



New Materials for Organic Photovoltaics

by

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Declaration

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Abstract

This thesis has investigated commercialization of organic solar cells with incorporated low cost, high efficiency donor PDCBT polymer and acceptor ITIC small molecular compound materials to improve the efficiency, lifetime of devices, and critically to keep material large scale production cost as low as possible. The thesis includes a review on device performance from new organic photovoltaic materials fabricated in the literature published to date.

Firstly, methodology based on selection of contemporary donor acceptor materials for the upscaled application will be discussed and comparison of these new materials versus benchmark compounds will be introduced.

The large scale organic synthesis of traditional active layer materials such as poly(3-hexylthiophene) P3HT polymer, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM or C₆₀-PCBM), ICxAs fullerenes and poly(3,4-ethylenedioxythiophene):poly(styrene) sulfonate (PEDOT:PSS) conducting polymer is undertaken. Then, PDCBT polymer and ITIC small molecule compounds are synthesised on a small scale and improvements and challenges encountered during the preparation is discussed in terms of translation to large scale synthesis. The characterization of standard P3HT:PCBM and PDCBT:ITIC organic solar cell performance, in contrast to the PDCBT:ITIC NP devices manufactured at the University of Newcastle during the course of this PhD will be examined to demonstrate device efficiency improvements over the time of this research project (2016-2022). Furthermore, to further examine and broaden the understanding of the chemistry and physics of large-scale synthesis, flow chemistry, as a method of production for selected materials is examined this work.

Although, vigorous recent progress has been made in the development of novel photoactive materials and the COE has already demonstrated the economical production of >100 m² of printed organic solar at ~1% power conversion efficiency, the challenge of highly efficient, long lifetime and low-cost material application at large scale production still exists.

Finally, optimisation of bulk heterojunction blend in OPV devices was examined to address existing issue of cost limitation for high performance new generation materials. This thesis demonstrates how we can identify, synthesise, test, and scale up new active layer materials for use in large scale roll-to-roll printed organic BHJ and nanoparticulate solar cells, to improve the power conversion efficiency while maintaining a low cost of the solar modules.

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Abbreviations and Definitions

AFM	Atomic force microscopy
AM1.5	Reference solar spectrum for photovoltaic performance evaluation
Ag	Silver
Al	Aluminium
ASNP	Aqueous Solar Nanoparticles
BHJ	Bulk heterojunction
CPDT	Cyclopenta[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene's
DBP	Dibenzo([f,f0]-4,40,7,70-tetraphenyl)diindeno[1,2,3-cd:10,20,30-Im]perylene
Device	: an organic solar cell
DTBT	Dithieno[30,20:3,4;200,300:5,6]benzo[1,2- <i>c</i>][1,2,5]thiadiazole
DR3TSBDT	Benzo[1,2- <i>b</i> :4,5- <i>b'</i>]dithiophene (BDT)
Efficiency	Power conversion efficiency
EQE	External quantum efficiency
Exciton:	A coulombically bound electron-hole pair
E _g	Bandgap
EtOH	Ethanol
FF	Fill factor
FBT-Th ₄ (1,4)	5,6 – difluorobenzothiadiazole-(1,4- quarterthiophene)
GRIM	Grignard metathesis
HTL	Hole transport layer
¹ H NMR	Proton nuclear magnetic resonance spectroscopy
HOMO	Highest occupied molecule orbital
I _{sc}	Short-circuit current
ITIC	3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3- <i>d</i> :2',3'- <i>d'</i>]-s-indaceno[1,2- <i>b</i> :5,6- <i>b'</i>]dithiophene (ITIC
ITO	Indium-tin oxide
ICBA	Indene: C ₆₀ bisadduct
ICMA	Indene: C ₆₀ monoadducts
ICTA	Indene: C ₆₀ trisadducts
ICxA	Indene: C ₆₀ multiadducts
IPA	Isopropanol

IQE	Internal quantum efficiency
ISC	Short circuit current
I–V	Current-voltage
KWh	Kilowatt hour
J _m	Maximum current density
J _{sc}	Short circuit current density
J–V	Current density–voltage
LBG	Low band gap
LCOE	Levelised cost of electricity
LUMO	Lowest unoccupied molecular orbital
MeOH	Methanol
M _n	Number average molecular weight
M _w	Weight average molecular weight
NP	Nanoparticle
o-DCB	o-Dichlorobenzene
OLED	Organic light emitting diode
OPV	Organic photovoltaic
P3HT	Poly(3-hexylthiophene)
PCBM	[6,6]-phenyl C60-butyric acid methyl ester
PC ₇₀ BM	Phenyl-C ₇₀ -butyric acid methyl ester
PCE	Power conversion efficiency
PE	Photoelectron energy
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PDI:	Polydispersity index
PDCBT	Poly[5,5'- bis(2-butyloctyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-alt-5,5'-2,2'-bithiophene]
PSCs:	Polymer solar cells
PTB1	Poly ((4,8- bis(octyloxy)benzo(1,2-b:4,5-b') dithiophene-2,6-diyl) [2-((dodecyloxy)-carbonyl) thieno(3,4-b) thiophenediyl])
PPDT2FBT	Poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c]-[1,2,5]thiadiazole)]
PTB1	Poly ((4,8- bis(octyloxy)benzo(1,2-b:4,5-b') dithiophene-2,6-diyl) (2-((dodecyloxy)-carbonyl) thieno(3,4-b) thiophenediyl))
PBDB-T-2F (PM6)	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
rr-P3HT	Regioregular-poly(3-hexylthiophene)

R2R	Roll-to-roll
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
STXM	Scanning transmission X-ray microscopy
UVO	UV ozone
UV-vis	UV-visible spectroscopy
V _m	Maximum voltage
V _{OC}	Open circuit voltage
ZnO	Zinc oxide
WBG	Wide band gap
Y6 (BTP-4F)	2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile

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Publications Currently Arising from this Thesis

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Kamilla Sivunova, Warwick Belcher, Natalie Holmes, Furqan Almyahi, Riku Chowdhuri and Paul Dastoor “Novel nanoparticles fabrication from photovoltaic materials (PDCBT:ITIC)”. Poster presented at 4th International Conference on Emerging Advanced Nanomaterials (ICEAN), Newcastle, Australia, 2022

Chapter 1: Introduction

1.1 Overview

This chapter will discuss the basics of organic photovoltaic technology and introduce a number of recently published highly efficient polymer and small molecule OPV materials. In particular, the focus is on leading candidates for large area roll-to roll (R2R) OPV production [1]. The chapter will also discuss economically viable chemical production methods, such as batch and flow chemistry, and demonstrate large scale synthesis [2] of benchmark and contemporary molecular donor and acceptor materials, towards the goal of high performance, long lifetime and low cost large scale OPV [3].

1.2 Background

Currently, due to increasing global energy demand and concerns related to climate change, solar energy, and photovoltaic technology (PV) has attracted worldwide attention as an environmentally friendly, clean, and very abundant renewable energy source [1], [4]. In particular, organic photovoltaics (OPV) is a promising contemporary PV technology. Recent progress has been made in the development of novel photoactive OPV materials for converting sun light into electrical energy [5], [6], as well as the demonstration of OPVs low cost, flexibility, and high throughput roll-to-roll production [7], [8]. It is estimated that by 2025, 7.5 % of total Australian energy demand will be met by PV solar panels [9]. High consumption of PV resulted in decrease of its average cost by 85 % between 2010-2020 [10]. Accordingly, the cost will decrease further, the more PV market grows.

In the mid-twentieth century, in 1953 (six years after the discovery of the p-n junction effect by William B. Shockley, Walther H. Brattain, and John Bardeen, which earned them the Nobel prize for the transistor in 1956), the first silicon solar cell with an efficiency of around 4 % was developed [11]. A few decades later, in the 1970s (semi)conducting conjugated polymers were discovered and developed by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, who received the 2000 Nobel Prize in chemistry for this work [11]. There are a number of advantages in using conjugated polymers in comparison to inorganic silicon materials in a PV device, such as lighter weight, and high flexibility [12].

The first report of an OPV was Ching Tang's publication of an organic donor/acceptor solar cell with an efficiency of 1 % in 1986 [13]. In that solar cell, a planar bilayer junction of an electron and a hole accepting material (a perylene tetracarboxylic derivative and copper phthalocyanine respectively) was utilised [14]. The next major achievement in OPV was the development of the bulk heterojunction, wherein a mixture of donor and acceptor materials are co-deposited in a single solution-processed layer within the electronic device, leading to a significant improvement in power conversion efficiency [15]. The discovery of the BHJ led to a rapid increase in the number of OPV publications over the last two decades, with recent OPV efficiencies reported in excess of 18 % in laboratory cells and above 8.5 % in multi-cell modules [16]–[18]. Even though conventional silicon solar cells have reached efficiencies of 20 % [19] and hold the world record solar efficiency of 46 % [20], there are significant disadvantages to the technology, such as the expensive crystalline silicon semiconductor material and complex fabrication procedure. In comparison, the

advantages of organic solar cells are low weight and fabrication cost, mechanically flexibility, short energy payback times, low environmental impact (in particular nanoparticles) and high throughput manufacture using established large scale roll-to-roll (R2R) production [15], [21].

There has been much research done for better understanding of the organic solar cell working principle and the structure/property relationships with different materials in the device [22]. Recent progress in OPVs over the past two decades has also included the improvement of traditional polymerization methods [23], [24], developing new synthetic routes [25], and designing novel high performance donor and acceptor materials for application in high efficiency solar cells [26]–[30]. Some of the benchmark OPV material syntheses (e.g. P3HT and PCBM) are quite mature now and have even achieved semi-commercial production in a few commercial projects/companies (e.g. the now bankrupt Konarka OPV company) [31]. Development of experimental methods to achieve low production cost, high output and maximum purity for novel, higher performance materials, is now a growing area of research, both in the field [32] and for my PhD project.

1.3 Photovoltaic technology and the operating principle of PV solar cells

PV technology has evolved through a significant amount of research and development work since the discovery of conducting polymers in the 1970s [33]. The basic physical and chemical phenomenon for direct conversion of sunlight into electricity inside a solar cell is performed by a photogeneration principle called the photovoltaic (PV) effect. [34] There are a range of different types of photovoltaic modules, including both inorganic and organic

devices. These types can then be further divided into various forms of inorganic devices such as amorphous [35], thin film [36], and crystalline [37] silicon, gallium arsenide, cadmium telluride, and others; and organic-based and organic-containing devices such as organic photovoltaics (OPV), dye sensitized solar cells (DSSC) and perovskite solar cells (PVSK). We will first consider the inorganic solar cell as a background technology for this study and then the focus of the discussion will shift to organic photovoltaics for this review [38]. The origin of semiconductivity in organic solar cells is established by the primary operation principle called photogeneration. The OPV cell is basically a semiconductor diode, where initially photons are absorbed by a semiconductor material and form electron-hole pairs called excitons. The key parameter that defines the contribution of photons to this photogeneration process is the bandgap energy (E_{gap}) of the semiconductor i.e. if the photon has an energy $h\nu < E_{\text{gap}}$ then no contribution will occur, whereas when the energy $h\nu > E_{\text{gap}}$ then each of photons will be absorbed to form an exciton, with a subsequent rapid loss of excess thermalisation energy ($h\nu - E_{\text{gap}}$). In the following step, charge separation takes place, where excitons are separated by the devices internal electric field into electrons and holes which travel to the respective electrodes in the solar cell. Therefore, the established “optimum” for E_{gap} ($\sim 1.1\text{eV}$) is a maximum of energy, roughly half of the incident solar energy, that can be transferred from sunlight to excitons [37].

1.3.1 First developed silicon solar cells

In inorganic solar cells, silicon semiconductors have an electron structure with a higher energy conduction band and a lower energy valence band separated by an energy band gap ranging from 0.1 – 2.2 eV (Figure 1.1). In order to manipulate and improve device

conductivity, doping of the semiconductor material is required to achieve an excess in the number of electrons (n-type) or holes (p-type) to form a p-n junction [39] [40] [41] [42].

