>
<th>E_g,opt (eV)ᵇ</th>
<th>E_g,elec (eV)ᶜ</th>
<th>IP (eV)ᶜ</th>
<th>EA (eV)ᶜ</th>
<th>EA (eV)ᵈ</th>
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</thead>
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<tr>
<td>FTR</td>
<td>9.58</td>
<td>499</td>
<td>500</td>
<td>2.15</td>
<td>2.14</td>
<td>5.53</td>
<td>3.39</td>
<td>3.59</td>
</tr>
<tr>
<td>CN-FTR</td>
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<td>516</td>
<td>516</td>
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<td>2.09</td>
<td>5.58</td>
<td>3.49</td>
<td>-</td>
</tr>
<tr>
<td>FBR</td>
<td>5.47</td>
<td>489</td>
<td>509</td>
<td>2.14</td>
<td>2.13</td>
<td>5.70</td>
<td>3.57</td>
<td>3.73</td>
</tr>
<tr>
<td>CN-FBR</td>
<td>7.93</td>
<td>499</td>
<td>515</td>
<td>2.08</td>
<td>2.14</td>
<td>5.82</td>
<td>3.68</td>
<td>-</td>
</tr>
</tbody>
</table>

Measured in a) dilute CHCl₃ solution; b) thin film, spin-cast from CHCl₃ solution (5 mg ml⁻¹); c) CV of acceptors in CH₂Cl₂ solution (3 x 10⁻⁴ M) with 0.3 M TBAPF₆ electrolyte; d) thin film CV in acetonitrile with 0.1 M TBAPF₆ electrolyte using ITO as the working electrode.

Measurement of the ionisation potential (IP) and electron affinity (EA) values by cyclic voltammetry reveals the effect that the different chemical moieties have on the frontier energy levels of the materials. Figure 3.15 illustrates this variation with the IP and EA values measured in solution plotted alongside the HOMO and LUMO values calculated by
DFT. It should be noted that the DFT calculations were carried out for molecules in the gas phase and so these values can only be taken as an approximation to the HOMO and LUMO energies. Meanwhile, the measurement of IP and EA in the solution state does not account for solid-state interactions, nor does it take into account how these values are affected in the BHJ blend, however these measurements do allow for an effective comparison of the modification of energy levels within a series such as this. From Figure 3.15 it can be seen that FTR has the smallest IP and EA (5.53 eV and 3.39 eV, respectively), which is due to the electron-rich thiophene units on either side of the fluorene core with only the rhodanine units in this case to stabilise the energy levels. It should be noted that the EA of FTR measured by CV in the thin film (3.59 eV) indicates that in the solid state there should be sufficient energetic offset between the LUMO of FTR and that of wide bandgap polymers such as P3HT (EA measured alongside as 3.2 eV) for electron transfer to take place, so that FTR can still be used as an acceptor. When the thioketone group on rhodanine is substituted for the more electron withdrawing dicyanovinyl group in CN-FTR, both the EA and IP are increased, but the effects on the EA is slightly greater (difference of 0.1 eV, vs 0.05 eV for IP), resulting in a marginally decreased optical and electrochemical bandgap for the dicyanovinyl adduct. Upon substitution of the thiophene for the more electron withdrawing benzothiadiazole group in FBR, a further increase in both EA and IP is observed, and likewise for the dicyanovinyl adduct CN-FBR, a further increase in both EA and IP is observed (with the EA affected somewhat more than the IP). Due to the high solubility of both dicyanovinyl adducts in acetonitrile under the experimental conditions used to measure thin-film CV, it was not possible to obtain EA values for these derivatives in the solid state; however, the values obtained for FTR and FBR at least follow a similar trend to the solution measurements. In this way, a series of molecules was shown with slightly offset HOMO and LUMO energies along the series, but with the bandgap relatively unaffected. As well as being of potential interest for fundamental charge transfer and other studies, such a series can be useful for optimising a certain donor-acceptor combination. In addition, studies are underway into the use of these acceptor materials in combination, in the form of a ternary blend device structure with one donor and two different, energetically offset acceptors.
3.3.4 Crystal Packing of Dicyanovinyl Rhodanine Derivatives

Specular X-ray diffraction was carried out (by Christian Nielsen) to evaluate the effect of thiophene substitution on the crystal packing properties of the materials. Figure 3.16 demonstrates the complete absence of crystalline reflections for FBR, as discussed in 3.1.4, and similarly for the dicyanovinyl adducts CN-FBR. By contrast, FTR (Figure 3.16 (b)), shows several pronounced crystalline reflections which are enhanced with thermal annealing, suggesting that the more planar molecular structure of the thiophene containing analogue allows for stronger intermolecular interactions and the formation of a crystal lattice which is not observed in films of the more twisted FBR acceptor. It should be noted that this difference is also observed in the ability to grow needle-like crystals of FTR from solution, while FBR could not be recrystallised from solution. CN-FTR also exhibits some weak diffraction peaks (Figure 3.16 (d)) but with significantly reduced intensity, implying that the dicyanovinyl groups may hinder the crystal packing somewhat in this case.
3.3.5 Morphology of P3HT Blends with FBR and FTR Acceptors

From X-ray diffraction it is clear that the thiophene containing acceptor FTR is significantly more crystalline than the BT analogue FBR. Differential scanning calorimetry (DSC) was carried out on drop-cast samples of the neat materials and 1:1 blends with P3HT, as presented in Figure 3.17, in order to compare the extent of crystallisation within the blends. As discussed in 3.2.7, neat FBR undergoes an endothermic melt ($T_m$) at 200 °C, but in the blend with P3HT there is no transition corresponding to the acceptor. In the case of FTR, the neat material exhibits an exothermic crystallisation ($T_c$) around 137 °C followed by a melt at 173 °C. The presence of a cold crystallisation peak close to the $T_m$ of the acceptor indicates that this material has a relatively low crystallisation rate under drop-casting conditions, but that heat-activated crystallisation does occur at temperatures within the range typically used for annealing P3HT solar cells. Furthermore, both of these exo- and endothermic transitions are present in the drop-cast blend sample with P3HT, which implies that, unlike FBR, the planar thiophene based acceptor is able to crystallise to some extent.
within the blend. The $T_c$ and $T_m$ of FTR, as well as the $T_m$ of P3HT, have still been slightly depressed within the blend relative to the neat samples, however, implying that there is still some miscibility of the two components.

![Figure 3.17: First heating cycles measured by DSC at (5 °C/min) on drop-cast samples of (a) FBR, P3HT and P3HT:FBR blend; (b) FTR, P3HT and P3HT:FTR blend. Thermograms are offset vertically for clarity.](image)

### 3.3.6 Photoluminescence Quenching of FBR and FTR Blends

In order to determine the effect of this enhanced acceptor crystallisation on the exciton dissociation properties of the films, photoluminescence quenching (PLQ) experiments were carried out (by Ching-Hong Tan) as presented in Figure 3.18, with corresponding absorption spectra given in the Appendix. As discussed in 3.2.6, the FBR emission in the P3HT:FBR as-cast blend is quenched with 99% efficiency (95% for the annealed blend), while the P3HT emission is likewise very efficiently quenched (96% as-cast, 93% annealed) in the sample excited at 600 nm in Figure 3.18 (b). For the P3HT:FTR blends, the PL quenching efficiency of the acceptor is slightly reduced at 89% in the as-cast blend, and 85% after annealing, while the P3HT emission is 94% quenched before and after annealing. This slight reduction in PL quenching efficiency for both donor and acceptor indicates that the P3HT:FTR blends are slightly more phase separated than the FBR blends, which suffered from problems of excessive recombination because of the highly intermixed blend morphology.
Figure 3.18: PL quenching efficiency of (a) FBR (excited 380 nm) and (b) P3HT (excited 600 nm) in P3HT:FBR blends (as-cast and annealed at 100 °C, 15 min); PL quenching efficiency of (c) FTR (excited 370 nm) and (d) P3HT (excited 600 nm) in P3HT:FTR blends (as-cast and annealed at 100 °C, 15 min).

3.3.7 Photovoltaic Performance with of FBR and FTR with P3HT

Based on the encouraging PL quenching results discussed above, which appeared to indicate a more phase separated morphology for the P3HT:FTR blend compared to P3HT:FBR, OPV devices were fabricated with P3HT and FTR as the acceptor for comparison, using the same inverted architecture and identical procedures for device fabrication. As shown in Figure 3.19 and Table 3.4, this change in structure was not found to result in improved photovoltaic performance. Rather, a reduction in all photovoltaic parameters was found for these blends, with an overall PCE of only 2%. In particular, a $V_{oc}$ of only 0.74 V is achieved for the thiophene analogue, compared to 0.82 V for FBR. This is despite the higher-lying LUMO energy of FTR, which would be expected to result in a larger $V_{oc}$ for this blend. Elsewhere, devices fabricated in the conventional architecture with P3HT:FBR blends have demonstrated open circuit voltages of up to 1.0 V and PCE of 3.1%, and similar results have
been found in our lab with this acceptor in conventional devices (Ching-Hong Tan, unpublished data). The reduced $V_{oc}$ in inverted devices implies a possible difference in interactions at the blend-electrode interface, which may be due to differences in vertical phase separation for the two blends, however further studies, including e.g. depth profiling by dynamic secondary ion mass spectrometry (D-SIMS), or X-ray photoelectron spectroscopy (XPS) would be needed to confirm this. The FF and $J_{sc}$ are also lower for the P3HT:FTR blend, although PL quenching experiments suggest that exciton dissociation is highly efficient for this blend and therefore the offset between the LUMO of P3HT and FTR (estimated by cyclic voltammetry as -3.2 eV and -3.6 eV, respectively) is sufficient for electron transfer. It should be noted that the inverted P3HT:FTR devices reported herein were not fully optimised and it is therefore possible that their performance could be improved. Therefore, it is not possible to determine conclusively whether this more phase-segregated morphology was beneficial or not for this system. Nevertheless, it is evident from Figure 3.19 (b) that the overlapping absorption spectra of FTR and P3HT still leads to a very narrow EQE profile, which limits the amount of photocurrent that can be produced in this blend as for the P3HT:FBR blend. In order to overcome this problem, it would be necessary to either significantly alter the bandgap of the acceptor to complement that of P3HT, or match the acceptor with a low bandgap donor polymer. The latter approach is currently under investigation with a range of donor materials, and it has been found that blends with FBR and the fluorinated benzothiadiazole polymer $\mu Y_4$ give up to 7.7% PCE with $J_{sc}$ values of over 11 mA cm$^{-2}$ as well as a high $V_{oc}$ of 1.1 V (Derya Baran, manuscript in preparation). This result also demonstrates the excellent potential of these acceptors to act as fullerene replacements with a variety of polymer donors.
Figure 3.19: (a) J-V data and (b) EQE spectra of P3HT:FBR, P3HT:FTR and P3HT:PC\textsubscript{60}BM devices measured under AM1.5G illumination at 100 mW cm\textsuperscript{-2}.

Table 3.4: Photovoltaic Performance of Optimised P3HT:Acceptor (1:1) Devices.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm\textsuperscript{-2})</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PC\textsubscript{60}BM</td>
<td>9.07</td>
<td>0.59</td>
<td>0.66</td>
<td>3.53</td>
</tr>
<tr>
<td>P3HT:FBR</td>
<td>7.95</td>
<td>0.82</td>
<td>0.63</td>
<td>4.11</td>
</tr>
<tr>
<td>P3HT:FTR</td>
<td>6.05</td>
<td>0.74</td>
<td>0.44</td>
<td>1.97</td>
</tr>
</tbody>
</table>

3.4 Conclusions

In this chapter, a new linear acceptor design was introduced that is easy to synthesise in two simple steps, allowing for the structure to be easily modified to tune the optoelectronic and crystal packing properties, as well as offering the potential for this material to be produced commercially on a large scale. This offers an intrinsic advantage over fullerene acceptors, for which the costly synthesis and difficult purification are widely considered to be a significant prohibitive factor. The design in question involves a central 9,9'-dioctylfluorene core (A), flanked by a second unit B, capped with rhodanine derivatives (C) via a vinyl linkage. The first acceptor presented using this design, FBR, incorporates benzothiadiazole and 3-ethylrhodanine in the B and C positions, respectively (Chapter 3.2). FBR demonstrated several advantageous properties as an acceptor for OPV, namely its strong absorption in the visible region of the spectrum, reversible reduction behaviour with the ability to accept at least two electrons reversibly and a LUMO energy that is higher-lying than that of PC\textsubscript{60}BM,
allowing it to achieve a larger open circuit voltage ($V_{oc}$) in P3HT:acceptor devices. Lastly, the non-planar molecular structure of FBR almost completely prevented the material from crystallising, at least on any length scale observable in these measurements. While this property helps prevent the formation of large crystalline domains beyond the length scale of exciton diffusion, as is commonly an issue with small molecule acceptors as well as with fullerene acceptors over extended lifetimes, it was found that this lack of any acceptor crystallisation or aggregation also lead to a sub-optimum morphology in which the donor and acceptor components were too well mixed. This led to increased charge generation in the P3HT:FBR blend compared to P3HT:PC$_{60}$BM blends, but also faster charge recombination which limited the short circuit current ($J_{sc}$) achieved. Another factor limiting the $J_{sc}$ is the essentially overlapping absorption profile of the acceptor with that of P3HT, meaning that photocurrent is generated over only a relatively narrow region of the spectrum. Despite these factors, OPV devices with FBR as the acceptor outperformed the reference P3HT:PCBM devices, largely owing to $V_{oc}$ enhancement, with a maximum power conversion efficiency of 4.1% which is among the highest non-fullerene acceptor devices with P3HT that have been reported.$^{172}$ Furthermore, it was shown that lateral diffusion and large-scale aggregation of this acceptor was reduced relative to PC$_{60}$BM, offering the potential for improved morphological stability, and the use of an inverted device architecture offers further stability in terms of the reactivity of the electrode and interlayer materials compared to conventional devices.

In the second part of this chapter, a series of linear acceptors was presented based on the FBR design, with small changes to the molecular structure allowing the frontier energy levels of the molecule to be varied. By substituting benzothiadiazole unit for the more electron rich thiophene, both the IP and EA of the material was reduced, while the addition of dicyanovinyl groups to the periphery of the molecule was used to increase the IP and EA. In this way, a series of four molecules was developed with slightly offset frontier energy levels from each other, but with the IP and EA both affected by roughly the same amount so that the optical bandgap was largely unchanged across the series. The materials did, however, exhibit a clear difference in crystallinity when comparing the benzothiadiazole and thiophene derivatives FBR and FTR, as the more planar FTR showed pronounced crystal
packing by XRD in contrast to the essentially amorphous FBR. This enhanced crystallinity appeared to have some effect on the phase segregation in P3HT:acceptor blends, with evidence of acceptor crystallisation within the P3HT:FTR blend shown by DSC, as well as a slight reduction in PL quenching efficiency being demonstrated for the P3HT:FTR blends. OPV devices with FTR as the acceptor and P3HT as the donor did not show any improvement in device performance, however, with a reduction in all photovoltaic parameters compared to the P3HT:FBR devices. The low $V_{oc}$ that was achieved in the inverted architecture, in this case, was tentatively assigned to differences in vertical stratification between the two blends, although this device data was also not fully optimised and further studies would be needed to investigate this issue. In any case, each of the acceptors presented in this series face the same problem of an absorption spectrum which overlaps with that of P3HT, thereby limiting the $J_{sc}$ in terms of the breadth of photocurrent generation across the incident solar spectrum. While devices with FBR and complementary, low bandgap polymers have demonstrated higher efficiencies up to 7.7% PCE (manuscript in preparation), there is still significant motivation to improve the efficiency of P3HT based devices due to the reasons already discussed. To address this challenge, the structure of the acceptor should be altered in order to reduce its optical bandgap, and the results of this approach are presented in Chapter 4.
Chapter 4:
Extended Linear Acceptors with an Indacenodithiophene Core

\[ \text{R = n-octyl} \]
\[ \text{R = 2-ethylhexyl} \]
\[ \text{O-IDTBR} \]
\[ \text{EH-IDTBR} \]
4.1 Introduction

The conclusions from Chapter 3 indicated two ways in which the molecular design of FBR could be changed in order to improve the photovoltaic performance with P3HT. Firstly, the spectral absorption should be modified in order to complement that of P3HT so that a greater portion of the incident solar spectrum could be harvested as photocurrent. Secondly, the miscibility with P3HT should be reduced sufficiently to deliver a more phase-separated microstructure with reduced charge recombination in the blend. In order to address both these aspects at once, the 9,9'-dioctylfluorene core on FBR was replaced with the more extended indacenodithiophene (IDT). The donation of electrons from the sulphur atom lone pairs into the π-system makes indacenodithiophene more electron rich relative to fluorene, which should have the effect of raising the HOMO energy of the molecule, as well as facilitating molecular orbital hybridisation when coupled with more electron deficient units, further contributing to raise the HOMO and lower the LUMO as discussed in Chapter 1.2.3.

The larger number of delocalised electrons in IDT also contributes to reducing the bandgap through conjugation effects. Lastly, the incorporation of flanking thiophenes in the fused IDT system helps to promote a more planar structure compared to fluorene, through the reduced steric effects between the α-protons on IDT and adjacent units, as well as through the increased quinoidal character of the bond. Similarly to fluorene, the side chains on IDT are attached to the sp³ hybridised bridging carbon atoms and are therefore projected out of the plane of the molecule, which can help to control the degree of aggregation without preventing intermolecular close contacts. With the narrow optical bandgaps, low conformational disorder and high charge carrier mobilities that this moiety offers, IDT (and its Ge- or Si-bridged analogues) has been incorporated into several high performing semiconducting polymers for photovoltaic and field effect transistor applications. Indeed, high hole mobilities of up to 3.6 cm²/Vs have been demonstrated for IDT-BT copolymers¹⁷³ and recently these polymers have been found to be approaching “disorder-free” transport which is thanks in part to the rigid planarity of the IDT-BT backbone, which appears to be relatively resilient to side-chain disorder.¹⁷⁴

On the basis of the properties outlined above, the incorporation of IDT into the small molecule acceptor design of FBR was expected to narrow the optical bandgap as well as
increase the planarity, and therefore molecular packing, of the acceptor to promote a greater
degree of crystallinity in the material. In this sense, the use of IDT is similar in approach to
the use of thiophene in the flanking position as presented in Chapter 3.3 with the molecules
FTR and CN-FTR. However, here we are able to retain the favourable electron withdrawing
properties of the benzothiadiazole unit to stabilise the LUMO energy, and the resulting
acceptor-donor-acceptor (A-D-A) character can furthermore help reduce the bandgap via
MO hybridisation. It has also been previously shown that the alkyl chain length and the
degree of branching can have a significant effect on the optoelectronic and aggregation
properties of IDT-BT\textsuperscript{175} polymers as well as other systems.\textsuperscript{176,177} For this reason, IDT
moieties with both linear (n-octyl) and branched (2-ethylhexyl) side-chains were synthesised
for comparison. P3HT was again chosen as the donor polymer for the devices reported
herein, to provide a direct comparison with the P3HT:FBR system as well as for the reasons
of scalability previously discussed.

### 4.2 Replacing the Fluorene in FBR with Indacenodithiophene

#### 4.2.1 Synthesis of IDTBR Acceptors

The indacenodithiophene (IDT) core was synthesised according to literature procedures,\textsuperscript{175,178}
using either linear n-octyl (O-IDTBR) or branched 2-ethylhexyl (EH-IDTBR) side-chains at
the alkylation step. Brominated IDT was then stannylated and reacted with 7-bromo-2,1,3-
benzothiadiazole-4-carboxaldehyde via Stille coupling, followed by Knoevenagel condensation
with 3-ethylrhodanine to give O-IDTBR and EH-IDTBR in 60% and 30% final yields,
respectively (See Figure 4.1). Stille coupling was used in this instance due to the well-
documented instability of thiophene boronic esters under basic Suzuki conditions, with the
high rate of hydrolytic deboronation prior to the aryl-aryl coupling often reducing the
product yields.\textsuperscript{179-181} However, the use of highly toxic organotin compounds would
considerably limit any potential industrial scale-up of this material and hence other routes
are currently under investigation for this synthetic step. Nevertheless, it should be noted
that the stannylation of n-octyl and 2-ethylhexyl IDT does not appear to have been hitherto
reported in the literature (Scifinder substructure search, December 2015). Both acceptors are
stable up to 350 °C according to thermogravimetric analysis (see Appendix) and highly soluble in common organic solvents such as chloroform at room temperature, as well as non-halogenated solvents such as o-xylene at slightly elevated temperatures (60 °C), which should enable the facile solution processing of OPV devices.

4.2.2 DFT Modelling of IDTBR Acceptors

In the case of FBR, a torsional angle of 35° was calculated between the fluorene core and the adjacent benzothiadiazole unit by DFT (B3LYP/6-31G*) as discussed in Chapter 3.2. By contrast, IDTBR was calculated to be essentially planar (1.3°) as shown in Figure 4.2 (b). This can be attributed to the increased quinoidal character of the phenyl-thienyl bond compared to the phenyl-phenyl bond, as well as the reduced steric twisting from adjacent alpha C-H bonds on the coupled phenyl rings. This increased planarity results in a more conjugated electronic structure so that the LUMO of IDTBR appears to be slightly more delocalised across the central unit relative to FBR, which could be beneficial in terms of

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Figure 4.1: Synthesis of O-IDTBR and EH-IDTBR acceptors.

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molecular oscillator strength and therefore molar absorption coefficient. However, it should be noted that the LUMO of IDTBR is still predominantly located on the periphery of the molecule rather than the central unit, which allows the energy of the HOMO to be tuned through replacement of the central unit whilst having less of an effect on the high-lying LUMO energy, thereby maintaining a similarly high $V_{oc}$ as obtained with FBR.

![Chemical structures and minimum energy conformations of (a) FBR and (b) IDTBR](image)

**Figure 4.2.** Chemical structures and minimum energy conformations of (a) FBR and (b) IDTBR calculated (with methyl replacing n-octyl or 2-ethylhexyl groups) using Gaussian (B3LYP/6-31G*) to visualise the LUMO and HOMO.

### 4.2.3 Optoelectronic Properties of IDTBR Acceptors

The increase in electron density offered by the addition of thiophene units in IDTBR, along with the increased MO hybridisation arising from the A-D-A structure for this molecule, are manifested in a significantly reduced optical bandgap for the IDTBR acceptors relative to FBR. Figure 4.3 shows the UV-vis absorption spectra of EH- and O-IDTBR in solution, as-cast thin film and thermally annealed thin film, and these results are also summarised in Table 4.1. Whereas the absorption maximum of FBR was observed at 489 nm in CHCl$_3$ solution, both IDTBR acceptors exhibit absorption maxima at 650 nm in solution. In addition, the molar absorption coefficients of the IDTBR acceptors in CHCl$_3$ solution are $1 \times 10^5$ M$^{-1}$ cm$^{-1}$ which is almost twice the value of FBR and around 26 x higher than that of
PC$_{60}$BM at its maximum absorption wavelength in CHCl$_3$ solution (400 nm), demonstrating the potential of these molecules to contribute significantly more to the photocurrent relative to fullerene acceptors.

Figure 4.3: UV-vis absorption spectra of (a) EH-IDTBR and (b) O-IDTBR in chloroform solution (1.5 x 10$^{-5}$ mol l$^{-1}$), thin film (spin-coated from 10 mg ml$^{-1}$ chlorobenzene solution) and thin film annealed at 130 °C for 10 min.

While the linear O-IDTBR and branched EH-IDTBR have very similar absorption profiles in solution, as shown in Figure 4.3, the as-cast thin film absorption of the linear analogue is red-shifted by 40 nm relative to the branched version, with a further bathochromic shift of 41 nm upon annealing at temperatures above 110 °C and up to 140 °C (see Figure 4.4 (a)). The shoulder observed at shorter wavelengths, which has been previously attributed to solid-state aggregation in IDT-BT polymers,$^{175}$ also becomes more pronounced with thermal annealing. By contrast, the absorption of EH-IDTBR is not affected by annealing, indicating that the alkyl chains have a significant effect on the tendency of the material to crystallise in the thin film. At least in terms of absorption, it appears that the more red-shifted absorption of the linear chain analogue would be preferable in providing a more complementary absorption profile to that of P3HT.
Table 4.1: Optoelectronic Properties of O-IDTBR and EH-IDTBR Acceptors

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon ) ( (10^4 \text{ M}^{-1} \text{ cm}^{-1})^a )</th>
<th>( \lambda_{\text{max}}^{\text{soln.}} ) (nm) (^a)</th>
<th>( \lambda_{\text{max}}^{\text{film}} ) (nm) (^b)</th>
<th>( \lambda_{\text{max}}^{\text{ann.}} ) (nm) (^c)</th>
<th>( E_{g}^{\text{opt.}} ) (eV) (^b)</th>
<th>EA (eV) (^d)</th>
<th>IP (eV) (^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-IDTBR</td>
<td>9.9</td>
<td>650</td>
<td>690</td>
<td>731</td>
<td>1.63</td>
<td>3.88</td>
<td>5.51</td>
</tr>
<tr>
<td>EH-IDTBR</td>
<td>10.3</td>
<td>650</td>
<td>673</td>
<td>675</td>
<td>1.68</td>
<td>3.90</td>
<td>5.58</td>
</tr>
</tbody>
</table>

Measured in \(^a\) CHCl\(_3\) solution; \(^b\) thin films spin-coated from 10 mg ml\(^{-1}\) CB solution; \(^c\) annealed at 130 °C for 10 min; \(^d\) cyclic voltammetry carried out on the as-cast thin films in acetonitrile with 0.1 M TBAPF\(_6\) electrolyte; \(^e\) estimated from the electrochemical EA and the optical \( E_{g} \).