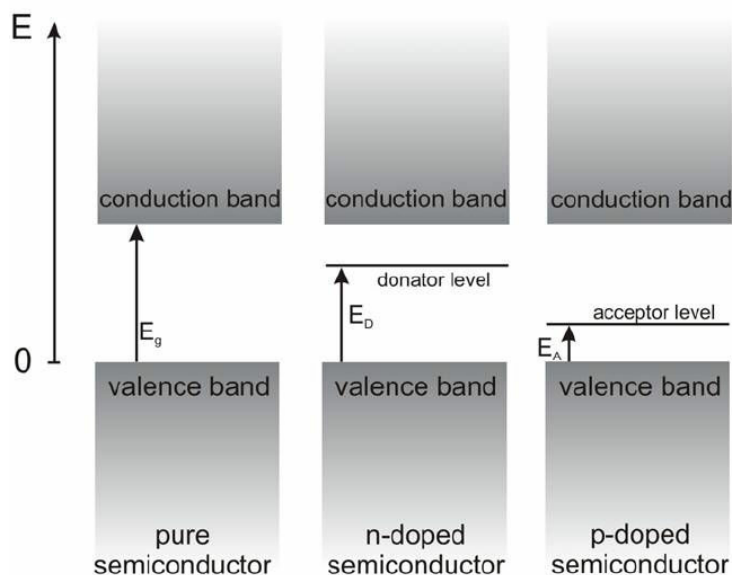


Figure 1.1 Diagram of energy bands for pure and doped semiconductors [43]

Upon contact of a p-type doped material with an n-type semiconductor wafer, electrons transfer from the region of high electron concentration (n-type), across the p-n junction, into the area of low electron concentration (p-type) resulting in a net charge transfer (Figure 1.1) and the establishment of an internal electric field. After light is absorbed by silicon, free electrons and holes are formed across the junction and directed by the electric field towards their respective electrodes [44]. The high dielectric constant of the silicon ($\epsilon_r \sim 11.7$) [45] means that excitons spontaneously undergo charge separation, since the resultant charges are well shielded from each other. An organic semiconducting material's electronic properties are defined by π bond delocalization over the entire molecule and quantum mechanical production of a bonding (π -orbital) and anti-bonding (π^* -orbital) orbital localized within the

conjugated polymers. The band gap is the energy difference between the valence band or lowest energy π orbital (lowest unoccupied molecular orbital, LUMO) and the conduction band or highest energy π^* orbital (highest occupied molecular orbital, HOMO) describes the optical properties of organic material. The majority of semiconducting polymers used in OPV devices have a band gap between 1.5-3 eV [39][40], and thus absorb light in the visible region of the spectrum.

In organic bulk heterojunction solar cells, a commonly used n-type material is a fullerene derivative, which is a pure carbon molecule consisting of at least 60 carbon atoms (Figure 1.13). This n-type material has strong electron accepting and conducting properties). Common p-type materials are conjugated polymers which conduct holes (Figure 1.10). Examples of these solar cells' materials are shown in Section 1.3.3.1 and Section 1.3.3.2 in this chapter. In recent times there is a move to use non-fullerene acceptor molecules (NFAs) since the optical properties and electronic energy levels of NFAs can be readily tuned and they have proven to be more thermally stable than fullerenes in OPV devices [46] Together, a blend of these n-type and p-type materials form the active layer of the OPV device. An acceptor material is required since the low dielectric constant of organic materials (2-4) prevents the spontaneous charge separation of the generated exciton and instead a material interface must be utilised to facilitate the charge separation. The key feature of most conducting polymers that function as electron donor materials is a high absorption region that matches the solar spectrum. The basic differences between inorganic and organic solar cells are shown in Figure 1.2. Firstly, in inorganic solar cell, by placing p-type and n-type semiconductors next to one another a p-n junction is created. The p-type

semiconductor, which has one less electron, attracts the electron from n-type semiconductor. When sunlight hits the surface of semiconductor, a photovoltaic effect happens. An electron is generated and is attracted towards the n-type semiconductor. This results in more negatives in the n-type semiconductors and more positives in p-type semiconductor. Organic solar cell's sunlight conversion to electricity occurs by lightabsorption of donor-acceptor material and formation of an exciton. Once the exciton is generated, it diffuses within the active layer to donor-acceptor interface. The dissociation of exciton from the LUMO of the donor to the LUMO of the acceptor occurs and collection of free charge carriers takes place at the electrodes.

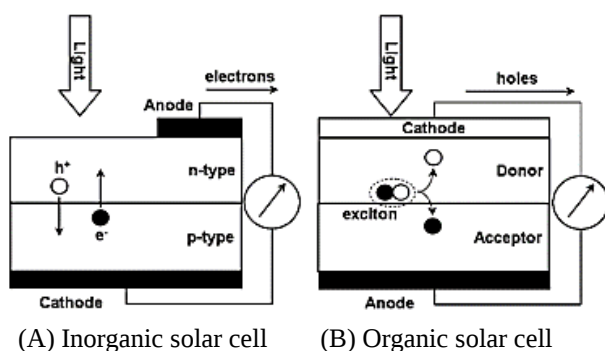


Figure 1.2 A simple inorganic silicon solar cell (A) and a heterojunction organic solar cell (B). These two simple schemes represent carrier generation difference between inorganic and organic solar cells [19]

1.4 Organic solar cell basics

In this section, the basic structure and operation of OPV devices are considered. Initially, the working principle of devices is discussed, with the comparison between bilayer

heterojunction and bulk heterojunctions emphasised. Then the standard BHJ device structure, organic photovoltaic materials, and a summary of characterization methods of OPV devices are outlined. Characterization methods discussed include current and voltage (IV) testing, to check the device efficiency; optical techniques for light absorption measurement; and spectral response tools for determining the number of photons converted to photocurrent at different wavelengths of light. Understanding of the OPV materials' properties impact on these factors is very important for effective device fabrication and will also be discussed.

1.4.1 Operation principles of OPVs and bulk heterojunction (BHJ) solar cells

The first bilayer heterojunction OPV device consisting of two organic layers with different electronegativities, namely copper phthalocyanine (CuPc) and a perylene derivative exhibited a reasonable power conversion efficiency of 1 % [47]. The compound structures are shown in Figure 1.3 below. In this device architecture, the copper phthalocyanine functioned as a p-type material and the perylene derivative as the n-type semiconductor [47].

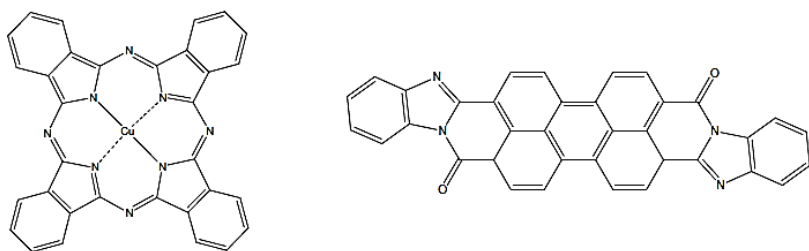


Figure 1.3. The two organic compounds used in Tang's heterojunction solar cells. Copper phthalocyanine (left), and a perylene derivative (right) [47]

An improved bilayer heterojunction structure with fullerene (C_{60}) functioning as a more efficient acceptor material (PCE = 1.7 %) was then introduced by Sarifitci (1992) [48] and the bulk heterojunction concept development was later shown by Yu Gang (1995) [49]. (Figure 1.4). The bulk heterojunction morphology resulted in further improvements to device efficiency, as by increasing the donor acceptor interface area, whilst maintaining charge transport pathways within the device, the BHJ active layer allowed for both efficient exciton dissociation as well as effective charge transport.

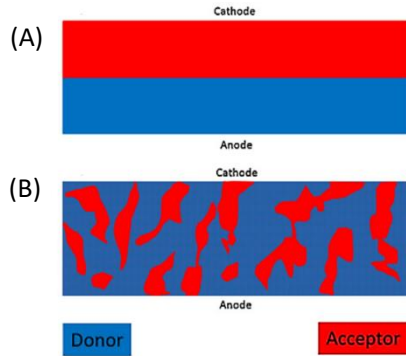


Figure 1.4. (A) bilayer heterojunction arrangement; (B) bulk heterojunction morphology [21]

The first step in the operation of an OPV is the absorption of a photon by the active layer materials, as shown in Figure 1.5. Light absorption leads to the creation of an exciton within the active layer electron donor (p-type) and electron acceptor (n-type) material blend. The binding force of exciton depends on their initial separation (into free charges) distance according to the photon energy and the dielectric constant. High dielectric constant of the material is increasing the separation distance. Therefore, the binding electric force between the electrons and holes in the excitons gets smaller. And consequence of low dielectric

constant is a strongly bound excitons in the materials. The efficiency of organic solar cells still behind the inorganic solar cells due to their low dielectric constant and charge transport [50]. The next step is the diffusion of formed exciton through the active layer and once the exciton reaches a donor-acceptor interface, charge separation occurs. Dissociation of the exciton forms free electrons and holes that are transported to the respective electrode through regions of donor (hole transport) and acceptor (electron transport) [39].

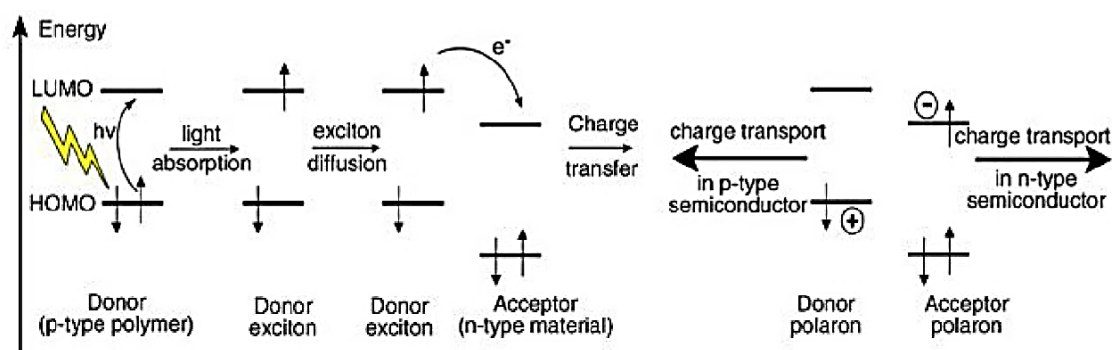


Figure 1.5. Charge generation for photoenergy conversion mechanism in bulk heterojunction organic solar cells [39]

In terms of energy levels of donor and acceptor materials in BHJ solar cells, analysis by Coakley and McGehee [51] showed that if all photons with higher energy than the band gap are assumed to be absorbed, each electron's energy is equal to the band gap energy minus the energy lost during the charge transfer process (Δ_{LUMO}), therefore energy losses will be in the order of 0.1 eV. From this electron transfer to an electron acceptor, the optimum theoretical efficiency can be derived as a function of the band gap of a conjugated polymer (Figure 1.6). It is estimated that a maximum PCE of ~15 % could be reached using an ideal absorber with a band gap of 1.75 eV [21].

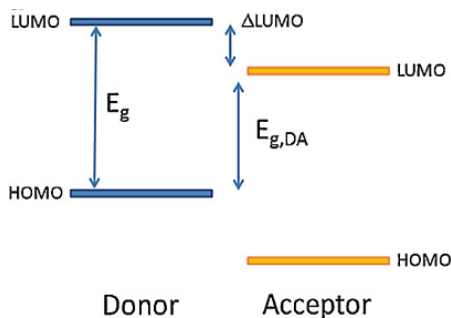


Figure 1.6. Optimum efficiency alignment of the energetic levels of a donor acceptor system in BHJ e.g. $E_{g,DA}$ is often called the effective band gap [21]

1.4.2 Device architecture

There are two major types of OPV device architectures. A typical BHJ device is a multilayered structure, and the order of these layers will define the device structure geometry as normal (or standard) architecture or inverted architecture (Figure 1.7 (A) and (B)). The difference in the inverted structured device is that the metal cathode is deposited on the substrate, whereas the first layer in the standard device is typically a coating of indium-tin oxide (ITO) i.e., an optically transparent anode vacuum deposited on the substrate. The transparent electrodes absorption of visible light should be as low as possible, as device illumination must occur through this face. Due to its high conductivity and optical transparency of 90 % [52], ITO on a glass or flexible plastic substrate has historically been the most commonly used anode material for OPV devices.

In a typical device, a thin layer of the conducting polymer mixture poly(3,4-ethylenedioxythiophene) and poly (styrenesulfonate) (PEDOT:PSS, Figure 1.8) that assists

charge extraction (by acting as an electron blocking layer) and minimises short-circuits through the device, is then spin-coated onto the ITO layer.