Cyclic voltammetry was carried out in the as-cast thin films of the acceptors to measure the reduction potential, from which electron affinity (EA) was calculated as described in Chapter 5. From Table 4.1 it can be seen that both EH-IDTBR and O-IDTBR have a similar EA around 3.9 eV. The EA of P3HT was measured for comparison to be 3.2 eV, which should give sufficient energetic offset to provide a driving force for electron transfer between these materials. The ionisation potential (IP) of the acceptors, estimated from the optical bandgap and electrochemically determined EA, was found to be slightly smaller for O-IDTBR compared to EH-IDTBR, which may be due to the enhanced planarisation effect of O-IDTBR arising from the additional intermolecular interactions of the more aggregated material. The energy offset between the IP both acceptors and of P3HT (measured alongside to be 5.1 eV) also appears to be suitable for efficient photoinduced hole transfer.

![Figure 4.4: (a) UV-vis absorption spectra of O-IDTBR thin films, as-cast and annealed (10 min) at different temperatures; (b) Absorption coefficient \( \alpha \) of EH-IDTBR as-cast thin film compared with common low bandgap donor polymers (see Figure 4.17 for structures), where \( \alpha \) was calculated by \( \alpha = 1/d \times \ln(1/T) \).]
Another interesting observation is that IDTBR (branched chain version) demonstrates significantly stronger absorption in the thin film relative to typical low bandgap polymers such as PTB7, as shown in Figure 4.4 (b), as well as having a higher extinction coefficient than is typically reported for P3HT.\textsuperscript{182-184} This opens the opportunity for an exciting new concept in the design of OPV active layer materials. Whereas traditionally the donor polymer is used as the primary light absorber and the fullerene exists mainly to accept and transport electrons, it is possible, in a case such as this where the acceptor is highly absorbing, that the acceptor could instead act as the primary low bandgap light absorber instead, donating holes on light absorption in the same way that donor polymers traditionally donate electrons on light absorption. This could open the possibilities for using wide bandgap ‘donor’, or hole transport materials alongside the low bandgap ‘acceptor’.

4.2.4 Crystal Packing of IDTBR Acceptors

As discussed in Chapter 4.1, one of the limiting factors of FBR was its lack of crystallinity, causing it to mix excessively with the polymer rather than form pure domains. This intimately mixed morphology led to charge recombination losses, which limited device performance. One of the design principles of the new IDTBR acceptors was therefore to increase the planarity of the backbone in order to induce crystallisation and the formation of pure acceptor domains. Specular X-ray diffraction (XRD) was used to compare the crystallinity of the O-IDTBR and EH-IDTBR acceptors in films that were spin-coated at 600 rpm from CHCl\textsubscript{3} (measurements carried out by Christian Nielsen). While FBR showed no sign of crystallinity by this method even after thermal annealing (Chapter 3.2.4), both O-IDTBR and EH-IDTBR give strong diffraction peaks that are enhanced with annealing, as shown in Figure 4.5, which clearly indicates an increase in crystalline order for the more planar IDT based acceptors. The effect of annealing above 110 °C also appears to be more pronounced for the linear chain analogue, in accordance with the change in UV-vis absorption spectra as described in 4.2.3.
The crystal structure of O-IDTBR was also resolved by X-ray crystallography (Andrew White), revealing monoclinic crystallisation in the space group P2₁/c for these single crystals grown by slow evaporation in CHCl₃. Further detailed crystallographic data are given in the Appendix. This is in contrast to FBR, for which no observable crystals could be grown from solution even after repeated attempts. Meanwhile, EH-IDTBR could also be recrystallized from CHCl₃ solution but diffraction quality crystals have not yet been obtained for this compound. In agreement with the DFT calculations, the crystal structure of O-IDTBR demonstrates a highly planar molecular backbone, although with is a slight asymmetry in the IDT-BT linkage dihedral angles (1.1° and 5.9°) as shown in Figure 4.6. This crystal structure also confirms the molecular conformation of energy minimised O-IDTBR structure, with the sulphur atoms on IDT oriented in the same direction as the thiadiazole group on BT (cis). Interestingly, this is in contrast to the most stable conformation calculated for IDT-BT polymers as well as for related thiophene-thiadiazole units, for which the unfavourable steric interaction between adjacent C-H protons (and attractive N---H interactions) leads to the opposite conformation (trans) being generally favoured. This difference could be explained by the presence of stabilising N---S non-bonding interactions as proposed elsewhere, which have been said to arise from donation of the nitrogen lone pair into low-lying empty orbitals on the sulphur, although it could also be that the orientation for this particular molecule is determined by the side-chains or the packing. It
should be noted that an analogous molecule bearing 4-hexylphenyl side-chains on the IDT has been published elsewhere and the same cis orientation was calculated as the energy-minimised structure in this case. Some degree of disorder in the side-chains can also be seen in Figure 4.6 and 4.7. While the first 3 or so carbons in the chain have a more rigid orientation perpendicular to the plane of the molecule, the carbons further from the molecule appear to have significant thermal disorder, which may be giving rise to different side-chain conformations. Indeed, no side-chain melt is observed by differential scanning calorimetry (Figure 4.8) for these molecules, indicative of a reasonable degree of side-chain disorder.

Figure 4.7 demonstrates a type of columnar π-stacking for this compound, with the substituents in each molecule offset with respect to the centre, in an alternating fashion. In this way, there does appear to be at least some degree of π-overlap in the crystal despite the presence of large, disordered alkyl chains which project out of the plane of the molecule, although it is not straightforward to determine how this would relate to transport properties.

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**Figure 4.6:** Crystal structure of O-IDTBR with colour coded atoms: C (dark grey), N (blue), O (red), S (yellow) and H (light grey).
Differential scanning calorimetry (DSC) measurements were carried out on drop-cast samples of the neat materials to study their thermal transitions. From the first heating cycle shown in Figure 4.8, it is apparent that O-IDTBR undergoes an exothermic crystallisation transition with an onset temperature of 108 °C and $T_c$ of 115 °C, which explains the strong effect on the UV-vis absorption properties after annealing at temperatures above 110 °C. No such thermally induced crystallisation occurs during the heating cycle of EH-IDTBR at such temperatures, hence the different optical response of the acceptors to annealing. Both acceptors demonstrate slightly elevated melting temperatures (225 °C and 219 °C for O-IDTBR and EH-IDTBR, respectively) compared to FBR (200 °C), further evidencing a higher degree of self-organisation in the IDTBR acceptors. In addition, both new acceptors appear to recrystallise upon cooling from the melt, whereas FBR could not be recrystallised on cooling after the initial melt, as discussed previously.
4.2.5 Photovoltaic Devices with IDTBR Acceptors

Solar cells were fabricated (by Shahid Ashraf and Amber Yousaf) using P3HT as the donor polymer due to its widespread availability and potential for technological scale-up, as already discussed. Inverted devices (glass/ITO/ZnO/P3HT:IDTBR(1:1)/MoO₃/Ag) were made due to the improved environmental stability relative to the conventional devices,¹⁶⁹,¹⁹³ which allowed for devices to be tested under ambient conditions. Active layer blends were spin-coated from chlorobenzene solution under ambient conditions without using any solvent additives. The films were annealed for 10 min at 130 °C in order to promote crystallisation of P3HT, as described previously, as well as that of the acceptor in the case of O-IDTBR. Figure 4.9 (a) shows the J-V curves of the best performing optimised devices, with the average and highest performing device data summarised in Table 4.2 for devices with an active area of 0.045 cm² and measured under simulated AM1.5G illumination at 100 mW cm⁻². Both acceptors yielded high open-circuit voltages (0.7-0.8 V) relative to reference PC₆₀BM devices reported in Chapter 3.2.5 (0.59 V) and this difference can be related to the smaller electron affinities of these materials. The IDTBR acceptors also generate higher short circuit currents compared to the P3HT:PC₆₀BM device, which may be related to the increased visible wavelength absorption, and therefore photocurrent generation, of these new acceptors. A higher average $J_{sc}$ of 13.9 mA cm⁻² is achieved from the O-IDTBR device, compared to 12.1 mA cm⁻² for EH-IDTBR. This can be at least partially explained by the
broader EQE profile of the linear chain analogue, which extends beyond 800 nm due to the red-shifted absorption of the acceptor upon annealing as described in 4.2.3. Although the \( V_{oc} \) and fill factor (FF) are both slightly lower for the linear chain analogue, the enhanced \( J_{sc} \) leads to an overall increase in average PCE of 6.3\% for O-IDTBR (maximum PCE 6.4\%) compared to 6.0\% for EH-IDTBR. At the time of writing, this is the highest published efficiency for non-fullerene acceptor devices with P3HT. It is also significantly higher than the reference PC\(_{60}\)BM:P3HT device efficiency of 3.5\% (Chapter 3.2.5), despite the reduced active layer thickness of 75 nm for the IDTBR devices compared to 150 nm for the fullerene based device.

![Figure 4.9: (a) J-V curves of optimised IDTBR:P3HT (1:1) solar cells; (b) EQE spectra (solid lines) of optimised IDTBR:P3HT (1:1) solar cells alongside normalised thin film absorption spectra of blends (dotted lines).](image)

Table 4.2: Photovoltaic Performance of Optimised IDTBR:P3HT (1:1) Solar Cells. (Average values shown in parenthesis were obtained from 8-10 devices.)

<table>
<thead>
<tr>
<th></th>
<th>( J_{sc} ) (mA cm(^{-2} ))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-IDTBR:P3HT</td>
<td>14.1 (13.9±0.2)</td>
<td>0.73 (0.72±0.01)</td>
<td>0.62 (0.60±0.03)</td>
<td>6.38 (6.30±0.10)</td>
</tr>
<tr>
<td>EH-IDTBR:P3HT</td>
<td>12.2 (12.1±0.1)</td>
<td>0.77 (0.76±0.01)</td>
<td>0.64 (0.62±0.02)</td>
<td>6.03 (6.00±0.05)</td>
</tr>
</tbody>
</table>
4.2.6 Morphology of IDTBR:P3HT Blends

Grazing incidence X-ray diffraction (GIXRD) was carried out by Zhengrong Shang to investigate the extent of crystallisation of donor and acceptor in the blends. Figure 4.10 shows the GIXRD patterns of neat O-IDTBR and EH-IDTBR films and 1:1 blends with P3HT, where samples were prepared using the same conditions used for solar cell active layers. It is evident that O-IDTBR forms a more ordered film than EH-IDTBR, with a narrow out-of-plane distribution of crystallites as indicated by the sharp diffraction peaks. In the blend, O-IDTBR crystallites become more isotropically distributed with polycrystalline rings observed in the diffractogram. The peak positions of these rings match with the diffraction peaks of neat O-IDTBR, as can be elucidated from peak analysis and chi-Q plots and shown in Figure 4.11 and 4.12. This suggests that the presence of P3HT may change the crystallite size and distribution of O-IDTBR but does not change its lattice structure. This is in sharp contrast to the GIXRD of FBR:P3HT blends shown in Chapter 3.2.7, which demonstrated no visible crystallisation of the acceptor, and this supports a more phase-separated morphology for the O-IDTBR blends as was the objective.