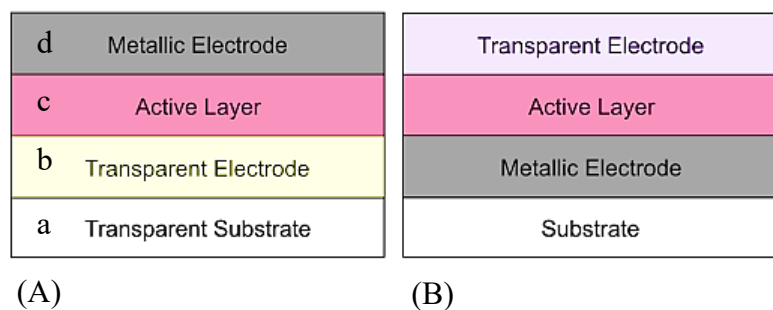


Figure 1.7. Normal or standard device structure (A) is (a) transparent substrate ITO, (b) transparent electrode PEDOT:PSS, (c) active layer a blend of donor acceptor material, (d) metallic electrode Ca or a metal oxide such as ZnO and inverted device structure (B) [53]

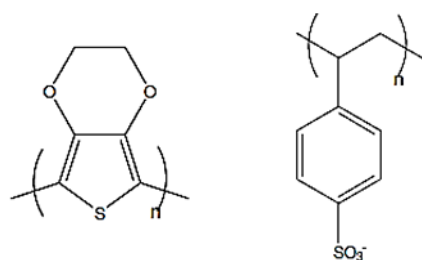


Figure 1.8. PEDOT (left) and PSS (right) structures

The primary light absorbing layer of the solar cell is referred to as the active layer, which consists of a blend of donor and acceptor materials. Typically, the donor will be a polymer, and the acceptor a fullerene, however both donors and acceptors can be polymers or small

molecules. The electron donating semiconducting polymer and electron-accepting fullerene absorb sun light, generate excitons, and produce photocurrent.

Onto the active layer is typically deposited a thin interlayer such as Ca or a metal oxide such as ZnO, which assists in the extraction of electrons (or holes, in the case of an inverted architecture device) from the active layer blend into the top electrode. The final layer deposited, typically by vacuum deposition, to complete the device is a metal cathode. A typical cathode is a low-work function metal such as aluminium, usually with a thickness between 80-150 nm [54], due to its high conductivity, low cost, and relatively low boiling point. Other materials are also commonly used such as silver [55], particularly in devices with inverted architecture, with the relative work functions of the electrode materials determining the flow of electrons and holes within the device (Figure 1.9).

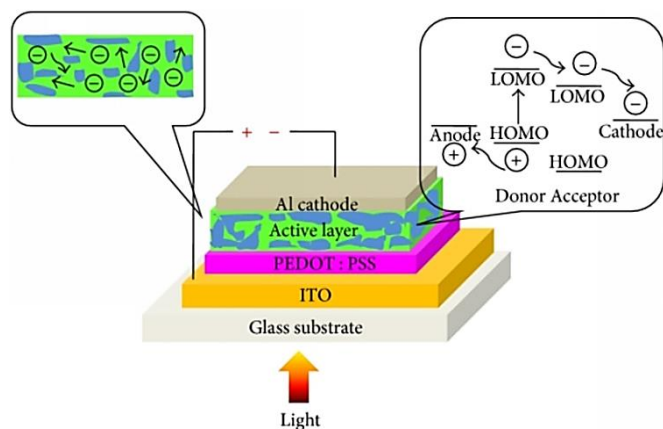


Figure 1.9. BHJ device structure [55]

Organic photovoltaic performance strongly depends on the material properties of the donor-acceptor photoactive layer. These materials determine such device parameters as the

internal electric field, film morphology, the generation and recombination rate of the carrier charges, and the formation of ohmic contacts within the device. To achieve high performance, OPV materials should have following properties [22]:

- (1) appropriate LUMO and HOMO energy levels in relation to other device materials;
- (2) an optical absorption region with relatively low or narrow bandgap;
- (3) a high acceptor (e.g. fullerene, small molecule, polymer) with optimal energy levels;

It is important to consider that these properties are interdependent. HOMO and LUMO energy levels variations, for example, will change the band gap energy [32]. These factors will be discussed in more detail throughout this thesis.

1.4.3 Organic photovoltaic materials

In this section, benchmark photovoltaic materials which are now being actively used in OPV, are discussed, followed by a further discussion of novel high-performance donor-acceptor materials arising from contemporary OPV research. The application of photoactive materials in OPV relies on the concept of charge photogeneration through maximum light absorption and optimal charge carrier transport [56]. When the polymer material has a low ionization potential, it can release an electron out of the material's HOMO or valence band, and therefore it will act as an electron donor. When the molecular material has a high electron affinity it can accept an additional electron into the LUMO or conduction band, and it will perform as an electron acceptor material. Common acceptor

materials are C₆₀ and C₇₀ fullerene and their derivatives. The energy separation between the HOMO and LUMO levels of donor acceptor materials will be the energy band gap of 0.1-1 eV within the device [57]. Recently, materials incorporating donor-acceptor regions within a single molecular structure have shown an increase in popularity in OPV research. For an effective band gap, the approach widely used is to apply the donor-acceptor (D-A) hybridization technique, where alternation of electron-rich and electron-poor segments that are built in along the polymer backbone takes place. The choice of monomers is the key parameter to control the band gap and energy levels, since the HOMO and LUMO levels of a polymer are almost entirely determined by the HOMO and LUMO of the donor and acceptor units [58].

1.4.3.1 Common donor materials

Conjugated polymers based on polythiophene and poly(*p*-phenylenevinylene) were traditionally the commonly used donor materials in the organic solar cells. Due to π -bond electron delocalization in the conjugated backbone in these materials, they have both good conductivity and stability; also, the absorption profiles lie with the visible solar spectrum, and they have efficient electron transfer to electron accepting fullerene species [59]. The most commonly used early organic photovoltaic donor materials were poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene (MDMO-PPV) and poly(3-hexylthiophene-2,5diyl) (P3HT). An alkoxy polythiophene derivative poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene (MDMO-PPV) has dialkoxy side chains which improves the solubility of this polymer and a π - π^* electronic energy gap which improves the absorption of photons in the visible solar spectrum compared with the non-

derivatised PPV [60] (Figure 1.10 (B)). The maximum efficiency for PPV-based devices is around 2.5 % [61].

In comparison to MDMO-PPV which was popular only in the early days of the field, P3HT remains in high demand due to many advantages such as easy synthesis, high charge carrier mobility, and good processability (Figure 1.10 (A)) [62][58]. The limiting factor for P3HT is a relatively large band gap of 1.9 eV that means the polymer can harvest only 22 % of photons from the sun [63]. There have therefore been various modified PT derivatives, such as P3HDTT, PT-C3 and PDCBT, developed to improve the absorption spectrum of the polymer. The P3HDTT derivative contains fewer electron-donating groups; this lowers the HOMO level and thus results in a higher open circuit voltage (V_{OC}) of 0.82 V (PCE 3.4 %) than P3HT in OPV devices. More recently, PT-C3 polymer with carboxylate substituents represents another OPV donor material with an improved V_{OC} of 0.78 V (PCE 3.87 %). One of the most recent PT derivatives is poly[5,5'-bis(2-butyloctyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-alt-5,5'-2,2'-bithiophene] (PDCBT), where attached electron-withdrawing carboxylate substituents reduce the HOMO level from the -4.90 eV observed in P3HT to -5.26 eV for PDCBT with a minor effect on the optical bandgap but a considerably improved V_{OC} to 0.91 V which results in a PCE of 7.2 % [26], Figure 1.10 (C).

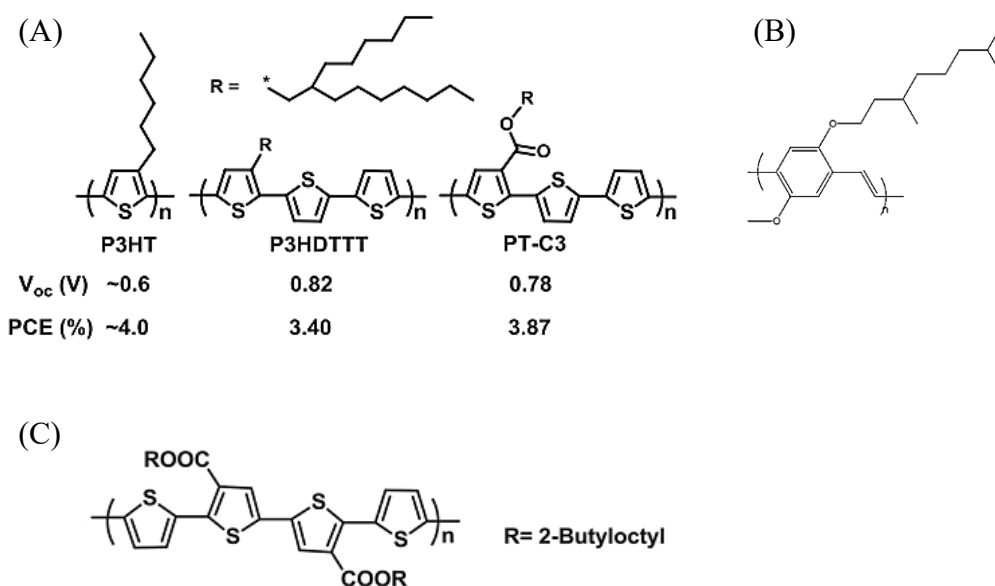


Figure 1.10. Common donor polymer materials: (a) poly(3-hexylthiophene-2,5diyl) (P3HT) [64] and two PT derivatives with various side groups [26]; (b) poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene (MDMO-PPV) [60]; (c) PDCBT donor material [26]

Poly(3-hexylthiophene) (P3HT)

The polythiophene class of polymers was first investigated in 1986 [65]. The most studied electron donor and hole transporting materials are functionalised polythiophenes [66]. However, there was an initial limitation caused by the poor solubility of unsubstituted polythiophene's (PT) at high molecular weight during the polymerisation process, where precipitation was often observed. In order to solve this issue, poly(3-alkylthiophenes) with improved solubility were developed. The 3-hexyl derivate (i.e. poly(3-hexylthiophene), P3HT) was selected as the optimum chain length for a simple PT derivative, and P3HT is

now known as a classic photovoltaic donor material with such key features as high solubility in common solvents such as chloroform and chlorobenzene, a straightforward synthetic route and high quality crystalline thin film production with wide range of practical and potential applications [67]. During the modern (Grignard metathesis, GRIM) synthesis methods of PT derivatives, the dissymmetry of the 3-alkylthiophenemagnesium halide monomer yields highly regioregular P3HT (RR-P3HT) with head-to-tail couplings in the structure, which is illustrated in Figure 1.11 [67]. The advantages of the regioregular P3HT include better π -orbital overlap and less contortion in the backbone which improves the conductivity of the polymer.

The simple two-step synthesis of RR-P3HT is represented in Figure 1.12, where first the dibromo-3-alkylthiophene monomer is treated with an alkyl Grignard reagent, yielding 2-bromo-5-chloromagnesium-3-alkylthiophene as the major regiochemical isomer. In the next step, Ni(dppp)Cl_2 catalyses the formation of RR-P3HT, which is later recovered by quenching in acidified methanol, often with addition of a chelating agent to assist removal of residual metal species such as magnesium and nickel. The filtered residue is then purified by Soxhlet extraction to remove unreacted monomer, oligomers, insoluble high molecular weight species, and metal species [68].

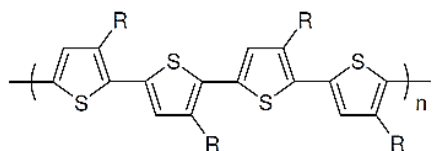


Figure 1.11. The regioregular RR-P3HT structure, where $\text{R} = \text{C}_6\text{H}_{13}$ [69]

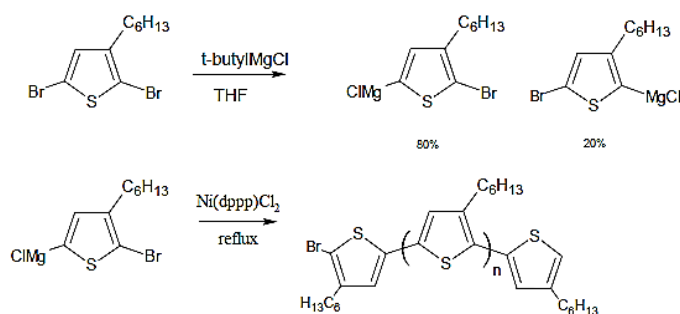


Figure 1.12. Grignard metathesis polymerization P3HT synthesis [68]

1.4.3.2 Common acceptor materials

C_{60} or Buckminsterfullerene (“buckyball”) is the base representative of the fullerenes group. The key purpose of incorporating fullerenes in the donor-acceptor blend within the active layer of device is their ability to dissociate excitons due to their strong electron affinity, and their good conductivity to assist in transport of electrons to the electrode. The first observation of fullerene assisted photocurrent generation was in MEH-PVV: C_{60} polymer solar cells [70]. However, the limiting factor was the solubility of C_{60} in common organic solvents. The acceptor [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM or C_{60} -PCBM) was therefore developed which has a much higher solubility and processability and enabled a subsequent increase in device performance. The structures of a range of common acceptor fullerene materials are shown in Figure 1.13.

For the standard synthesis route of PCBM, following the original Hummelen (1995) paper, the adduct is prepared as the *p*-tosylhydrazone derivative which is then reacted with C_{60} fullerene in the presence of a base. The intermediate fulleroid is then heated or irradiated to convert the fulleroid to the fullerene PCBM, as seen in Figure 1.14 [71]. In comparison

to PC₇₀BM which has ellipsoidal symmetry, PC₆₀BM has a very low light absorption ability due to the spherical shape that affects the electron transitions within the molecule [72]. Another fullerene derivative, synthesised from PCBM (or as a reaction by-product from PCBM synthesis) is bis [C₆₀] PCBM, which improves the V_{OC} of solar cells by introducing a greater energy offset between the HOMO of the donor material and LUMO of the acceptor due to the higher LUMO energy of bis [C₆₀] PCBM [73].

One issue with fullerene acceptors is their strong tendency for diffusion through the polymer and self-aggregation over time, which is accelerated by heat, resulting in morphological degradation of the OPV [74]. Furthermore, due to their relatively high electron affinity, which is difficult to decrease, fullerenes are fairly limited in being able to achieve a high V_{OC} [75]. Currently, the most successful fullerene to use in a P3HT:fullerene device is the indene-C₆₀-bisadduct (ICBA), which has a relatively small electron affinity, with potential to increase device V_{OC} above 0.8 V. ICBA has a relatively simple synthesis route (Figure 14), where firstly, the mixture of C₆₀ fullerene and indene in 1,2-dichlorobenzene is heated at reflux for two days, to give a mixture of mono-, bis-, tris-, and higher adducts. However, despite the simple synthesis, it is due to the low solubility in solvents required for chromatographic purification that ICBA is an expensive fullerene to manufacture with a market price of ~\$1700/g, compared to PC₇₁BM with the price of ~\$900/g and PC₆₁BM of ~\$300/g [58]. A simplification of the purification procedure by extraction of unreacted C₆₀ from the mixture of adducts, pioneered by the Centre for Organic Electronics (COE) at the University of Newcastle for use in low-cost R2R OPV, gives rise to a mixture called ICxA (where x is mono-, bis-, or tris-adducts of C₆₀ fullerene

of average ICMA:ICBA:ICTA ratio of 36:52:12), with the ICBA as a majority product. This mixture of indene adducts can replace PCBM in P3HT:PCBM OPVs and gives similar power conversion efficiency at a much lower cost to produce [8].

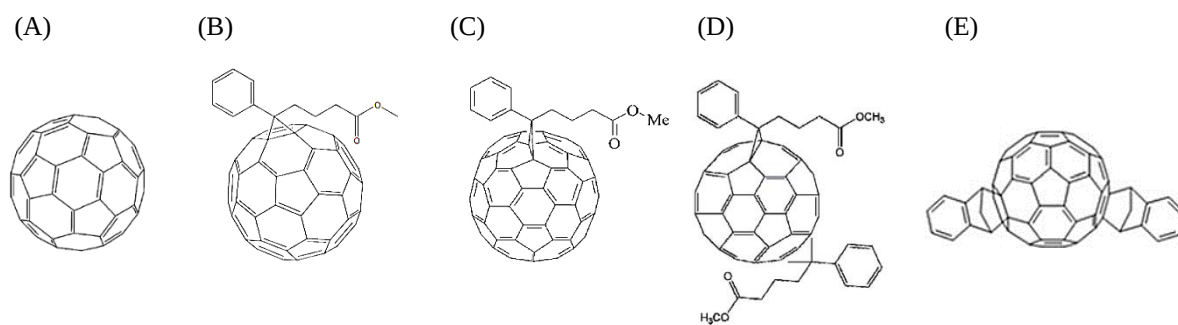


Figure 1.13. (A) buckminsterfullerene C_{60} ; (B) [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM or C_{60} -PCBM); (C) C_{70} -PCBM (D) bis[C_{60}] PCBM; (E) ICBA [69]

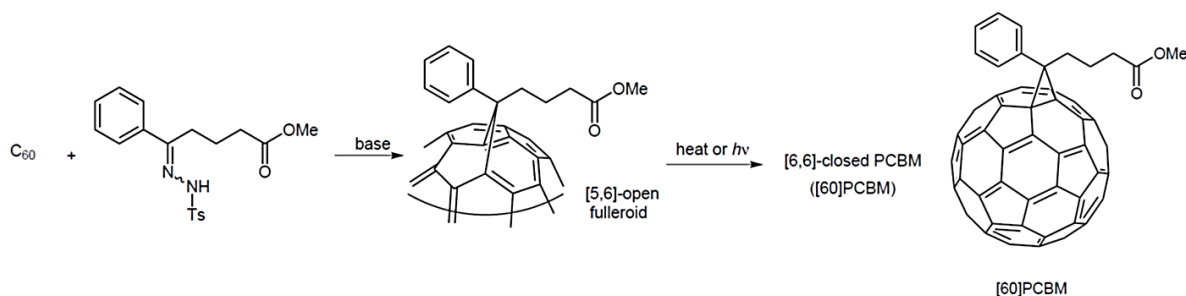


Figure 1.14. PC₆₀BM synthesis [71]

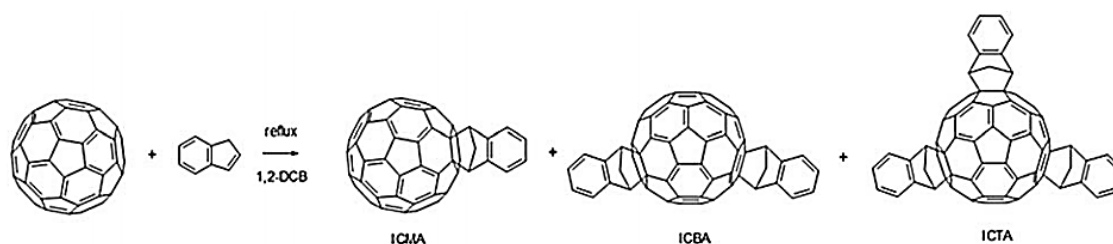


Figure 1.15. Synthesis of ICBA, ICMA and ICTA [8]

1.4.3.3 Contemporary high efficiency donor-acceptor materials: PDCBT and ITIC

During the past decade, hundreds of donors, acceptors and conjugate donor-acceptor organic photovoltaic materials have been synthesised and investigated with improved absorption of light, formation of charges and charge transport for better PSC efficiency [58]. Even though a large amount of research has focused on reducing the energy band gap for increasing light harvesting efficiency, band gap decrease may also result in thermalisation of charge carriers formed by the absorption of high-energy photons, that can decrease the external quantum efficiency and the PCE of low band gap based solar cells as well. Another disadvantage of low band gap (LBG) polymers is that their generated excitons within the interlayer materials result in their separation into free charges with very low V_{OC} for LBG devices. So far, in terms of LBG polymers, only a few conjugated polymers among the large number of polymer donors could display PCE over 5 % in PSCs with active layer thickness of ~ 200 nm or thinner [76]. Finally, solar cells based on wide band gap polymers (WBG) represent higher values V_{OC} and EQE, that is an advantage for wide applications in OPV field [28].

Contemporary photovoltaic materials survey

The lack of coherency between high performance active layer material selection and their critically important criteria such as synthetic complexity, costing and large scale application was identified by T.P. Osedach et al. [77] in 2013 and three years later this research area gap was analysed more detailed by Riccardo Po et al. [2]. As described in this chapter, after critical literature review and the careful analysis of a number of promising active layer candidate materials, selected materials for my thesis are PDCBT as a donor and ITIC and an acceptor. These materials meet the following criteria, which we have identified as crucial to the successful scale up and commercialization of OPV:

- High efficiency
- Printable using large scale R2R methods
- Relatively simple PDCBT and ITIC chemical structures
- Relatively easy synthetic routes
- Economic viability (See Chapter 3)
- Reduced production costs at scale
- Favorable device lifetime

The maximum solar cell efficiency reported for PDCBT with ITIC as an acceptor is 10.16 % with no impact on the device performance upon thickness variation of active layer, which is a significant benefit for R2R printing [78]. Also, PDCBT's advantages, such as insensitivity to thermal treatment, additives and strong degradation resistance of the active layer, in comparison to the P3HT:PCBM blend [26][79] are favorable for production using a printing process such as R2R. In terms of the chemical synthetic methods of these two selected materials discussed in this introduction, it is critical to emphasise the simplicity of synthetic routes that enable mass production in a cost-effective manner. Finally, a major step forward in choosing these promising high efficient, cost effective candidate materials is the relatively simple sustainable production methods and chemical structures, which allow for practical large scale R2R application and commercialised mass production [80].

T.P. Osedach et al. considered several important factors of photovoltaic materials such as complexity of synthesis, as well as the purification methods which can have a crucial effect on the scalability and use of these materials in the OPV field [77]. They surveyed the compounds production cost (\$ per g) versus the number of synthetic steps, which is illustrated in Figure 1.16, where the PTB1 (poly ((4,8- bis(octyloxy)benzo(1,2-*b*:4,5-*b'*) dithiophene-2,6-diyl) [2-((dodecyloxy)-carbonyl) thieno(3,4-*b*) thiophenediyl])) [81] polymer with 14 number of steps represents a very high cost material in comparison to common P3HT, whereas DBP (dibenzo([f,f0]-4,40,7,70-tetraphenyl) diindeno[1,2,3-*cd*:10,20,30-*Im*]perylene) [82] donor material has a relatively simple synthesis method and purification which reduces costs considerably, comparing to those, our selected materials: PDCBT and ITIC represent both simplicity in synthesis and average material cost of

production. Though examination and costing of a series of materials of various synthetic complexity, a linear relationship between the cost and complexity of the synthesis was observed (Figure 1.16), suggesting a cost per synthetic step (at the kilogram of product scale) of between \$6.39 per gram step and \$31.00 per gram step [77] depending on the complexity of the material.

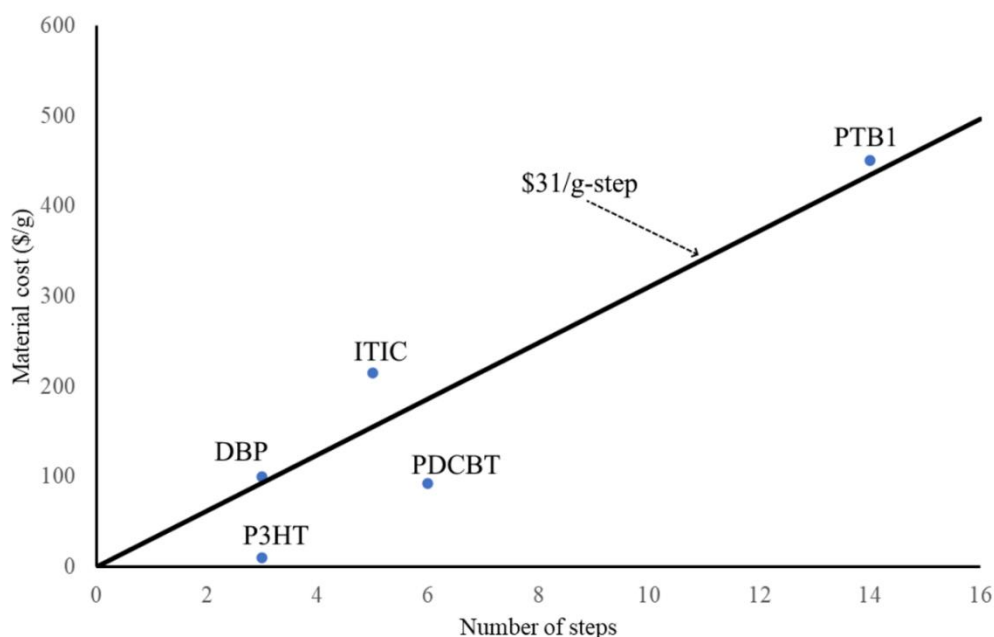


Figure 1.16. Linear plot with the cost (\$ per g) versus the number of the synthesis steps

A similar method of analysis to quantify the complexity of synthesis and the suitability for scale-up of a selection of common donor materials was presented by Riccardo Po et al. as the synthetic complexity index (SC) for donor photoactive materials [2]. SC index calculations are examined further in Chapter 3. The synthetic complexity index has clear implications for the cost of commercialising OPV technology, as well as the environmental impact of producing materials at scale, and should be evaluated along with device

efficiency and lifetime when considering future large-scale application of any novel developed OPV materials.

Another interesting calculation of efficiency and lifetime effect of solar cells modules on the cost of electricity generated by these modules has been performed by C.J. Mulligan et. al [83]. By integrating the OPV modules data, an estimation of commercial scale levelised cost of electricity (LCOE) is derived. The average lifetime levelised electricity generation cost calculation is introduced in the following Equation 1.1:

$$LCOE = \frac{\sum_{t=0}^n (C_t / (1 + r)^t)}{\sum_{t=0}^n (E_t / (1 + r)^t)} = \frac{C_{NPV}}{E_{NPV}}$$

Equation 1.1 LCOE calculation [83]

Where, C_t is the total cost of generation in the time, t , E_t is the total energy generation per square metre in the time period, t , r is the discount rate, and n is the system's life. As a result, an estimated LCOE of \$0.20 /kWh for device efficiencies of 3 % and lifetimes of three years and LCOE \$0.13 /kWh for of 5 % efficient devices with and five years, respectively, was calculated [83]. The relative dependence of LCOE on efficiency and the lifetime of the OPV module is demonstrated in Figure 1.17 below, which illustrates the decrease in the LCOE with increase of these two parameters.