The neat film of EH-IDTBR demonstrates an out-of-plane peak centered at \( Q_x = 1.69 \text{ Å}^{-1} \) (just visible in Figure 4.10 (c)) as well as several rings in its diffraction pattern. The peak most probably results from a certain portion of “face-on” \( \pi \)-stacking in the EH-IDTBR aggregates, while the rings indicate that the film also contains a considerable amorphous fraction. When EH-IDTBR is blended with P3HT, a new peak appears at around \( Q_x = 0.5 \text{ Å}^{-1} \) (more easily seen in the chi-Q plot, Figure 4.12 (b)) which partially overlaps with the broad P3HT alkyl peak at 0.4 Å\(^{-1}\). This peak does not correspond to any features that can be seen in the neat EH-IDTBR diffraction pattern, suggesting that EH-IDTBR crystallises in a different orientation or a different polymorph when in the presence of P3HT. It should also be noted that the diffraction pattern of P3HT in the blends is the same as that widely reported for pure P3HT films.\(^{194}\)
Figure 4.10: 2D GIXRD of (a) O-IDTBR; (b) O-IDTBR:P3HT (1:1); (c) EH-IDTBR; (d) EH-IDTBR:P3HT (1:1). Films were processed using the same conditions as described for optimised devices (annealed at 130 °C for 10 min).

Figure 4.11: Line cuts from GIXRD chi-Q plots of (a) EH-IDTBR and EH-IDTBR:P3HT blend at 87.5-92.5°; (b) O-IDTBR and O-IDTBR:P3HT blend at 87.5-92.5°; (c) O-IDTBR and O-IDTBR:P3HT blend at 40-50°.
Figure 4.12: Chi-Q plots of (a) EH-IDTBR (b) EH-IDTBR:P3HT; (c) O-IDTBR and (d) O-IDTBR:P3HT. Diffraction intensity is integrated over two ranges of Chi = 87.5-92.5° and 40-50° and plotted against whole wave vector Q.

DSC measurements were also carried out on drop-cast blends of the acceptors with P3HT to further investigate the extent of crystallisation within the blend. The DSC of FBR:P3HT shown in Chapter 3.2.7 only exhibits a melting endotherm for P3HT upon heating, which is broadened and depressed by as much as 20 °C due to the disruption in packing caused by the presence of FBR. However, the lack of any phase transitions relating to the acceptor suggests that there are no pure acceptor domains in this blend. By contrast, the heating cycles of O-IDTBR and EH-IDTBR blends with P3HT (Figure 4.13) show both endothermic (as well as exothermic, in the case of O-IDTBR) transitions from the acceptors in addition to the P3HT melt, indicating that these acceptors are still able to crystallise to some degree in the blend. Furthermore, the melting temperature of P3HT is only depressed by 10 °C in the IDTBR blends, suggesting that the crystallisation of P3HT may be less significantly disrupted by these acceptors compared to FBR and this factor could be advantageous in terms of hole mobility in the blend.
Figure 4.13: DSC first heating cycles of (a) O-IDTBR, O-IDTBR:P3HT (1:1) and P3HT; (b) EH-IDTBR, EH-IDTBR:P3HT (1:1) and P3HT. Measurements were carried out at 5 °C/min under nitrogen on samples drop-cast from CHCl₃ solution. Thermograms are offset vertically for clarity.

4.2.7 Charge Carrier Mobility and Charge Extraction in IDTBR:P3HT Devices

The charge carrier mobility of both donor and acceptor materials in an OPV device can be affected by morphology, field or carrier densities in bulk heterojunction active layers during device operation, therefore to obtain reliable charge carrier mobility measurements of the IDTBR:P3HT blend systems, photo-induced charge carrier extraction in a linearly increasing voltage (photo-CELIV) measurements were conducted (by Derya Baran and Nicola Gasparini). Average performance EH-IDTBR:P3HT and O-IDTBR:P3HT devices (80-90 nm) were used for these measurements which had an active area of 4 mm² (See Chapter 5 for further details). Figure 4.14 shows the photo-CELIV transients of the two systems, recorded by applying a linearly increasing reverse bias pulse of 2 V/60 µs with a delay time (tₐ) of 50 µs. The charge carrier mobility (µ) was calculated from the measured photocurrent transients using the following equation:

\[
\mu = \frac{2d^2}{3At_{max}^2 \left[1 + 0.36 \frac{\Delta j}{j(0)}\right]} \quad \text{if } \Delta j \leq j(0)
\]

where \(d\) is the active layer thickness, \(A\) is the voltage rise speed \(A = dU/dt\), \(U\) is the applied voltage, \(t_{max}\) is the time corresponding to the maximum of the extraction peak, and \(j(0)\) is
the displacement current. The effective mobilities for the charge carriers in the O-IDTBR:P3HT and EH-IDTBR:P3HT blends were found to be $5.4 \pm 0.4 \times 10^{-5}$ cm$^2$/Vs and $5.0 \pm 0.3 \times 10^{-5}$ cm$^2$/Vs, respectively, after averaging over various delay times. The O-IDTBR:P3HT blend shows slightly higher charge carrier density (the integrated area of the photo-CELIV curve at 1 µs delay time) than the branched chain analogue system, therefore a higher $J_{sc}$ would be expected for the O-IDTBR devices, which would be reflected in the overall PCE.

Figure 4.14: (a) Photo-CELIV of IDTBR:P3HT solar cells at 1 µs delay times; $t_{\text{max}}$ (when extraction current is at its max value) for O-IDTBR:P3HT and EH-IDTBR:P3HT is 4.7 and 4.3 µs, respectively; (b) Average charge carrier densities measured in O-IDTBR:P3HT and EH-IDTBR:P3HT devices at open circuit as a function of $V_{oc}$ determined by CE for different bias light intensities.

Charge carrier density ($n$) using charge extraction (CE)$^{197-199}$ measurements were also carried out (Derya Baran and Nicola Gasparini) to investigate the origin of the reduced $V_{oc}$ in O-IDTBR compared to EH-IDTBR solar cells. All samples were operated at $V_{oc}$, but under different background illumination intensities (See Chapter 5), followed by shorting in the dark to enable charge extraction. The average $n$ that was measured as a function of $V_{oc}$ is depicted in Figure 4.14 (b). At equivalent charge densities, O-IDTBR devices exhibit approximately 40 meV lower $V_{oc}$ (see shaded region, corresponding to ca. 1 sun irradiation) relative to EH-IDTBR devices. This shift in $n(V_{oc})$ indicates a 40 meV smaller electronic bandgap for O-IDTBR devices, which is consistent with the reduced open circuit voltage.
(0.73 V) measured for O-IDTBR:P3HT devices compared to EH-IDTBR:P3HT devices (0.77 V). This reduced $V_{oc}$ can be explained by the more ordered microstructure of O-IDTBR:P3HT blends, as indicated by GIXRD and DSC measurements, which results in a reduced electronic bandgap in the bulk.

4.2.8 Photoluminescence Quenching of IDTBR:P3HT Blends

Photoluminescence (PL) studies were carried out by Ching-Hong Tan on the IDTBR:P3HT blends and neat films and the PL quenching efficiency (PLQE) was obtained by comparing the relative emission between the neat and blend films as shown in Figure 4.15. The selected range in the PL measurement is mainly focused on the IDTBR emission wavelength. The films were excited at 680 nm in order to selectively excite the IDTBR acceptors, with the PL quenching assigned to hole transfer from IDTBR excitons to P3HT. For the branched chain system, the PL of the acceptor is quenched with 89% efficiency, suggesting reasonably efficient hole transfer from acceptor excitons to the P3HT. For the linear chain analogue O-IDTBR, a modest decrease in PLQE (83%) is observed, indicating that the greater degree of crystallinity of O-IDTBR allows for the formation of pure acceptor domains on a lengthscale that is comparable to the exciton diffusion length of O-IDTBR. This is in contrast to the almost quantitative acceptor PL quenching that was observed for FBR:P3HT blends as reported in Chapter 3.2.6, supporting the theory that both IDTBR acceptors exhibit more pronounced phase separation compared to FBR.
Figure 4.15: Photoluminescence spectra of (a) EH-IDTBR, P3HT and EH-IDTBR:P3HT (1:1); (b) O-IDTBR, P3HT and O-IDTBR:P3HT (1:1) blends all excited at 680 nm. Note that P3HT does not absorb at this excitation wavelength. Neat films were measured as-cast and blend films were annealed at 130 °C for 10 min. All spectra are corrected for film absorption.

4.2.9 Charge Generation and Recombination Dynamics of IDTBR:P3HT Blends

Femtosecond-nanosecond transient absorption spectroscopy (TAS) was used to study the charge generation process, as detailed in Chapter 5 (Ching-Hong Tan and Stoichko Dimitrov). Transient spectra of EH-IDTBR and O-IDTBR blends are given in the Appendix, wherein the acceptors are selectively excited at 680 nm. The neat EH-IDTBR and O-IDTBR films were also excited using the same excitation wavelength and density. Because of the spectral overlap of exciton and polaron signals, the spectra were analysed by deconvolution of the blend spectra from the neat P3HT, neat IDTBR and polaron spectra at selected time delays. Deconvolution of the blend spectra using the neat data allowed the temporal evolution of the polaron signal to be extracted, as shown in Figure 4.16. For both blends, polaron growth kinetics were observed on a similar timescale to acceptor exciton decay. This indicates reasonably efficient charge separation from IDTBR excitons which is consistent with the photocurrent generation from IDTBR light absorption observed in the EQE data (Figure 4.9 (b)). The rise of the polaron signal, and decay of acceptor absorption, were fitted to single exponential functions. For EH-IDTBR:P3HT, the polaron rise kinetics, and decay kinetics of EH-IDTBR exciton absorption, primarily exhibit time constants of 10-20 ps. Only a small fraction (10-20%) of the polaron generation appears to occur within the instrument response. By contrast, for the FBR:P3HT blends at least 50% of polaron
generation was observed to be instrument response limited, which is consistent with a more phase segregated morphology for EH-IDTBR compared to FBR. Slower polaron formation and exciton decay is observed for O-IDTBR:P3HT (60-120 ps), indicating more delayed polaron generation for this blend which is consistent with our PLQE results. Relatively slow (100s of picoseconds) polaron generation has previously been reported from acceptor excitons in polymer:PC_{60}BM blends, and this was correlated with exciton diffusion within pure PC_{60}BM domains to the donor-acceptor interface.\textsuperscript{23,200} Therefore it appears likely that the slow polaron generation kinetics observed herein are also limited by the kinetics of exciton diffusion within pure IDTBR domains, which is again consistent with a more phase separated blend morphology relative to P3HT:FBR. Charge recombination is also apparent in Figure 4.16 with the decay of the polaron signal at longer time delays. These kinetics appear to be slower for O-IDTBR compared to EH-IDTBR, which can again be associated with greater phase segregation in the O-IDTBR:P3HT blend.

Figure 4.16: Rise and decay of photogenerated EH-IDTBR and O-IDTBR polaron absorption, obtained by deconvolution of ultrafast transient absorption spectra of the EH-IDTBR:P3HT and O-IDTBR:P3HT films excited at 680 nm, 2 \(\mu\)J cm\(^{-2}\). Films were fabricated according to device active layer spin-coating conditions with annealing at 130 °C for 10 min.
4.2.10 IDTBR:P3HT Solar Cell Stability

In terms of the technological implementation of OPV materials, oxidative stability is an essential consideration as discussed already in Chapter 1.4.5. For many of the record high efficiencies reported in recent years using low bandgap polymers, all aspects of the device fabrication and measurement must be carried out under inert conditions in order to achieve these impressive results. By contrast, the efficiencies reported herein for IDTBR:P3HT devices were obtained for devices that were processed and measured in air, except for a brief thermal annealing step which was carried out in a nitrogen glovebox. This improved stability is partly due to the inverted architecture used, which means that there is no need for encapsulation of these devices. For some conventional cells, by contrast, the use of reactive metals such as Ca as the top electrode can result in efficiencies of zero after a few days of storage in air without encapsulation, in addition to the degradation caused by the acidic PEDOT:PSS electron-blocking layer. In order to further investigate the stability of O-IDTBR:P3HT devices to air, aging measurements were carried out alongside a reference PC<sub>60</sub>BM:P3HT device, as well as devices fabricated using the polymers: PTB7, PCE-10 and PCE-11, which are three of the most widely reported high efficiency polymers. The active layer recipes used for these polymer-fullerene devices were the optimised procedures taken from the literature or from the polymer supplier, as detailed in Chapter 5. All cells were fabricated in an inverted architecture to provide a fair comparison. After the initial (stabilised PCE) measurement was taken, solar cells were stored in the dark under ambient conditions between measurements, in line with the ISOS-D-1 shelf storage protocols for OPV stability testing. Subsequent PCE values were normalised to the corresponding initial values and plotted against air exposure time, as presented in Figure 4.17 alongside the relevant polymer structures. The absolute PCE values are plotted in the Appendix. It is clear from this data that O-IDTBR:P3HT devices demonstrate the least degradation out of the materials studied. Indeed, after an initial drop in performance within the first 60 hours, the PCE remains relatively stable with only a slight reduction in efficiency and even after 1200 hours in air, the PCE was still 73% of its initial value. By contrast, the efficiency of all of the high performance donor polymer devices had fallen to zero after this time. This may be partly due to degradation caused by 1,8-diiodooctane (DIO), which is required here to
control the morphology, in particular the aggregation of PC$_{70}$BM, in these devices.$^{107}$ Table 4.3 lists the initial and final PCE values for the devices measured along with their T$_{80}$ and T$_{50}$ lifetimes, which are defined as the time taken from the beginning of the decay period until the efficiency reaches 80% and 50% of its initial value, respectively.$^{203}$ The O-IDTBR:P3HT devices display significantly improved lifetimes, with a T$_{80}$ of 808 hours compared with only 8.5 hours for the least stable PCE-10 and PCE-11 devices. It is also significantly longer than the reference PC$_{60}$BM:P3HT device which exhibited a T$_{80}$ of 69 hours. This further demonstrates the potential of this new acceptor design to feature in scalable, stable solar cells with practical working lifetimes. Additional studies under illumination would be useful to determine the device stability under operating conditions.

**Figure 4.17:** Oxidative stability of O-IDTBR:P3HT device efficiencies (normalised PCE) in comparison with PC$_{60}$BM:P3HT and high performance polymer:fullerene systems (polymer structures shown). Devices were stored under ambient conditions in the dark between measurements. Dotted lines correspond to normalised PCE values at T$_{80}$ and T$_{50}$. 

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Table 4.3: Oxidative Stability of O-IDTBR:P3HT Devices in Comparison with Selected Polymer-Fullerene Devices.

<table>
<thead>
<tr>
<th></th>
<th>Initial PCE (%)</th>
<th>( T_{80} ) (hr)</th>
<th>( T_{50} ) (hr)</th>
<th>PCE 1200 hr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PC}_{60}\text{BM:P3HT (1:1)} )</td>
<td>3.50</td>
<td>69</td>
<td>1182</td>
<td>1.35</td>
</tr>
<tr>
<td>O-IDTBR:P3HT (1:1)</td>
<td>5.85</td>
<td>808</td>
<td>(-)*</td>
<td>4.29</td>
</tr>
<tr>
<td>( \text{PC}_{70}\text{BM:PTB7 (1:1.5)} )</td>
<td>5.05</td>
<td>43</td>
<td>188</td>
<td>(-)**</td>
</tr>
<tr>
<td>( \text{PC}_{70}\text{BM:PCE-10 (1:1.5)} )</td>
<td>8.90</td>
<td>8.5</td>
<td>78</td>
<td>(-)**</td>
</tr>
<tr>
<td>( \text{PC}_{70}\text{BM:PCE-11 (1:1.4)} )</td>
<td>8.45</td>
<td>8.5</td>
<td>78</td>
<td>(-)**</td>
</tr>
</tbody>
</table>

*PCE did not fall to 50% of initial value within time period measured. **No photodiode behaviour.

In addition to oxidative stability, the morphological stability of the O-IDTBR:P3HT blends was investigated. One of the problems with many fullerene based acceptors is the growth of large scale aggregates or crystallites over time from the meta-stable blend morphology. This aggregation process is often investigated using polarised optical microscopy during accelerated aging of the films with thermal annealing.\textsuperscript{123,163} For this study, films of O-IDTBR:P3HT and \( \text{PC}_{60}\text{BM:P3HT} \) were prepared on ZnO/ITO substrates according to device active layer parameters and these films were subjected to annealing at 140 °C for 1 hr. As shown in the micrographs in Figure 4.18, large (1-20 \( \mu \)m) aggregates appear after 1 hr annealing of the fullerene blend, whereas the O-IDTBR blend remains smooth and featureless after annealing, indicating that this new acceptor offers improved morphological stability over fullerene acceptors, at least in terms of lateral diffusion within the time limits of experiment.
4.3 Conclusions

In this Chapter, a new small molecule electron acceptor IDTBR was presented which is based on an indacenodithiophene core with benzothiadiazole and rhodanine flanking groups. The planarity of the molecule and delocalised electronic structure of this molecule, along with the push-pull molecular orbital hybridisation owing to the electron rich and electron poor moieties, results in a low bandgap material for which the thin film absorption is highly complementary to that of the donor polymer P3HT. This is in contrast to the fluorene based acceptors discussed in Chapter 3, for which the twisted molecular structure resulted in a relatively wide-bandgap material with almost the same absorption profile as P3HT. Because of this complementary absorption, significantly broader photon harvesting is achieved across the incident solar spectrum in the active layer for IDTBR:P3HT solar cells, which is reflected in higher short circuit currents and power conversion efficiencies relative to FBR:P3HT devices. Furthermore, the absorption onset in the solid state of this new IDTBR acceptor can be tuned by judicial choice of solubilising alkyl chains on the IDT unit. Linear (O-IDTBR) chains promote stronger intermolecular packing relative to branched (EH-IDTBR) chains, and thermal annealing can be used to enhance this self-aggregation. One
result of this is to further red-shift the absorption of O-IDTBR relative to the branched counterpart, giving a broader EQE profile, higher $J_{sc}$ and increased PCE from 6.0% to 6.4%, which is the highest efficiency reported for non-fullerene devices with P3HT as the donor. Charge extraction measurements at the same light intensity reveal that the electronic bandgap of O-IDTBR is smaller than that of EH-IDTBR, which can explain the slight difference in $V_{oc}$ measured for the different IDTBR derivatives. As well as affecting the optoelectronic properties, the enhanced intermolecular interactions of IDTBR also change the blend morphology. Compared to FBR, both IDTBR acceptors exhibit significantly increased crystallinity and the formation of ‘pure’ acceptor domains as evidenced by GIXRD and DSC studies. O-IDTBR in particular shows pronounced crystal packing upon annealing, which can explain the reduced optical bandgap. This crystallisation results in greater phase segregation for the linear analogue, which is in turn manifested in reduced PL quenching of the acceptor emission for the O-IDTBR:P3HT blend, as well as a delayed polaron generation and slower recombination dynamics. In addition, these new materials were shown to be more air stable relative to the benchmark P3HT:PC$_{60}$BM device, and significantly more stable compared to devices made with the widely published low bandgap donor polymers: PTB7, PCE-10 and PCE-11, which give very high performance initially (up to 8.9% PCE) but degrade very quickly when exposed to air. Indeed, while these devices had all stopped working after the time period under measurement (1200 hrs), the O-IDTBR:P3HT cells still retained 73% of their initial PCE, further demonstrating the potential of these active layer materials for stable, commercialisable OPV technology in the future. In addition, optical microscopy revealed superior morphological stability for O-IDTBR blends with P3HT compared to PC$_{60}$BM blends, in terms of reduced lateral diffusion of the acceptor with thermally accelerated aging.

Finally, it is worthwhile to mention some other recently published research employing IDT-based small molecule acceptors. In this work, the IDT core is solubilised with bulky 4-hexylphenyl side-chains in order to reduce the degree of self-aggregation of the rigid, planar backbone. When electron deficient 2-(3-oxo-2,3-dihydroindene-1-ylidene)-malononitrile flanking groups are employed on the periphery, these materials demonstrated narrow optical
bandgaps and power conversion efficiencies of 6.3% paired with the high performance donor polymer PTB7-Th (PCE-10).

Very recently, derivatives of this acceptor with BT and 3-ethyl rhodanine flanking groups, following the same design as IDTBR, gave 5.1% PCE with P3HT as the donor. The slightly inferior device performance reported for these blends may be related to the slightly bulkier 4-hexylphenyl side-chains, which reduce the ability of the small molecule to self-aggregate in the way that the n-octyl derivatives reported herein are able. Nevertheless, it is encouraging to observe that high efficiencies are obtained from this acceptor design despite using different side-chains and even when the materials were synthesised and tested in other labs, illustrating that this is a robust molecular design.
Chapter 5:

Experimental Procedures
5.1 Materials and General Methods

All reagents and solvents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Acros Organics or TCI) and used as received, unless otherwise stated. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (Chapter 3) was synthesized by M. Kirkus according to literature procedures.\textsuperscript{143,144} 2,7-Dibromo-4,9-dihydro-4,4,9,9-tetraoctyl-s-indaceno[1,2-b:5,6-b']-dithiophene and 2,7-dibromo-4,9-dihydro-4,4,9,9-tetra(2-ethylhexyl)-s-indaceno[1,2-b:5,6-b']-dithiophene (Chapter 4) were synthesised by A. Wadsworth following literature procedures.\textsuperscript{175,178} P3HT for OPV devices was obtained from Flexink ($M_n$ ca. 40 kDa) and PC$_{60}$BM for reference samples/devices was purchased from Nano-C. PCE-10 and PTB7 were purchased from Ossila for the oxidative stability studies in Chapter 4. All reactions were carried out in an inert argon atmosphere using conventional Schlenk techniques unless otherwise stated.

5.2 Synthetic Procedures for Chapter 2

\begin{figure}
\centering
\includegraphics[width=0.2\textwidth]{1_1.png}
\caption{5-bromo-indan-1-one (5 g, 23.8 mmol) was dissolved in CHCl$_3$ (75 ml), giving a dark brown solution to which bromine (7.6 g, 47.5 mmol) was added dropwise with vigorous stirring. Stirring was continued for 2 h and argon was then bubbled through the solution into a bubbler of Na$_2$S$_2$O$_3$ (aq) for 2 h in order to remove excess bromine. The solvent was removed \textit{in vacuo} to give pale brown crystals which were washed with EtOH and dried to give 1.1 in 81\% yield (7.2 g). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.1$ Hz, 1H), 7.64 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.59 (s, 1H), 4.26 (s, 2H).}
\end{figure}
1.2: A flask containing 1.1 (7.0 g, 19 mmol) was connected to a Na$_2$S$_2$O$_3$ (aq) bubbler and heated with stirring at 220 °C for 1.5 h, after which gas evolution ceased. After cooling to room temperature, the solid was dispersed in 40 ml CH$_2$Cl$_2$ with 5 min ultrasound treatment; the product was then filtered off and washed twice more with CH$_2$Cl$_2$ and dried to give 1.0 g (26% yield) of insoluble yellow solid 1.2 which was used in the next step without further purification.

1.3: 1-bromo-4-hexyl benzene (5.0 g, 20.5 mmol) was dissolved in THF (80 ml) under argon and cooled to -78 °C for 30 min. 1.6 M n-BuLi in hexane was added (15.5 ml, 25 mmol) and the mixture stirred for a further 30 min before 4,4,5,5-tetramethyl-2-(propan-2-yloxy)-1,3,2-dioxaborolane (5 ml, 25 mmol) was added. The reaction was allowed to return to room temperature whilst stirring for 12 h, after which it was poured into iced water and extracted with diethyl ether, washed with water and brine, dried over MgSO$_4$ and the solvent removed in vacuo. The crude product was purified by column chromatography in 3:2 hexane: diethyl ether to afford 1.3 as a colourless liquid (4.08 g, 69%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91–7.65 (m, 2H), 7.23–7.11 (m, 2H), 2.75–2.53 (m, 2H), 1.72–1.51 (m, 2H), 1.31 (dt, J = 4.2, 2.6 Hz, 6H), 0.90 (td, J = 7.1, 3.7 Hz, 3H).
PHTr: A solution of 1.2 (0.8 g, 1.3 mmol) and 1.3 (2.23 g, 9.0 mmol) in THF (80 ml) was degassed with argon for 30 min, while a 2M K$_2$CO$_3$(aq) solution was also degassed with argon. Pd(PPh$_3$)$_4$ (0.18 g, 0.13 mmol) was added to the reaction flask and after degassing for a further 20 min, the K$_2$CO$_3$ (aq) solution (34 ml) was added and the reaction mixture was heated at 60 °C for 12 h. After cooling to room temperature, the reaction was poured into water and extracted with CHCl$_3$, washed with brine, dried over MgSO$_4$ and the solvent removed in vacuo. Flash column chromatography on silica gel with CHCl$_3$ as the eluent, followed by recrystallisation from MeOH/toluene have the product PHTr as a yellow waxy solid (0.58 g, 45 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.47 (d, J = 1.5 Hz, 3H), 7.73 (d, J = 7.8 Hz, 3H), 7.68 – 7.64 (m, 2H), 7.62 (dd, J = 7.8, 1.5 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H).