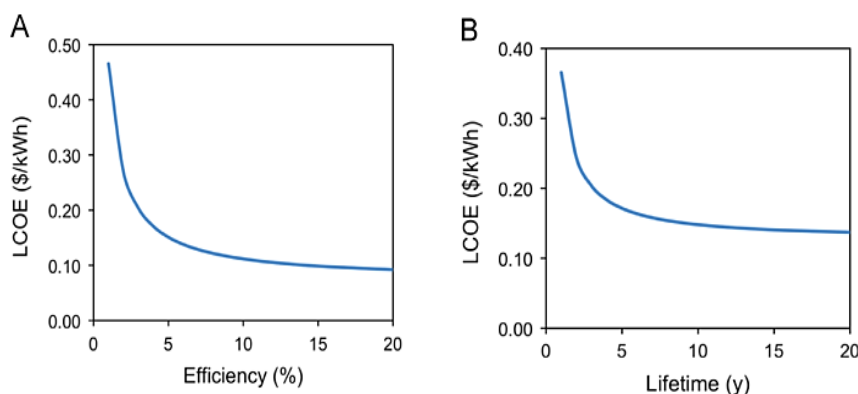


Figure 1.17. (A) The LCOE dependence on the efficiency and (B) Lifetime influence on LCOE [83] At that stage, in 2014, a 2 % efficient solar panel with 2-3 years lifetime showed potential in becoming achievable for replacement with the conventional solar technologies, which improves each year [83].

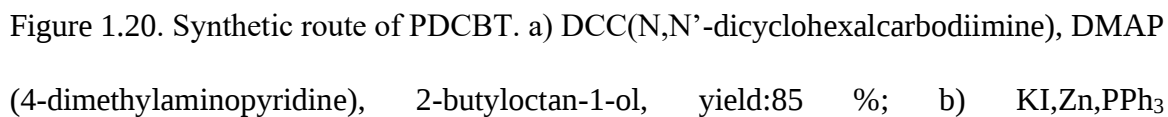
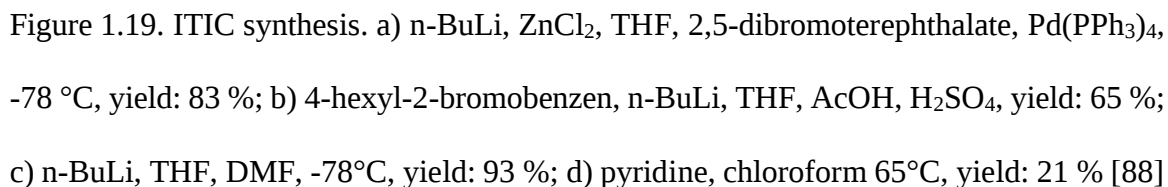
PDCBT and ITIC

The highest published power conversion efficiency of P3HT:PCBM is only 5.5 % [64], so solar cells with various other polymers and fullerenes have been studied in the literature in an attempt to drive the efficiency of OPVs higher [84][26][85][76][79]. A limiting factor of P3HT:PCBM BHJ device performance is the P3HT HOMO level of 4.9 eV, and therefore the absorption band is in the visible spectrum and makes PT:fullerene-based active layers more likely to be affected by oxygen that increases device degradation and therefore makes the process of PSC optimization more complex [26]. To address this issue, an organic benzothiadiazole polymer, named PDCBT [79], with a 30 % higher light absorption coefficient than P3HT [26] has been considered in combination with the small-molecule ITIC as a promising novel acceptor material. Due to PDCBTs deeper HOMO

level of 5.3 eV it combines well with PC₇₀BM but importantly, also with the much less expensive PC₆₀BM, as well as non-fullerene acceptors such as ITIC [85][86] which therefore makes it a strong candidate for development of organic photovoltaics at the large scale [87].

Recently, Zhan et al. synthesised a non-fullerene small-molecule with a low bandgap of 1.59 eV; 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) [88] and reached a maximum OPV efficiency of 6.8 % by combination with the donor polymer PTB7-Th. Due to the incompatibility of the absorption spectra in the short-wavelength region, some studies have reported ITIC's application with PT derivatives with a low band gap, however desirable PCEs were challenging to achieve. To overcome this issue, a new alkoxycarbonyl-functionalised PT derivative, poly[(4,4'-bis(2-butyloctoxycarbonyl)-[2,2'-bithiophene]-5,5'-diyl)-alt-(2,2'-bithiophene-5,5'-diyl)] [89] (PDCBT) was produced.

The relatively simple 4 steps synthesis route of ITIC and 5 steps synthesis route of PDCBT in addition to their non-complex molecular structures, offer the possibility to scale-up both PDCBT and ITIC (Figure 1.18, 1.19, 1.20), in comparison to common complex novel high-performance donor-acceptor materials syntheses [2][78].



(triphenylphosphine), $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$, 50°C yield: 70 %; c) $\text{CF}_3\text{COOH}/\text{CHCl}_3$, NBS (N-bromosuccinimide), yield: 60 %; d) toluene, $\text{Pd}(\text{PPh}_3)_4$, 110°C , yield: 76 % [26]

Zhan et al. also reported that the blends of P3HT:ITIC and PDCBT:ITIC exhibit very different photovoltaic properties. The optical absorption spectra of both P3HT and PDCBT are complementary with that of ITIC and are shown in Figure 1.21.

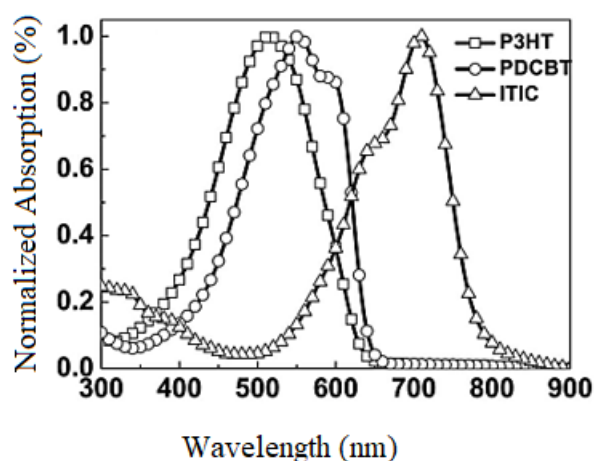


Figure 1.21. Normalised optical absorption spectra of P3HT, PDCBT, and ITIC in films [78]

PDCBT:ITIC and P3HT:ITIC based devices show maximum PCEs using chloroform as a processing solvent with a D/A weight ratio of 1:1, followed by thermal annealing at 160°C for 10 min. After the annealing process, the PCE of PDCBT:ITIC PSC was optimised to 10.16 %, with V_{OC} of 0.94 V, J_{SC} of 16.50 mA cm^{-2} , and FF of 65.67 % (Figure 1.22(a)), however thermal annealing brought smaller FF and V_{OC} but improved J_{SC} for the P3HT:ITIC devices with PCEs of only $\approx 1\%$ (Figure 1.22 (b)). From EQE measurements,

the P3HT:ITIC devices performed poorly across the entire response range from 300 to 800 nm, but for the PDCBT:ITIC solar cells, the EQE values were in the range of 60-70 % between 550–700 nm.

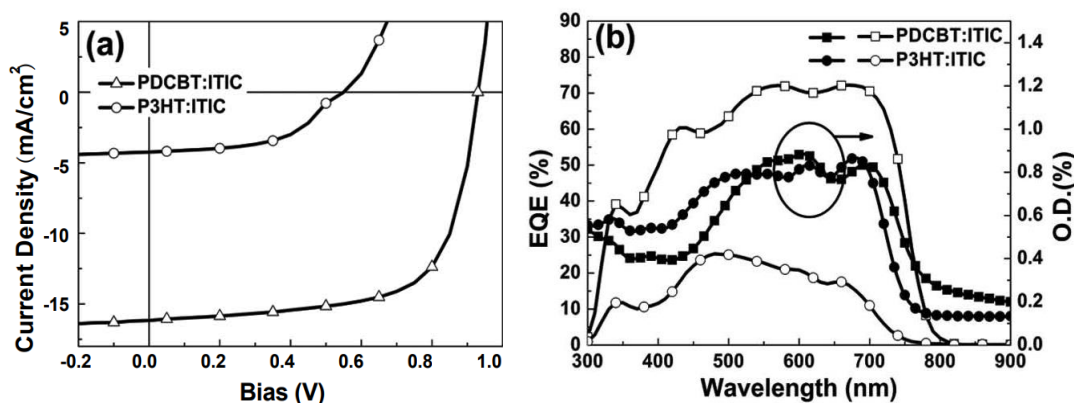


Figure 1.22. (a) J–V and (b) EQE curves and absorbance of PSCs based on PDCBT:ITIC or P3HT:ITIC processed under optimized conditions [78]

In comparison to more synthetically complex materials, PDCBT and ITIC have the desirable properties of having relatively few synthetic steps, which leads to reduced solvent and reagent waste, an issue of key importance when considering suitable polymers for upscale [78].

Development of PTs

PDCBT-2F

To control the energy levels of organic photovoltaic materials inside the solar cell, halogenation, and in particular fluorination, of these organic semiconductor materials has

been commonly used in the optimisation of chemical structures. By reducing of the HOMO and increasing the LUMO energy levels without changing light absorption, the V_{OC} is enhanced and this change, in principle, results in improved device PCE. For example, PDCBT-2F donor with, IT-M, methyl-end-capped ITIC derivative as the electron acceptor device demonstrates a PCE of 6.6 % with a very high V_{OC} of 1.13 V. However, a limitation of fluorination is that it is generally a low yielding reaction which increases the cost of the polymer synthesis and may hinder the commercial application. One example of a fluorinated polythiophene (PT) derivative, PDCBT-2F, is represented below in Figure 1.23 [90].

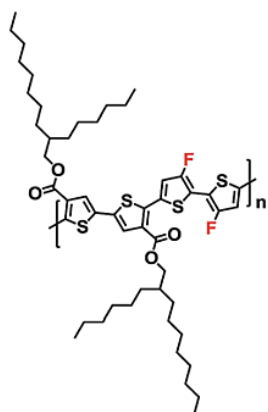


Figure 1.23. PDCBT-2F structure [79]

Another approach to manipulate the energy levels of PT and establish control over the polymer energy bandgap is the incorporation of electron-rich donor units in D/A conjugated polymers. These donor units represent fused and bridged thiophene-based ring systems as benzodithiophene (BDT), indacenodithiophene (IDT) and cyclopentadithiophene (CPDT)

with high electron density, where lone-pair donation from the sulfur atoms into the π -bonded system takes place [62].

Benzodithiophene-thienothiophene polymers (BDT) with reported efficiencies of >10 % in solar cells have been developed during the last decade. Commonly the thieno[3,4-*b*]thiophene (TT) ring system is used as a co-monomer for BDT, because of the added stability of the quinoidal structure (see Figure 1.24) which decreases the energy bandgap [58].

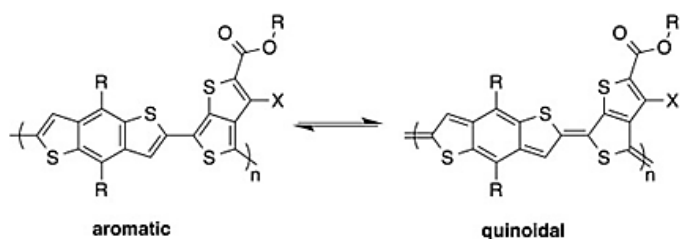


Figure 1.24. BDT-TT polymer structure. TT unit stabilises the quinoidal structure and planarises the polymer backbone [58]

Indacenodithiophene (IDT) has the structural feature of a ladder-type donor unit with a coplanar and extended ladder-like carbon framework, which results in an effective increase in the π -conjugation length and improved the charge carrier mobility. IDT has been used successfully with efficient non-fullerene acceptors. An IDT-based copolymer first developed by Ko et al. showed a PCE of 4.4 % with [6,6]-phenylC₇₁-butyric acid methyl ester (PC₇₁BM) [91][92] Figure 1.25 (a).

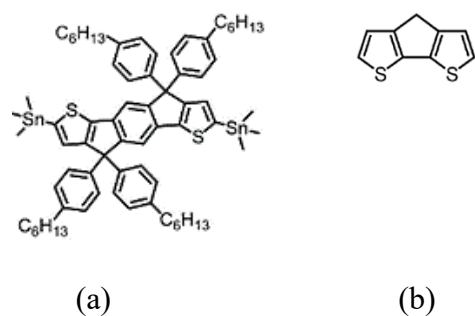


Figure 1.25. (a) IDT unit structure [92]; (b) CPDT Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene [93]

Cyclopenta [2,1-*b*:3,4-*b'*]dithiophene's (CPDT) have extended conjugation and strong intermolecular interaction due to two thionyl subunits with a bridging carbon at the 4-position of CPDT which can be functionalised by alkyl groups to increase the solubility and results in a low energy band gap [94], Figure 1.25 (b).

Fused-ring non-fullerene acceptors

A critical review of fused-ring non-fullerene acceptors for use in commercially viable OSCs is introduced in this section. It is known that employing non-fullerene acceptors in solar cells aids in photon harvesting. Altering the frontier molecular orbitals (FMOs) results in better tunability of the absorption level and increasing the photocurrent in bulk heterojunction devices.

Overcoming the significant drawbacks of fullerene-based acceptors, such as poor optical features and photostability of the active layer is critical to produce photo- and morphologically stable organic solar cells. Limitations in achieving chemical modification

of LUMO by the presence of additional functional groups (methano-adducts, amines or fluorine atoms on the phenyl unit of the adduct) and delocalisation of the LUMO level across the 3D carbon cage, results in poor tunability of the absorption spectrum in UV-visible region [95]. Additionally, tendency for aggregation (as a result of fullerene poor solubility) after the active layer has been cast, causes major morphological issues such as delamination and loss of operation of the device [96]. The aforementioned LUMO delocalisation is a critical aspect to maximise the open circuit voltage (V_{oc}) and thus improve bulk heterojunction device performance. Furthermore, active layer photostability [96] is a necessary, and indeed critical, component in reaching new heights in organic photovoltaics [97].

By contrast non-fullerene compounds and their recent chemical modifications offer new pathways to address the limitations of fullerene acceptors [30]. One of the main features of NFAs is better control over the frontier molecular orbitals (FMOs) of the acceptors, which allows for a variety of donor polymers to be incorporated in the active layer. In addition, NFAs can be readily modified to increase steric hinderance which prevents aggregation and allows enhanced solubility in common organic solvents compared to the fullerenes [97].

We will now consider NFAs with a focus on ITIC and its derivatives; 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (IEIC) is an acceptor with indaceno[1,2-b:5,6-b']dithiophene (IDT) core flanked by thiophene spacer units and dicyanovinylindan-1-one (DCI) terminal unit end groups (Figure 1.2 (a) and (b)) IEIC is a toxic compound and due to environmental concerns unlikely to be commercialised. By comparison to a non-toxic

ITIC has a indacenodithieno[3,2-b]thiophene (IDTT) core, instead of the IDT core in IEIC acceptor and does not contain the DCI units on the periphery which form a π -conjugated spacer. These changes result in extension of the electron donating core that forms a bandgap of 1.59 eV which is very similar to IEIC. The HOMO and LUMO levels are both shifted upwards by around 0.1 eV.

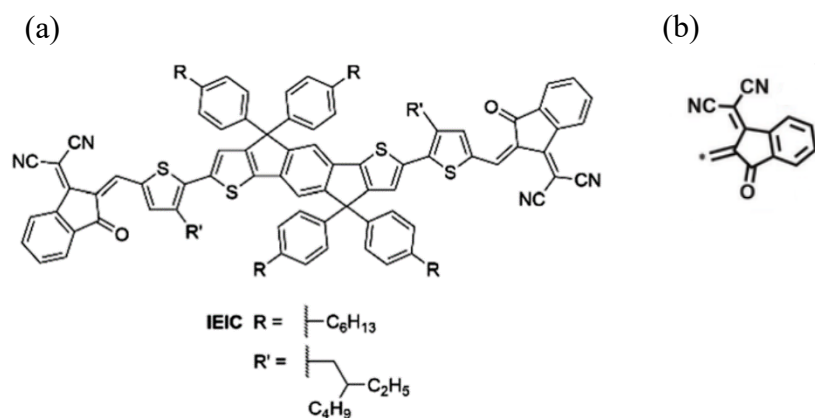
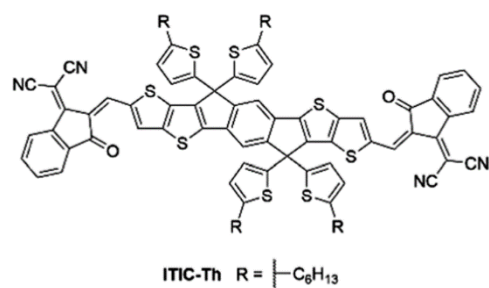
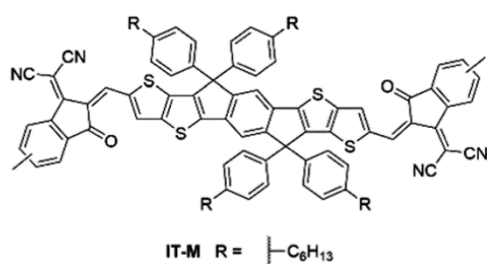


Figure 1.26 (a) IEIC structure [97] and (b) DCI terminal unit structure [71]

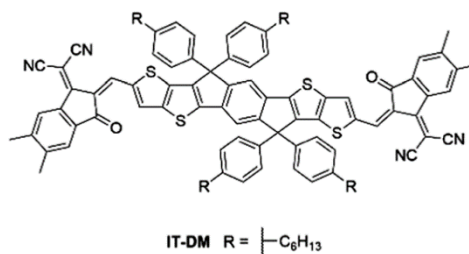
Another analogue of ITIC is ITIC-Th (Figure 1.27), where the phenyl units have been replaced by thienyl groups to work as solubilising sidechains. The HOMO and LUMO levels are lower comparing to ITIC, which results in the σ -inductive effect [97] with electron withdrawal from the thienyl parts. This ITIC analogue with the thienyl moieties has better electron mobility due to higher intermolecular interactions.



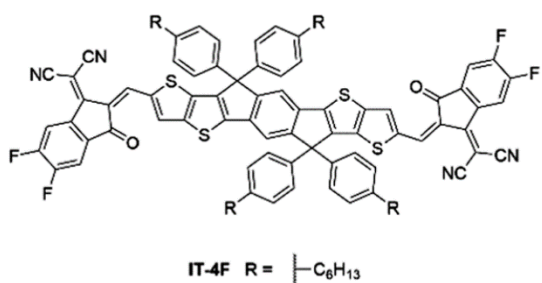
(a)



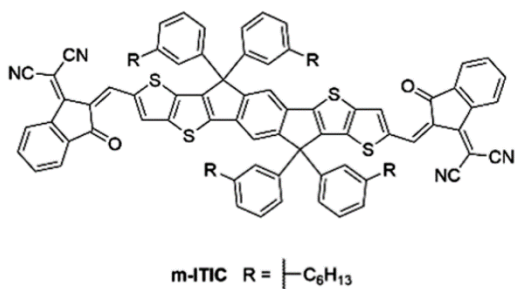
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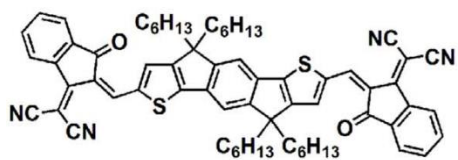
(c)



(d)



(e)



(f)

Figure 1.27 (a) ITIC-Th structure [97]; (b) IT-M; (c) IT-DM structures [97]; (d) IT-4F structure [97]; (e) m-ITIC structure [97]; (f) IDIC acceptor [98].

To increase the LUMO levels, further derivatives of ITIC (IT-M and IT-DM) were designed with methyl groups introduced onto phenyl ring of the DCI unit (Figure 1.27 (b) and (c)). This addition of electron donating groups raises the LUMO level 0.04 eV higher than ITIC for IT-M and of IT-DM the LUMO was 0.09 eV higher.

In the case of IT-4F (Figure 1.27 (d)), a similar approach is employed to IT-M and IT-DM, where the phenyl units of the DCI each contain two fluorine atoms instead of the methyl units introduced in the IT-M and IT-DM. This modification was expected to narrow the bandgap due to fluorination and increase intra- and intermolecular exchanges. As a result, it was observed that the HOMO and LUMO levels were lowered because of the strong electronegativity of the fluorine atoms. Also, the extinction coefficient of the molecule was improved, and the red shifted absorption spectrum was broadened due to stronger π - π bonding. All these effects result in higher electron mobility of this non-fullerene acceptor material.

m-ITIC is an isomerised ITIC derivative with the alkyl substituent moved from para- to meta- position on the phenyl rings. This change aimed to increase the delocalisation however the FMOs and optoelectronic properties remained the same as in ITIC. This side chain isomerisation does increase crystallinity (self-organisation) in m-ITIC compared it to the para-alkyl-phenyl ITIC (Figure 1.27 (e)). This change results in a modest increase in electron mobility for the m-ITIC acceptor ($\mu_e = 1.30 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in contrast to the ITIC acceptor blend ($\mu_e = 1.05 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). These comparisons were made for the m-ITIC and ITIC acceptors blended with J61 polymer [97] and result in more balanced charge transport in the blend for m-ITIC. Therefore, these structural changes made to the

ITIC base molecule (isomerization of aryl–alkyl chains) should be considered in order to improve structural and morphological properties of non-fullerene acceptors.

IDIC is a fused-ring electron acceptor (FREAs), which is based on indacenodithiophene (IDT) and indacenodithieno[3,2-*b*]thiophene (IDTT) electron-donating rings (Figure 1.27 (f)) [99]. The molecule was designed by deleting the benzene group side chain of ITIC and replacing with solubilising alkyl chains. IDIC has a planar structure and narrow bandgap comparing to fullerene acceptors which allows high performance (PCEs of 11.03 % in OSCs [99][100]).

In summary, most of solar cells with ITIC derivative acceptors exhibit performances with more than 8 % PCE on small scale devices [101][100]. To identify the best donor material for non-fullerene acceptors, Yuze Lin et.al. proposed 3 basic principles: (1) suitable energy levels, (2) complementary absorption and (3) morphology compatibility of donor material with the NFA. Following these criteria to match the donor to the non-fullerene acceptor will allow us, firstly to achieve higher exciton dissociation with small energy loss and high V_{OC} ; secondly to improve J_{SC} via increased incident photon conversion and finally, good morphology match will afford high charge separation for improved FF and J_{SC} [83]. The reason that ITIC is a superior acceptor among most NFA materials is due to its excellent compatibility with donor materials compared to P3HT:PC₆₀BM as an example. The best donor materials for ITIC reported are donor PTB7-TH with 2D-BDT unit resulting a PCE of 8.7 % [102], PBQ-0F with 2D-BDT unit with a PCE of 6.5 % [103], whilst PDCBT achieved a maximum PCE of 10.16 % [78] and PBDB-T with 2D-BDT has the highest PCE of 11.21

% [104], [105]. This brief review demonstrates that it is critical to carefully select the best matching donor material for the ITIC acceptor in order to achieve optimal efficiencies.

1.5 Device fabrication and performance control

Rapid progress in organic photovoltaics has led to power conversion efficiencies (PCE) of over 18 % [16] [17]. The reason for this improvement is not only the development of novel materials, but also specific fabrication methods and optimisation techniques for the solar cells [69]. For better free charge carrier extraction, photoexcitation must occur within proximity (<10 nm) of a material interface, or the exciton will recombine, and the photon energy will be lost. In bulk heterojunction devices a blend of polymer and fullerene (or NFAs) spin coated from a common solution create a larger interfacial surface for effective photogenerated charge separation and further transport of free charges to the appropriate electrodes [69].

1.5.1 Spin coating and the roll to roll printing process

Spin coating for small-scale fabrication and roll to roll for large-scale printing are widely applied techniques in device fabrication for the active layer blend deposition of OPV devices. The spin coating process, which is illustrated in Figure 1.28, involves evenly spreading an excess of active material solution onto a rotating substrate, where the angular velocity can be modified to achieve desired final thickness of the film. The solvent is “flash evaporated” and a well-blended active layer is deposited. Spin coating works well for laboratory-scale device fabrication but is limited in the size of substrates it can coat, e.g.,

the largest substrate reported for spin coating had a total active area of 108 cm², with dimensions of 15.2 x 15.2 cm and a PCE of 2.4 % [53].