6CN-PHTr: Malononitrile (0.12 g, 1.82 mmol) and PHTr (0.11 g, 0.127 mmol) were dissolved in dry chlorobenzene (10 ml). Pyridine (0.2 ml, 2.5 mmol) and TiCl$_4$ (0.14 ml, 1.4 mmol) were added and the reaction mixture was heated at 110 °C for 22 h after which the temperature was raised to reflux (145 °C) for a further 2 h. The reaction was then quenched.
with water and extracted with CH₂Cl₂, washed with brine, dried with MgSO₄ and the solvent removed in vacuo. The crude material was purified by column chromatography (1:2 hexane:CH₂Cl₂) to give 6CN-PHTr as a dark red solid (28 mg, 15%). ¹H NMR (400 MHz, CDCl₃) δ: 8.48 (d, J = 8.2 Hz, 3H), 7.84 (d, J = 1.7 Hz, 3H), 7.78 (dd, J = 8.3, 1.5 Hz, 3H), 7.64–7.55 (m, 6H), 7.38 (d, J = 8.2 Hz, 6H), 2.81–2.54 (m, 6H), 1.76–1.61 (m, 6H), 1.41–1.29 (m, 12H), 0.93–0.88 (m, 9H).

**FFTr**: 1.2 (0.1 g, 1.6 mmol) and 9,9-dioctyfluorene 2-boronic acid pinacol ester (0.5 g, 0.97 mmol) were dispersed in THF (20 ml) degassed with argon for 30 min, meanwhile a 2M K₂CO₃(aq) solution was degassed with argon. Pd(PPh₃)₄ (18.5 mg, 0.016 mmol) was added to the reaction flask which was then degassed for a further 10 min. The K₂CO₃(aq) solution (4.2 ml) was then added and the reaction mixture was heated at 60 °C for 12 h. After cooling to room temperature, the reaction was poured into water, extracted with CHCl₃, washed with brine and dried over MgSO₄ and the solvent removed in vacuo. Flash column chromatography on silica gel with hexane:CHCl₃ (1:3) as the eluent, followed by recrystallisation from EtOH/CH₂Cl₂ yielded 0.13 g (53 %) of FFTr as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 3H), 7.99 (d, 3H), 7.90 (m, 9H), 7.79 (m, 6H), 7.38 (m, 9H), 1.5-1.1 (m, 84H), 0.8 (s, 18H).
**6CN-FFTr**: A solution of FFTr (0.1 g, 0.064 mmol) and malononitrile (60 mg, 0.9 mmol) in chlorobenzene (12 ml) was cooled to 0 °C. TiCl$_4$ (0.07 ml, 0.64 mmol) and pyridine (0.1 ml, 1.2 mmol) were then added dropwise. After 30 min, a further 80 mg (1.2 mmol) malononitrile was added and the mixture was stirred overnight at 110 °C. The reaction was then cooled to room temperature, quenched with water (20 ml), extracted with CH$_2$Cl$_2$, washed with water and brine and dried over MgSO$_4$. The crude material was purified by column chromatography with 1:1 hexane:CH$_2$Cl$_2$ as the eluent to yield 6CN-FFTr as dark red solid (45 mg, 42 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (d, 3H), 8.0 (d, 3H), 7.92 (m, 9H), 7.81 (m, 6H), 7.71 (m, 9H), 7.41 (m, 12H), 1.5-1.2 (m, 84H), 0.81 (s, 18H).

### 5.3 Synthetic Procedures for Chapter 3.2

**3.1**: N-Thionyl aniline (10.1 ml, 90 mmol) was added drop-wise to a solution of 2,3-diaminotoluene (5.0 g, 41 mmol) in toluene (60 ml) and the mixture was heated at 90-100 °C for 2 h, with the reaction monitored by thin layer chromatography (2:1 hexane:EtOAc) to ensure full conversion of the starting material. The solvent was then removed in vacuo and the residue was redissolved in CH$_2$Cl$_2$, washed with 2M HCl, water, brine and dried over MgSO$_4$, followed by removal of the solvent. The crude product was purified by column chromatography on silica gel (3:1 hexane:EtOAc) to yield **3.1** as a colourless oil (5.05 g,
\[ \text{1H NMR (400 MHz, CDCl3)} \delta: 7.82 (d, J = 8.8 \text{ Hz, 1H}), 7.47 (dd, J = 8.9, 6.7 \text{ Hz, 1H}), 7.33 (dt, J = 6.6, 1.4 \text{ Hz, 1H}), 2.74 (s, 3H). \]

3.2: Bromine (2.46 ml, 48 mmol) was added slowly to a solution of 3.2 (7.2 g, 48 mmol) in 50 ml HBr (47% aq). The reaction mixture was heated to 80 °C for 30 min after which time a solid had precipitated; heating at 130 °C was then continued overnight. The reaction was neutralized with Na\(_2\)SO\(_3\) (aq) solution, extracted with CH\(_2\)Cl\(_2\) and dried over MgSO\(_4\) to give 3.2 as a pale yellow solid (6.5 g, 59%). \[ \text{1H NMR (400 MHz, CDCl3)} \delta: 7.73 (d, J = 7.4 \text{ Hz, 1H}), 7.27 (d, J = 7.0 \text{ Hz, 1H}), 2.70 (s, 3H). \]

3.4: A mixture of 3.3 (5.5 g, 24 mmol), N-bromosuccinimide (12.8 g, 72 mmol) and benzoyl peroxide (1.16 g, 4.8 mmol) were dissolved in chlorobenzene (50 ml) and stirred overnight at 80 °C. After cooling to room temperature, the succinimide precipitate was removed by filtration and water was added to the filtrate which was then extracted with CH\(_2\)Cl\(_2\) and dried over MgSO\(_4\). Column chromatography on silica gel with hexane/CH\(_2\)Cl\(_2\) (9:1) as eluent followed by recrystallization from EtOH afforded 3.4 as a white crystalline solid (5.3 g, 57%). \[ \text{1H NMR (400 MHz, CDCl3)} \delta: 7.97-7.91 (m, 2H), 7.41 (s, 1H). \]
3.5: A solution of **3.4** (3 g, 7.8 mmol) in 95% formic acid (30 ml) was refluxed at 110 °C for 2 h, then cooled to room temperature and poured into water. The resulting precipitate was filtered and washed with water until the filtrate was of neutral pH, then dried to give **3.5** as an off-white crystalline solid (1.75 g, 93%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 10.74 (s, 1H), 8.09 (s, 1H, $J$ = 7.7Hz), 8.06 (d, 1H, 7.6Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 188.38, 154.08, 152.39, 132.11, 131.73, 126.89, 121.94.

![Diagram of 3.5](image)

3.6: A solution of **3.5** (0.78 g, 3.2 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.90 g, 1.4 mmol) in THF (30 ml) was degassed for 1 h before addition of Pd(PPh$_3$)$_4$ (60 mg, 0.04 eq) and subsequent degassing for 1 hr. K$_2$CO$_3$ solution (1M, 5 ml) was then added and the reaction was heated under argon at 80 °C overnight. After cooling to room temperature, the reaction was quenched with water and extracted with CH$_2$Cl$_2$. Flash column chromatography on silica gel with CH$_2$Cl$_2$ as the eluent, followed by recrystallization from CH$_2$Cl$_2$/hexane, afforded **3.6** as a yellow solid (0.35 g, 49%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 10.81 (s, 2H), 8.35 (d, $J$ = 7.3 Hz, 2H), 8.10-7.96 (m, 8H), 2.15-2.11 (m, 4H), 1.18-1.11 (m, 20H), 0.89-0.80 (m, 4H), 0.76 (t, J=6.8 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: δ 188.99, 153.93, 152.07, 141.79, 140.83, 135.76, 132.55, 128.94, 126.88, 126.25, 124.46, 120.51, 55.67, 40.14, 31.79, 30.00, 29.21, 24.00, 22.59, 14.04.
**FBR**: 3-Ethylrhodanine (0.24 g, 1.47 mmol) and 7 (0.35 g, 0.49 mmol) were dissolved in tert-butyl alcohol (15 ml) by gentle heating. Piperidine (2 drops) was then added and the mixture heated at 85 °C overnight. After cooling to room temperature, the crude product was purified by flash column chromatography on silica gel (CH$_2$Cl$_2$) followed by recrystallization from CH$_2$Cl$_2$/ethanol, yielding FBR as a dark red solid (0.38 g, 78%); mp = 190-201 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.57 (s, 2H), 8.08 (dd, $J =$ 7.8 Hz, 1.7 Hz, 2H), 8.04 (d, $J =$ 1.4 Hz, 2H), 7.94 (d, $J =$ 7.8 Hz, 4H), 7.82 (d, $J =$ 7.5 Hz, 2H), 4.26 (q, $J =$ 7.1 Hz, 4H), 2.14-2.10 (m, 4H), 1.34 (t, $J =$ 7.1 Hz, 6H), 1.19-1.10 (m, 10H), 0.89-0.82 (m, 4H), 0.77 (t, $J =$ 6.8 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 193.16, 167.52, 154.61, 153.54, 152.03, 141.54, 136.97, 135.80, 131.08, 128.68, 127.59, 127.30, 125.68, 125.60, 124.17, 120.43, 55.61, 40.18, 39.97, 31.81, 30.03, 29.22, 24.01, 22.60, 14.06, 12.33. MS (MALDI-TOF): m/z calc for C$_{53}$H$_{56}$N$_6$O$_2$S$_6$ 1000.3; found 1002.4 (M$^+$ +1).

### 5.4 Synthetic Methods for Chapter 3.3

**3.7**: Malononitrile (0.70 g, 10.6 mmol) and ethyl isothiocyanate (1.0 ml, 11.6 mmol) were dissolved in acetonitrile (40 ml). 1,8-Diazabicyclo[5.4.0]indene-7-ene (DBU) (1.6 ml, 10.6 mmol) was added and the mixture was stirred for 30 min before ethyl 2-bromoacetate (2.0 ml, 18.0 mmol) was added slowly. After stirring at room temperature for 1 h, the mixture was heated at reflux for 3 h then stirred at room temperature overnight. The solvent was
removed in vacuo and the mixture was acidified with 2 M HCl (50 ml), then extracted twice with CHCl₃ (2 x 50 ml). The organic phase was washed with water and brine, dried over MgSO₄ and the solvent removed in vacuo. Recrystallisation from hexane/CH₂Cl₂ afforded 3.7 as dark yellow crystals (1.24 g, 61%). ¹H NMR (400 MHz, CDCl₃) δ 4.19 (q, 2H), 4.00 (s, 2H), 1.36 (t, 3H). ¹³C NMR (101 MHz, CDCl₃) δ: 171.50, 171.44, 112.78, 111.65, 56.57, 40.67, 32.38, 13.96. MS (ES-ToF): m/z calc for C₈H₇N₃O₈ 193.03; found 192.02.

**CN-FBR:** A solution of 3.6 (0.15 g, 0.21 mmol) and 3.7 (0.12 g, 0.63 mmol) in t-BuOH (15 ml) was heated gently to dissolve the starting materials, before piperidine (2 drops) was added and the reaction was then heated overnight at 85 °C. After cooling to room temperature, the mixture was poured into water and extracted with CH₂Cl₂, washed with water and brine, and purified twice by flash column chromatography on silica gel with CH₂Cl₂. The product was then precipitated from CH₂Cl₂/MeOH to give **CN-FBR** as a dark red solid (0.19 g, 83%). ¹H NMR (400 MHz, CDCl₃) δ: 8.69 (s, 2H), 8.10 (dd, 2H), 8.06 (d, 2H), 8.04 (q, 8H), 4.39 (q, 4H), 2.32–1.94 (m, 4H), 1.46 (t, 6H), 1.20–1.05 (m, 16H), 0.90–0.81 (m, 6H), 0.76 (t, 6H); ¹³C NMR (101 MHz, CDCl₃) δ: 14.04, 14.20, 22.58, 24.02, 29.21, 30.02, 31.77, 40.16, 40.75, 55.66, 56.35, 112.09, 112.99, 119.18, 120.56, 124.26, 124.62, 127.51, 128.79, 131.43, 132.35, 135.60, 138.09, 141.73, 152.14, 153.55, 154.15, 166.06, 166.29.
3.8: A solution of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (2.50 g, 3.89 mmol) in dimethoxyethane (20 ml) was degassed for 1 hr before addition of 5-bromo-2-thiophenecarboxaldehyde (1.39 ml, 11.7 mmol) and Pd(PPh₃)₄ (0.22 g, 0.19 mmol). After further degassing for 1 hr, an already degassed Na₂CO₃ solution (2M) was added (12 ml) and the mixture was heated overnight at 90 °C. The reaction was then cooled to room temperature and extracted with CH₂Cl₂, dried over MgSO₄ and the solvent removed in vacuo. Flash column chromatography on silica gel (CH₂Cl₂) followed by recrystallization from CH₂Cl₂/methanol gave 3.8 as a yellow solid (1.8 g, 76%). 