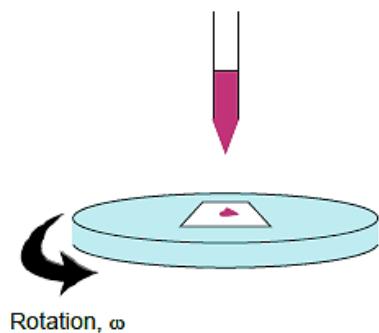


Figure 1.28. Spin coating technique [53]

Roll-to-roll (R2R) processing of organic electronic materials from solution at high speed across large areas is a key technique in OPV upscaling. With rapid printing on large areas a new challenge of material selection and availability becomes significant and many challenges for selection and synthesis of large-scale materials exist. Even the most commonly printed materials such as P3HT and PCBM encounter several challenges on the R2R printing scale, such as surface energy compatibility of specific substrate materials to the ink formulations, temperature control across the entire module during the various steps of R2R processing and equipment maintenance after repeated use of machines to maintain uniformity in printed patterns over time.

Wide application of large-scale OPV by R2R processing (See Figure 1.29) promises a bright future for the technology but depends significantly on the development of new high efficiency, low cost and stable materials suited to this new fabrication scale [72]. This thesis

addresses this issue and deals fundamentally with the selection, up-scaling and trialling of materials for R2R printing of OPV.

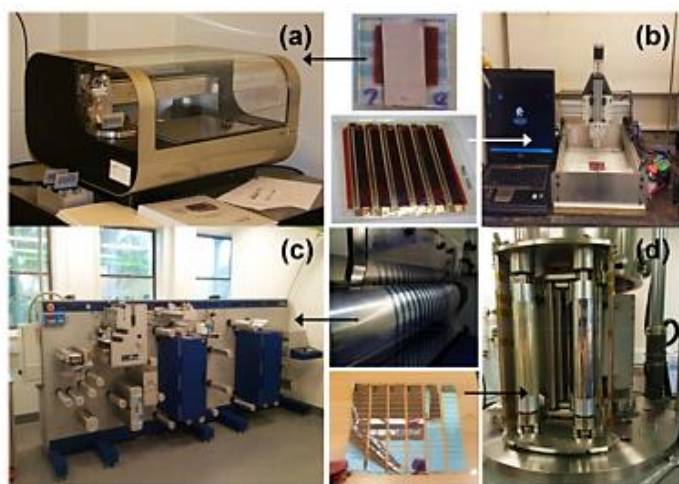


Figure 1.29. Printing equipment facilities at the Centre for Organic Electronics. (a) Dimatix inkjet printer, (b) blade coater and custom-built single head automated slot die, (c) roll-to-roll solar coating line from Grafisk Maskinfabrik and (d) roll-to-roll sputter coating unit from Semicore Inc. Fabricated samples are represented in the middle images (a)-(d) respectively [7]

1.5.2 Annealing

A common method to optimise OPV device morphology and performance is heating above or close to the polymer's glass transition temperature. This technique is known as annealing. The ideal thermal annealing treatment was shown by Y.Kim et. al, to be 140 °C for 4 minutes for a P3HT:PCBM active layer at 1:1 material ratio with the maximum efficiency of 3 % for films from chlorobenzene (CB) and 2.3 % for 1,2-dichlorobenzene

(DCB) solvents. Figure 1.30 illustrates the AM 1.5 I - V characteristics of annealed and unannealed P3HT:PCBM CB devices, where the maximum FF and J_{SC} were achieved at 140 °C for 4 minutes thermal annealing and performance decreases with increasing temperature as this dramatically reduces the J_{SC} [106]. Thus, it is now very common to see P3HT-based device fabrication performed using an annealing temperature of 140 °C for 4 minutes, conditions which I have also adopted in my device fabrication within this thesis.

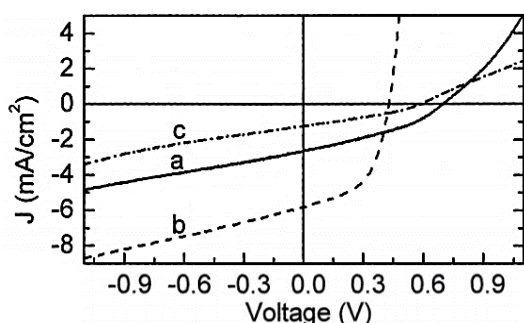


Figure 1.30. AM 1.5 I - V characteristics of P3HT:PCBM (1:1) films of the chlorobenzene a) unannealed solar cell; b) annealed solar cell at 140 °C for 4 min in air, and c) annealed solar cell at 230 °C for 4 min in air [106]

1.5.3 Solvent

The morphology of the active layer blend inside the device is strongly influenced by deposition solvent choice. For instance, in BHJ P3HT:PCBM blend devices, the films made from chloroform, toluene, chlorobenzene and xylene solutions are schematically represented in Figure 1.31. These images are diagrams of annealed films reconstructed from the results of atomic force microscopy (AMF) investigation, where black areas correspond to pure PCBM phases and white to pure P3HT phases with the characteristic

lengths observed. These images give an insight into how solvent modification can be used to optimise OPV active layer morphology. For instance, the most beneficial solvent for hole collection near the hole collecting electrode is the film spun from chlorobenzene solvent, due to a higher P3HT accumulation at this interface. Consequently, charge collection by increased sunlight harvesting occurs and directly improves the PCE of the solar cell [107]. Typically, thin active layers of ~ 100 nm are considered the optimal thickness for high performance in P3HT-based OPV devices. However, thick active layers with high PCE may in some instances be better suited to large scale printing technology (e.g. reduced risk of short circuiting when using thickly printed layers) and therefore more effective for the light harvesting [56].

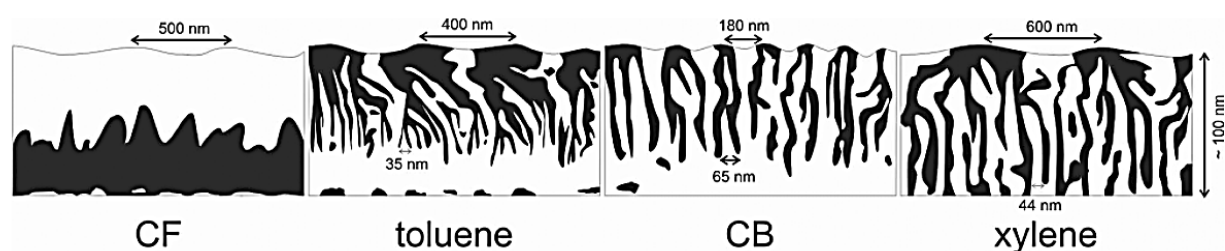


Figure 1.31. Schematic morphology of annealed P3HT:PCBM films spun from chloroform, toluene, chlorobenzene and xylene [108]

1.5.4 Donor/acceptor ratio

The active layer blend donor (D) and acceptor (A) ratios can also have a significant impact on solar cell efficiency, due to the influence on the crystalline order, morphology, and separation of the blend phases. Therefore, the optimum D:A ratio depends on the materials selection and can vary widely. For instance, a P3HT:PCBM blend of 1:1 or 1:0.8 ratio is

necessary to reach efficiencies over 4 %, whereas, for example, in a different D:A system Sun et al. developed BHJ solar cells from small molecule DTS(PTTh₂)₂:PC₇₁BM with donor-acceptor ratios of 7:3 and with a PCE of 6.7 %.

P3HT:PC₆₁BM active layer films with various donor acceptor ratios were studied by Huang et al. [107], where they examined the three-dimensional morphology of the films. Among all blend ratios (Figure 1.32), the highest efficiency was of a device with a 40 % PC₆₁BM ratio, with the efficiency attributed to a high crystallinity and dense network of P3HT nanowires within the active layer [107]. Even though advances in research have been made regarding optimum donor acceptor ratio blend determination, optimisation is a constant requirement whenever a new material system, or even new batch of material is investigated.

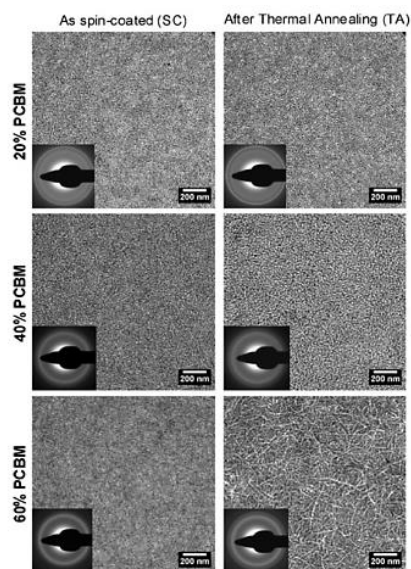


Figure 1.32. BF-TEM images of P3HT:PC₆₁BM films with different D/A ratios [107]

1.6 Device characteristics

There are several standard methods of organic solar cell characterisation which are used to benchmark device performance. These include current – voltage determination for the calculation of device efficiency, optical techniques for determination of light absorption of the active layer materials, and spectral response techniques for photon to photocurrent conversion at various light wavelengths.

Current-voltage (IV) characteristics

To investigate the properties of a solar cell, a graph of current I (or current density J) versus voltage V is commonly used. This measurement provides the necessary information for the power conversion efficiency of the device to be calculated. There is no photocurrent generated in a solar cell when it is in the dark, however when the solar cell is illuminated, it produces photo current and the IV graph shifts downward. Usually, a light source with an AM (air mass) 1.5 illumination spectrum is used when recording current-voltage curves. This light source simulates the accepted standard illumination conditions equivalent to sunlight that has reached the earth's surface at an angle of 48° . OPV devices are commonly illuminated at a fixed light intensity of 100 mW/cm^2 which simulates the light reaching the earth's surface. In order to measure IV curves of a solar cell under solar simulation, the voltage applied to the device is varied and the photocurrent produced under illumination at different applied potentials measured, from this data an IV or JV curve is plotted, Figure 1.33 [19].

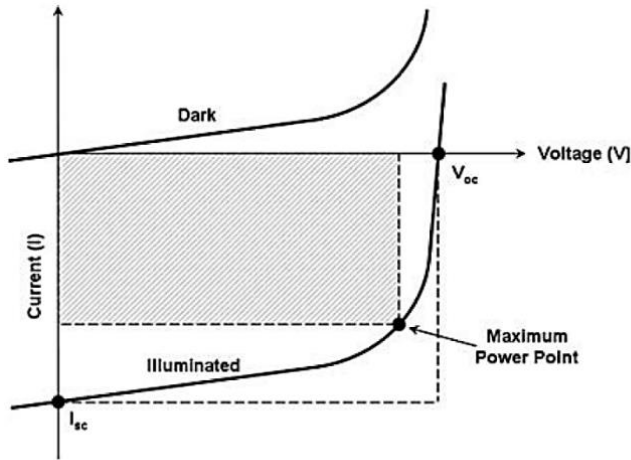


Figure 1.33. Current-voltage (IV) curve and detailed photovoltaic parameters for a BHJ solar cell [19]

A number of key device characteristics can be derived from the recorded data.

Power Conversion Efficiency (PCE) is given as the percentage of incident light energy (P_{in}) which has been converted into current by the device and is equal to output power divided by input power: Equation 1.2.

$$PCE = \frac{I_{mpp}V_{mpp}}{P_m} = \frac{I_{sc}V_{oc}FF}{P_m}$$

Equation 1.2 Power Conversion Efficiency (PCE) calculation

Short Circuit Current (I_{sc}) is the current that flows when the connected electrodes in the device are under light without external resistance or load at 0 V, i.e. at short circuit. The units of current density (J_{sc}) are mA/cm².

Open Circuit Voltage (V_{oc}) is the maximum voltage that a cell can perform at and it occurs during illumination without current flowing in the solar cell, i.e. at open circuit.

Maximum Power Point (MPP) is the maximal value of the power that is represented on an IV curve.

Fill Factor (FF) is the ratio between the actual cell power and theoretical maximum output. The value of fill factor value rises as the area of square formed within the IV curve increases. Equation 1.3

$$FF = \frac{I_{mpp}V_{mpp}}{I_{sc}V_{oc}}$$

Equation 1.3 Fill Factor (FF) calculation

Quantum Efficiency (QE), which is subdivided into two kinds being internal quantum efficiency and external quantum efficiency and evaluates the device efficiency in terms of energy function or incident radiation wavelength and combines the charge carriers with photons.

External Quantum Efficiency or Incident Photon to Current Efficiency (EQE or IPCE) calculates the losses through reflection and transmission. This is a key technique for accurate spectral response measurement of a device, where photocurrent is determined by the ratio of produced electrons for each incident photon absorbed by the photovoltaic material i.e. polymer: fullerene blend components across a range of wavelengths [69]. To convert power ($J.s^{-1}$) to the number of photons arriving per second and to convert current

($C.s^{-1}$) to the number of electrons arriving per second is achieved by the following Equation 1.4 below:

$$EQE = \frac{1240 J_{sc}}{\lambda I}$$

Equation 1.4 External Quantum Efficiency (EQE) calculation

where 1240 is a conversion factor, which combines Planck's constant, the elemental charge, the speed of light, and a scaling factor), J_{sc} is the short-circuit current density (mA/cm^2), λ (nm) is the wavelength of the incident light, and I is the incident irradiance (mW/cm^2).