1H NMR (400 MHz, CDCl₃) δ: 9.91 (s, 2H), 7.78-7.75 (m, 4H), 7.70 (dd, J = 8.2 Hz, 1.8 Hz, 2H), 7.64 (d, J = 1.6 Hz, 2H), 7.49 (d, J = 3.9 Hz, 2H), 2.05-1.97 (m, 4H), 1.15-1.02 (m, 20H), 0.78 (t, J = 7 Hz, 6H), 0.70-0.61 (m, 4H). 

13C NMR (101 MHz, CDCl₃) δ 182.68, 154.78, 152.27, 142.27, 141.64, 137.40, 134.59, 132.43, 125.73, 124.05, 120.79, 120.72, 55.57, 40.21, 31.74, 29.88, 29.14, 23.77, 22.57, 14.03.

FTR: 3-Ethylrhodanine (0.12 g, 0.74 mmol) and 3.8 (0.15 g, 0.25 mmol) were dissolved in t-BuOH (15 ml) with gentle heating. Piperidine (1 drop) was added and the mixture was heated overnight at 85 °C. After cooling to room temperature, the crude product was purified by flash column chromatography on silica gel (CH₂Cl₂) followed by recrystallization from CH₂Cl₂/methanol to yield FTR as a red solid (0.16 g, 71%). 

1H NMR (400 MHz, CDCl₃) δ: 8.89 (s, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 1.7
Hz, 2H), 7.46 (dd, J = 20.5 Hz, 4H), 4.21 (q, J = 7.1 Hz, 4H), 2.1-2.06 (m, 4H), 1.31 (t, J = 7.1, 6H), 1.19-1.0 (m, 10H), 0.77 (t, J = 7.0 Hz, 6H), 0.70-0.72 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 192.26, 167.52, 153.25, 152.44, 141.60, 135.69, 132.54, 125.46, 124.87, 120.89, 120.69, 120.32, 55.79, 40.42, 40.11, 31.90, 30.01, 29.62, 29.31, 23.92, 22.72, 14.18, 12.45.

**CN-FTR:** A solution of 3.7 (0.14 g, 0.74 mmol) and 3.8 (0.15 g, 0.25 mmol) in t-BuOH (15 ml) was gently heated to dissolve. Piperidine (1 drop) was added and the reaction mixture was heated overnight at 85 °C. After cooling to room temperature, the reaction was poured into water and extracted with CHCl$_3$, then washed with water and brine and dried over MgSO$_4$. Purification by flash column chromatography on silica gel (CHCl$_3$) followed by recrystallization from CHCl$_3$/MeOH afforded CN-FTR as a dark red solid (0.24 g, 99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.11 (s, 2H), 7.82–7.71 (m, 4H), 7.64 (d, J = 1.7 Hz, 2H), 7.56–7.50 (m, 4H), 4.35 (q, J = 7.2 Hz, 4H), 2.14 (dd, J = 10.7, 5.9 Hz, 4H), 1.43 (t, J = 7.1 Hz, 6H), 1.17–0.99 (m, 10H), 0.76 (t, J = 6.9 Hz, 6H), 0.64 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 173.86, 165.98, 165.59, 154.29, 152.50, 151.60, 141.83, 136.95, 135.69, 132.08, 129.06, 125.67, 125.08, 120.96, 120.23, 113.48, 55.76, 40.73, 40.23, 31.75, 29.81, 29.13, 23.78, 22.57, 14.04.
5.5 Synthetic Procedures for Chapter 4

4.1: A solution of 2,7-dibromo-4,9-dihydro-4,4,9,9-octyl-s-indaceno[1,2-b:5,6-b']-dithiophene (2.11 g, 2.42 mmol) in anhydrous THF (200 mL) was stirred at -78 °C for 30 min. n-BuLi (2.42 mL, 6.04 mmol, 2.5 M in hexanes) was added dropwise and the solution was stirred at -78 °C for 30 min followed by -10 °C for 30 min. After cooling again to -78 °C, trimethyltin chloride was added (7.26 mL, 7.56 mmol, 1M in hexanes) and the solution was allowed to return to room temperature overnight. The reaction was then poured into water and extracted with hexane, washed successively with acetonitrile to remove excess trimethyltin chloride and dried over MgSO₄ to yield 4.1 as a yellow oil (2.18 g, 86%). ¹H NMR (400 MHz, CDCl₃) δ: 7.25 (s, 2H), 6.97 (s, 2H), 1.97-1.91 (m, 4H), 1.86-1.78 (m, 4H), 1.23-1.05 (m, 48H), 0.83-0.80 (t, 12H, J=7Hz), 0.39 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ: 157.15, 153.47, 147.71, 139.24, 135.31, 129.55, 113.42, 53.06, 39.20, 31.87, 30.07, 30.03, 29.31, 24.17, 22.68, 14.14, -8.02. MS (ES-ToF): m/z calculated for C₅₄H₉₀S₂Sn: 1040.45; m/z found 1041.40 (M + H)⁺.

4.2: A solution of 4.1 (1.04 g, 1.0 mmol) and 2,1,3-benzothiadiazole-4-carboxaldehyde 3.5 (0.73 g, 3.0 mmol) in anhydrous toluene (40 mL) was degassed for 45 min before Pd(PPh₃)₄ (58 mg, 0.05 mmol) was added and this solution was heated at 100 °C overnight. The reaction mixture was then cooled and purified by flash column chromatography on silica mixed with potassium fluoride using CHCl₃ as the eluent. Further purification by column chromatography on silica using CH₂Cl₂/pentane (1:1) followed by precipitation from
methanol yielded 4.2 as a dark purple solid (0.93 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 10.72 (s, 2H), 8.27 (s, 2H), 8.25 (d, $J = 7.7$ Hz, 2H), 8.06 (d, $J = 7.5$ Hz, 2H), 7.45 (s, 2H), 2.05 (dt, $J = 59.3$, 12.9, 4.6 Hz, 8H), 1.05-1.2 (m, 38H), 0.99-0.81 (m, 10H), 0.77 (t, $J = 6.8$ Hz, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 188.44, 157.04, 154.02, 152.29, 147.00, 140.67, 136.44, 134.14, 132.87, 131.62, 124.87, 124.8, 122.80, 114.12, 54.43, 39.16, 31.79, 29.98, 29.29, 29.20, 24.29, 22.58, 14.04. MS (ES-ToF): m/z calculated for C62H78N4O2S4: 1038.5; m/z found 1041.40.

O-IDTBR: 4.2 (0.40 g, 0.39 mmol) and 3-ethylrhodanine (186 mg, 1.16 mmol) were dissolved in tert-butyl alcohol (30 mL). 2 drops of piperidine were added and the solution was left to stir at 85 °C overnight. The product was extracted with CHCl$_3$ and dried over MgSO$_4$. The crude product was purified by flash column chromatography on silica in CH$_2$Cl$_2$ and precipitated from methanol. The precipitate was collected and dried by vacuum filtration to afford O-IDTBR a dark blue solid (0.40 g, 78%). mp = 219-221 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.54 (s, 2H), 8.24 (s, 2H), 8.03 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.45 (s, 2H), 4.27 (q, $J = 8.0$ Hz, 4H), 2.18-1.96 (m, 8H), 1.35 (t, $J = 8.1$ Hz, 6H), 1.22-1.12 (m, 40H), 0.99-0.90 (m, 8H), 0.80 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 193.04, 167.59, 157.05, 154.63, 154.22, 151.77, 146.15, 141.02, 136.41, 131.37, 130.54, 127.29, 124.49, 124.25, 124.08, 123.82, 113.97, 54.38, 39.94, 39.19, 31.82, 30.02, 29.33, 29.24, 24.30, 22.61, 14.08, 12.35. MS (MALDI-ToF): m/z calculated for C72H68N6O3S8: 1324.5; m/z found 1326.0 (M + H)$^+$.  

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4.3: A solution of 2,7-dibromo-4,9-dihydro-4,4,9,9-tetra(2-ethylhexyl)-s-indaceno[1,2-b:5,6-b’]-dithiophene (1.09 g, 1.25 mmol) in anhydrous THF (40 mL) was stirred at -78 °C for 30 min. n-BuLi (1.25 mL, 3.12 mmol, 2.5 M in hexanes) was added dropwise and the solution was stirred at -78 °C for 1 hr. Trimethyltin chloride was then added (3.75 mL, 3.75 mmol, 1M in hexanes) and the solution was allowed to return to room temperature overnight. The reaction was then poured into water and extracted with hexane, washed successively with acetonitrile to remove excess trimethyltin chloride and dried over MgSO₄ to yield 4.3 as a yellow oil (1.16 g, 89%). ⁱH NMR (400 MHz, CDCl₃) δ: 7.28 (s, 2H), 6.99 (s, 2H), 1.96-1.88 (m, 8H), 1.87-1.82 (m, 8H), 0.99-0.46 (m, 60H), 0.37 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ: 157.40, 153.43, 147.51, 140.73, 135.20, 130.04, 113.95, 53.52, 43.59, 34.89, 32.20, 29.75, 28.74, 28.10, 22.67, 14.16, -8.16.

4.4: A solution of 4.3 (0.94 g, 0.90 mmol) and 2,1,3-benzothiadiazole-4-carboxaldehyde 3.5 (0.53 g, 2.17 mmol) in anhydrous toluene (30 mL) was degassed for 45 min before Pd(PPh₃)₄ (52 mg, 0.05 mmol) was added and this solution was heated at 110 °C overnight. The reaction mixture was then cooled and purified by flash column chromatography on silica mixed with potassium fluoride using CHCl₃ as the eluent. Further purification by column
chromatography on silica using CH$_2$Cl$_2$/pentane (1:1) followed by precipitation from methanol yielded 4.4 as a dark purple solid (0.40 g, 43%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 10.72 (s, 2H), 8.37-8.30 (m, 2H), 8.25 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 7.5 Hz, 2H), 7.49 (s, 2H), 2.15-2.05 (m, 8H), 1.05-0.85 (m, 40H), 0.74-0.50 (m, 20H). MS (ES-ToF): m/z calculated for C$_{62}$H$_{78}$N$_4$O$_2$S$_4$: 1038.50; m/z found 1038.50 (M$^+$.)

EH-IDTBR: 4.4 (0.20 g, 0.19 mmol) and 3-ethylrhodanine (93 mg, 0.58 mmol) were dissolved in tert-butyl alcohol (15 mL). 1 drop of piperidine was added and the solution was left to stir at 85 ºC overnight. The product was extracted with CHCl$_3$ and dried over MgSO$_4$. The crude product was purified by flash column chromatography on silica with CH$_2$Cl$_2$ as the eluent followed by precipitation from methanol to yield EH-IDTBR as a dark blue solid (0.20 g, 80%). mp = 218-220 ºC. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.53 (s, 2H), 8.27 (m, 2H), 7.99 (m, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.47 (s, 2H), 4.25 (q, J = 8.0 Hz, 4H), 2.07 (m, 8H), 1.34 (t, J = 8.0 Hz, 6H), 0.95-0.90 (m, 36H), 0.69-0.54 (m, 24H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 193.07, 167.58, 156.76, 154.63, 153.93, 151.80, 146.14, 140.46, 136.38, 131.37, 130.64, 127.31, 125.08, 124.51, 124.30, 123.73, 114.82, 54.19, 39.94, 35.13, 34.16, 28.64, 28.25, 27.26, 22.86, 14.18, 12.33, 10.60. MS (MALDI-ToF): m/z calculated for C$_{72}$H$_{88}$N$_6$O$_2$S$_8$: 1324.5; m/z found 1325.9 (M + H)$^+$. 

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5.6 Characterisation Techniques

$^1$H and $^{13}$C NMR spectra were collected on a Bruker AV-400 spectrometer at 298 K and are reported in ppm relative to TMS.

Mass spectrometry was carried out with either electrospray ionisation with time-of-flight detection (ES-ToF) or matrix assisted laser desorption ionisation with time-of-flight (MALDI-ToF).

UV-Vis absorption spectra were recorded on a UV-1601 Shimadzu spectrometer. Solution measurements were carried out in dilute ($10^{-5}$ M) CH$_2$Cl$_2$ (Chapter 2) or CHCl$_3$ (Chapter 3 and 4) solution. Extinction coefficients in solution were calculated by plotting the peak absorption against concentration for measurements at 4-5 different concentrations, and extracting the gradient of the linear fit in Origin. Thin film spectra were measured on films spin-coated onto glass or ITO substrates from CHCl$_3$ or CB solutions.

Cyclic voltammetry (CV) was performed using an Autolab PGSTAT101 potentiostat. For solution measurements (Chapter 2 and Chapter 3), the acceptors were dissolved in anhydrous and deoxygenated CH$_2$Cl$_2$ solution ($3 \times 10^{-4}$ M) with 0.3 M tetrabutylammonium hexafluorophosphate (TBA PF$_6$) as the supporting electrolyte. A three-electrode system consisting of a platinum disk working electrode, platinum mesh counter electrode and Ag/AgCl reference electrode was used, calibrated against ferrocene. Electron affinity (EA) and ionization potential (IP) values were calculated from the equations: $EA = (E_{\text{red}} - EF_c + 4.8) \text{ eV}$ and $IP = (E_{\text{ox}} - EF_c + 4.8) \text{ eV}$, where $E_{\text{red}}$ and $E_{\text{ox}}$ are taken from the onset of reduction and oxidation, respectively, and $EF_c$ is the half-wave potential of ferrocene measured in the same solution. For thin film measurements, the acceptors were spin-coated onto ITO coated glass substrates for use as the working electrode, alongside a platinum mesh counter electrode and Ag/AgCl reference electrode. Measurements were carried out in anhydrous and deoxygenated acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate (TBA PF$_6$) as the supporting electrolyte, and calibrated against ferrocene in solution using a platinum disk working electrode. Ionisation potential (IP) and
electron affinity (EA) values were calculated using the same equations as used for solution measurements.

**Thermal Gravimetric Analysis** (TGA) was carried out on a Pyris 1 Thermogravimetric Analyzer from Perkin Elmer on powder samples (2-4 mg) heated at a rate of 10 °C min⁻¹ under nitrogen.

**Differential Scanning Calorimetry** (DSC) experiments were carried out with a Mettler Toledo DSC822 instrument. Samples were prepared by drop-casting directly into the Al sample pan from CHCl₃ solution and allowing the solvent to evaporate under a flow of nitrogen. Samples were then heated at a heating rate of 5 °C min⁻¹ under nitrogen, except for the samples in Figure 3.4 which were measured at 10 °C min⁻¹ on the powder (not drop-cast) samples.

**Specular X-ray diffraction** (XRD) was carried out using a PANalytical X’Pert PRO MRD diffractometer equipped with a nickel-filtered Cu-Kα₁ beam and X’Celerator detector, using a current of 40 mA and accelerating voltage of 40 kV. Samples were prepared on Si(100) substrates by spin-coating at 600 rpm from CHCl₃ solution, except in Figure 3.4 where samples were drop-cast from CHCl₃ solution.

**Atomic force microscopy** (AFM) was carried out using a Dimension 3100 atomic force microscope in close contact (tapping) mode on the BHJ devices, or on thin films prepared from the same procedure.

**Photovoltaic devices** were fabricated with an inverted architecture (glass/ITO/ZnO/P3HT:Acceptor/MoO₃/Ag). Glass substrates were used with pre-patterned indium tin oxide (ITO). These were cleaned by sonication in detergent, deionized water, acetone and isopropanol, followed by oxygen plasma treatment. ZnO layers were deposited by spin-coating a zinc acetate dihydrate precursor solution (60 μl monoethanolamine in 2 ml 2-methoxyethanol) followed by annealing at 150 °C for 10-15 min, giving layers of 30 nm.
The active layers in Chapter 2 (device data shown in Appendix) were deposited from P3HT:truxenone (1:1) solutions in CB (20 mg ml\(^{-1}\)). Films were spin-coated at 3000 rpm and annealed in a glovebox for 10 min at 110 °C. In Chapter 3, the P3HT:acceptor (1:1) active layers were deposited from 16 mg ml\(^{-1}\) solutions in CHCl\(_3\)/o-DCB (4:1) by spin-coating at 5000 rpm, resulting in active layer thicknesses of approximately 80 nm. These films were then annealed in a glovebox for 15 min at 110 °C. Active layer thicknesses of 90 nm and 100 nm were also tested but these gave no further improvement in device performance. P3HT:PC\(_{60}\)BM (1:1) layers were spin-cast at 1500 rpm from 40 mg ml\(^{-1}\) solutions in o-DCB, followed by annealing in the glovebox at 130 °C for 20 min.

In Chapter 4, The P3HT:IDTBR (1:1) active layers were deposited from 24 mg ml\(^{-1}\) solutions in CB by spin-coating at 2000 rpm, followed by annealing at 130 °C for 10 min. Active layer thicknesses were 75 nm (averaged over 6 devices) for both acceptor blends. P3HT:PC\(_{60}\)BM (1:1) reference devices were prepared as described above.

The active layers used in the stability studies in Chapter 4 were prepared as follows:

**PTB7:PC\(_{70}\)BM (1:1.5):** Active layer solutions (D:A ratio 1:1.5) were prepared in CB with 3% DIO (total concentration 25 mg ml\(^{-1}\)). To completely dissolve the polymer, the active layer solution was stirred on a hot plate at 80 °C for at least 3 h. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N\(_2\) glove box at 1500 rpm.

**PCE-10:PC\(_{70}\)BM (1:1.5):** Active layer solutions (D:A ratio 1:1.5) were prepared in CB with 3% DIO (total concentration 35 mg ml\(^{-1}\)). To completely dissolve the polymer, the active layer solution was stirred on a hot plate at 80 °C for at least 3 h. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N\(_2\) glove box at 1500 rpm.

**PCE-11:PC\(_{70}\)BM (1:1.4):** Active layer solutions (D:A ratio 1:1.4) were prepared in CB/o-DCB (1:1 volume ratio) with 3% DIO (polymer concentration: 10 mg ml\(^{-1}\)). To completely dissolve the polymer, the active layer solution was stirred on a hot plate at 110 °C for at
least 3 h. Before spin-coating, both the polymer solution and ITO substrate are preheated on a hot plate. Active layers were spin-coated from the warm polymer solution on the preheated substrate in a N₂ glove box at 1000 rpm.

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

**Photo-CELIV (charge extraction by linearly increasing voltage)** measurements in Chapter 4 were carried out on P3HT:IDTBR devices illuminated with a 405 nm laser-diode. Current transients were recorded across an internal 50 Ω resistor of an oscilloscope (Agilent Technologies DSO-X 2024A). A fast electrical switch was used to isolate the cell and prevent charge extraction or sweep out during the laser pulse and the delay time. After a variable delay time, a linear extraction ramp was applied via a function generator. The ramp, which was 20 μs long and 2 V in amplitude, was set to start with an offset matching the Voc of the cell for each delay time. The geometrical capacitance is calculated as \( C = \frac{(\varepsilon \cdot \varepsilon_0 \cdot A)}{d} \) where \( A \) is the device area (4 mm²), \( \varepsilon = 3 \) and \( \varepsilon_0 = 8.85 \times 10^{-12} \) F m⁻¹ are the relative and absolute dielectric permittivity, respectively, and \( d \) is the active layer thickness (90 nm). \( C \) is then calculated as 1 nF. Assuming \( R_{load} = 50 \) nm, the \( RC \) value is 5 x 10⁻⁸ s. Assuming the electrical field (E) = 1 x 10⁵ V m⁻¹, the transient time (t) is calculated with the formula \( t = t_{\text{max}} \ast \sqrt{3} = 8 \times 10^{-6} \) s.
Charge extraction (CE) measurements were carried out by illuminating the devices in air with a 405 nm laser diode for 200 μs which was sufficient to reach a constant open-circuit voltage with steady state conditions. At the end of the illumination period, an analog switch was triggered that switched the solar cell from open-circuit to short-circuit (50 Ω) conditions within less than 50 ns. By adjusting the laser intensity, different open-circuit voltages were obtained which allowed a plot of charge carrier density over voltage to be generated. As described by Shuttle et al. a correction was applied for the charge on the electrodes that results from the geometric capacity of the device.

Photoluminescence (PL) Spectroscopy and Transient Absorption Spectroscopy (TAS) samples were spin-coated onto glass using the same conditions as for solar cells. Spectra were measured using a steady state spectrofluorimeter (Horiba Jobin Yvon, Spex Fluoromax 1). The spin-coated films were excited at 680 nm. Sub-picosecond TAS was carried out at 800 nm laser pulse (1 kHz, 90 fs) by using a Solstice (Newport Corporation) Ti:sapphire regenerative amplifier. A part of the laser pulse was used to generate the pump laser at 680 nm, 2 μJ cm⁻² with a TOPAS-Prime (Light conversion) optical parametric amplifier. The other laser output was used to generate the probe light in near visible continuum (450–800 nm) by a sapphire crystal. The spectra and decays were obtained by a HELIOS transient absorption spectrometer (450-1450 nm) and decays to 6 ns. The samples were measured in a N₂ atmosphere.
References


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Appendix

Chapter 2 Supplementary Data

Table S1: Photovoltaic Performance of P3HT:truxenone BHJ Devices

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<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
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Figure S1: Normalised UV-vis absorption spectra of PC$_{60}$BM in CH$_2$Cl$_2$ ($10^{-5}$ M) and thin film spin-coated from CHCl$_3$ solution (10 mg ml$^{-1}$).

Chapter 3 Supplementary Data

Figure S2: TGA of FBR heated at 10 °C/min under nitrogen.
Figure S3: Pico-second timescale transient absorption spectra of P3HT:FBR and P3HT:PC₆₀BM blends and neat P3HT pumped at 600 nm with 4uJ cm⁻² excitation density in (a) 1 ps and (b) 6 ns.

Figure S4: UV-vis absorption of P3HT:FBR and P3HT:FTR blends used for PLQE experiments.

Chapter 4 Supplementary Data

Figure S5: TGA of EH-IDTBR and O-IDTBR measured at 10 °C/min under nitrogen.
Figure S6: Femtosecond-transient absorption spectra of (a), (b) EH-IDTBR:P3HT and (c), (d) O-IDTBR:P3HT blends and pristine counterparts excited at 680 nm with 2\mu J/cm² density at (a), (c) 1 ps (exciton signature) and (b), (d) 6 ns (polaron signature).

Figure S7: Oxidative stability data (PCE) for O-IDTBR:P3HT devices alongside PCBM:P3HT and high performing polymer-fullerene devices.
Single Crystal Data of O-IDTBR

Single Crystal Data and Structure Refinement for O-IDTBR.

Formula C72 H88 N6 O2 S8
Formula weight 1325.96
Temperature 173(2) K
Diffractometer, wavelength Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system, space group Monoclinic, P2₁/c
Unit cell dimensions
  \( a = 13.7663(2) \, \text{Å} \), \( a = 90° \)
  \( b = 15.81032(17) \, \text{Å} \), \( b = 96.2928(12)° \)
  \( c = 32.7146(3) \, \text{Å} \), \( g = 90° \)
Volume, Z 7077.43(15) \, \text{Å}³, 4
Density (calculated) 1.244 Mg/m³
Absorption coefficient 2.709 mm⁻¹
F(000) 2824
Crystal colour / morphology Purple blocky needles
Crystal size 0.30 x 0.06 x 0.03 mm³
q range for data collection 2.718 to 73.557°
Index ranges \(-12 < h < 16, -11 < k < 19, -40 < l < 39\)
Reflns collected / unique 23351 / 13647 [R(int) = 0.0259]
Reflns observed \([F > 4σ(F)]\) 10573
Absorption correction Analytical
Max. and min. transmission 0.930 and 0.681
Refinement method Full-matrix least-squares on \(F^2\)
Data / restraints / parameters 13647 / 270 / 839
Goodness-of-fit on \(F^2\) 1.023
Final R indices \([F > 4σ(F)]\) \(R1 = 0.0647, wR2 = 0.1744\)
R indices (all data) \(R1 = 0.0824, wR2 = 0.1898\)
Largest diff. peak, hole 1.419, -0.564 eÅ⁻³
Mean and maximum shift/error 0.000 and 0.00
Bond lengths [Å] and angles [°] for O-IDTBR.

S(1)-C(18) 1.710(3)
S(1)-C(2) 1.750(3)
C(2)-C(3) 1.385(4)
C(2)-C(19) 1.448(4)
C(3)-C(4) 1.402(4)
C(4)-C(18) 1.375(4)
C(4)-C(5) 1.513(4)
C(5)-C(6) 1.534(4)
C(5)-C(44) 1.542(5)
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S(10)-C(11) 1.751(3)
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C(14)-C(15) 1.537(4)
C(14)-C(77) 1.542(5)
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C(16)-C(17) 1.396(4)
C(17)-C(18) 1.455(4)
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C(19)-C(20) 1.429(4)
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C(20)-C(24) 1.436(4)
N(21)-S(22) 1.610(3)
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