The quantum efficiency that is deals only with the process of absorbed photons is **Internal Quantum Efficiency (IQE)**.

1.7 Modern organic synthesis - flow chemistry and scale up

Flow and batch synthesis are the two main chemical production methods (Figure 1.34). The most common method is standard batch synthesis, which involves mixing of reagents and solvents in a flask or reaction vessel, product collection after the reaction occurs, then further purification of the discharged product [109]. However, a potential disadvantage for large scale batch synthesis is the issue of heat transfer and mixing which may affect the reproducibility of the reaction [110], which can then be problematic in R2R OPV production due to the large consumption of materials in printing trials and the effect of material quality and variation on device performance. In order to address this scale up

concerns, the flow chemistry synthesis for P3HT donor [111], [112] was introduced in this thesis.

Flow chemistry has been under development in the modern organic synthesis field over the past decade and allows continuous production of materials that are (ideally) scalable and reproducible at the same time [113]. H. Seyler et al. suggest that a Suzuki polycondensation method of synthesis performed by continuous flow chemistry is an ideal method to improve reaction time for appropriate systems [114]. Flow synthesis introduces the reagents continuously into the system and their formed products are simultaneously discharged during the flow.

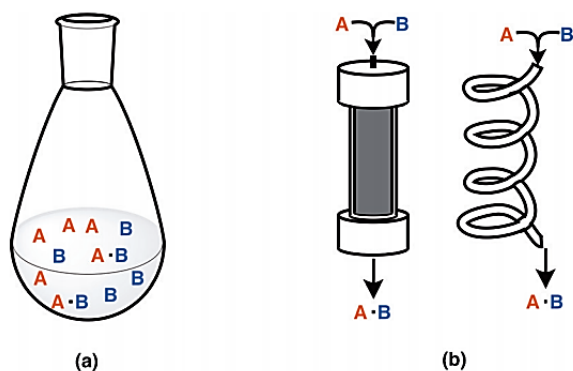


Figure 1.34. Batch synthesis method (a) and flow synthesis method (b) [109]

Recently the use of microreactors has become a popular tool for flow chemistry, whilst the dual pump, continuous flow synthesis setup is widely applied as well, due to the low cost and simplicity. The microreactor assembly (a type of a mixing device) was first described in the flow chemistry of an OPV material in the synthesis of rr-P3HT using GRIM catalyst in perfluoropolyether suspensions by Bannock et al. [115]. This study described a

continuous throughput of 0.9 g per 17 hours, clearly a limitation for adoption to large scale OPV [115]. Another J.H. Bannock et al. [116] paper introduced a droplet-based microfluidic reactor which achieved gram-scale P3HT synthesis by the GRIM method [116]. However, the major drawback of using the microreactor was the limitation in achieving a high area to volume ratio [117], so instead the authors transitioned to a pump system as more effective setup for scaling the flow reaction [118]. To apply pressure in order to force the liquid in the flow synthesis setup to move through the other components, pumps are used in the flow system, typically common syringe pumps with wide internal dimensions, which result in a suitably low back pressure, Figure 1.35.



Figure 1.35. Continuous flow synthesis equipment Harvard apparatus model 33 twin syringe pump 99.5 PSI max [119]

A dual pump system allows better control for flow chemistry reactions due to maintaining a constant flow rate with low back pressure. The first solution is taken up in an air-tight glass syringe and placed into pump 1, and similarly a separate second solution is taken up in an air-tight glass syringe and placed into pump 2 (see Figure 1.36).

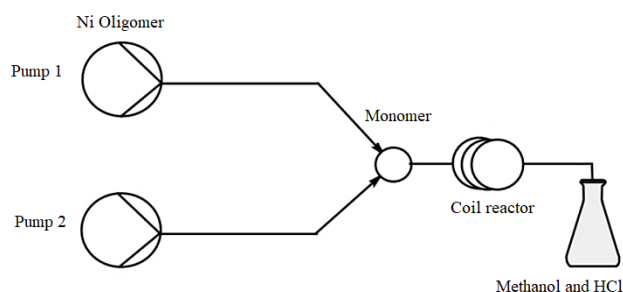


Figure 1.36. P3HT flow synthesis by utilizing dual pump system [68]

The most commonly used combination of units in flow chemistry system are represented in the scheme below with key components A-M, Figure 1.37 [120]. Components D (T-piece), F (static mixer chip), G (immobilised reagents) and H (reaction coil) play the most important role in the flow chemistry assemble. Further details of the flow chemistry apparatus design are discussed in Chapter 6.

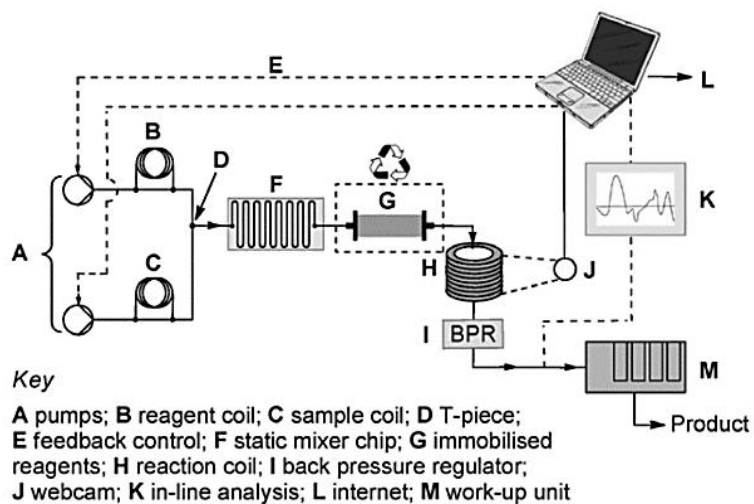


Figure 1.37. Scheme with key units in flow chemistry setup [120]

A new organic photovoltaic donor material PiEDOT (poly[isoidindigo-alt-3,4-ethylenedioxythiophene]) with a PCE of 3% in BHJ devices fabricated with PC₇₀BM as an acceptor material, was synthesised by a continuous flow method with high yields and appears economically feasible as a commercially scaled material. However, the difficulty of reproducing this conjugated polymer synthesis in large scale, identified a challenge in flow synthesis of this polymer [121]. An in-house built vapour technology flow chemical reactor system was introduced by M. Helgesen et.al, who suggest this method to synthesise PBDTTTz-4 (poly[thiazolo[5,4-d]thiazole4,5-bis(2-hexyldecyloxy)benzo[2,1-b:3,4-b0]dithiophene) donor polymer at the 10 g scale production. Devices of PCE 3.5 % with PCBM [122] were fabricated, using this in-house built flow chemistry system, which is illustrated in the Figure 1.38 below:



Figure 1.38. In-house flow chemistry setup. Where reactant solution (A) is heated by oven. The oven outlet-inlet (B) is connected to a pump (C) with a maximum output pressure of

400 bars was used. Resulting polymer was quenched in a collection reaction vessel (D) [122].

Proposed advantages of flow synthesis include [109][123]:

- Potentially less hazardous. The reaction is performed in an isolated system, which eliminates the contact with toxic materials.
- Better control over reaction performance and high reaction yield. The coil reactor allows efficient reagent mixing inside the tubing which leads to a higher reaction yield.
- Greater scope for scaling up a reaction. When planning an upscale of existing flow chemistry reaction, the flow system is not limited by the size of available glassware unlike in the batch chemistry.

Two significant challenges exist; purification of the product (solvent extractions, filtrations etc.) that may require industrial facilities due to the scale, and multistep reaction control, that requires computer control which is potentially prohibitively expensive for researchers [124]. Due to a limited number of publications and a gap in research conducted with respect to optimisation of methods and tools for flow chemistry synthesis, the current driving force is towards improving the methods of modern organic flow chemistry for large scale application by improving the physics of mixing in flow [113], [125], [126]. Significantly, whilst the flow chemistry field continues to grow there are still few publications which investigate the synthesis of polymeric OE materials [24], [25], [114], [120], [121], [127]–

[130]. This is in part due to the physical challenge in mixing materials in flow, especially since changing solubility of the polymeric product as the polymer chain grows can lead to precipitation of the product in the flow system and thus blockages. Consequently, not all synthetic processes are suitable for transition to flow chemistry. Nonetheless, for large scale OPV fabrication particularly using techniques such as R2R printing, large quantities of P3HT and other solar cell materials are required, quantities which are potentially not practical using batch chemistry. Therefore, flow chemistry with the ability to directly scale material production may be the best method of synthesis. This thesis will determine if flow chemistry is amenable to the synthesis of key new OE materials to aid material scale up.

Compatible Ni-catalyst systems were studied by H.Seyler et. al and their results for the continuous flow synthesis of P3HT showed challenge in using an *o*-tolyl–Ni catalyst in THF and Ni(dppp)Cl₂ in *o*-DCB due to their high reactivity in the continuous flow reaction. A schematic representation of their flow apparatus is shown in Figure 1.39 [111].

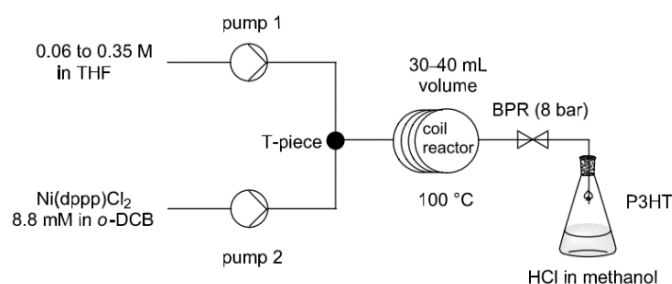


Figure 1.39. Scheme of flow chemistry reactor for continuous P3HT synthesis by flow, using *o*-tolyl–Ni catalyst 3 in THF and Ni(dppp)Cl₂ in *o*-DCB [111].

Two alternative methods to improve compatible Ni-catalyst solvent systems, were suggested by Kumar et. al (2014) [131] and Bannock et, al (2016) [129]. They both described rapid “flow” synthesis of high quality P3HT in reactors with residence times of between 1 – 2 minutes. Both authors used a combination of catalyst and solvent that is different to the commonly used Ni(dppp)Cl₂ (dppp=1,3-bis(diphenylphosphino)propane) /THF [68]:

Kumar et. al [131] used an EDOT:THF mix as the solvent, where EDOT was used to increase the solubility of the Ni(dppp)Cl₂ catalyst. Additionally, LiCl was employed to increase the reaction rate. They used a conventional (single phase) commercial flow synthesis apparatus (Asia Syrris microreactor; see Figure 1.40). However, despite appearing to operate the reactor at an elevated pressure, no mention was made of this parameter in the paper as well as for the percentage of conversion of monomer. Characteristics of the P3HT produced were $M_n \sim 15k$, PDI 1.1–1.3, $rr > 98\%$. This paper also highlighted the critical importance of mixing (particularly during initiation of the polymerisation) in achieving good results. The continuous flow reaction was performed using a relatively simple setup of micro reactor “chips”, micro mixer chips and syringe pumps.

By comparison, Bannock et. al [129] used 2-methyltetrahydrofuran (2MeTHF) as solvent and a synthesised Ni(dppp)Br₂ catalyst, using this combination in a (two-phase) droplet “flow” reactor. Characteristics of the P3HT produced: $M_n \sim 33k$, PDI 1.4 and $rr 93\%$.

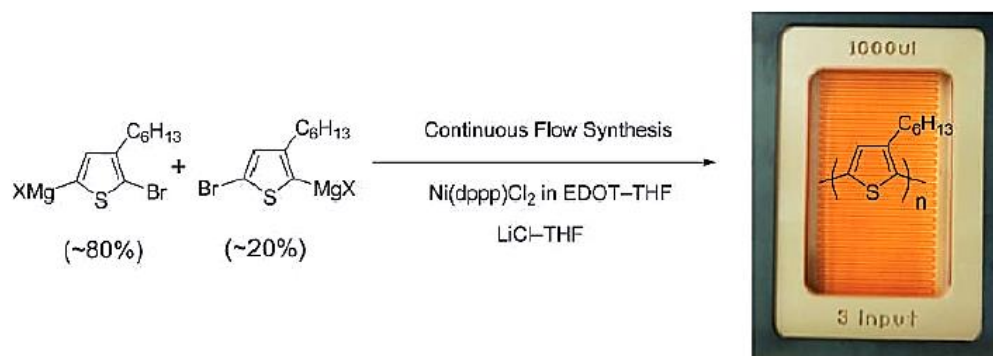


Figure 1.40. Asia Syrris microchip reactor of 1 mL for P3HT synthesis by continuous – flow reaction [112]

Continuous flow synthesis method has also been applied as a method for the production of fullerene derivatives such as PCBM and ICBA [132], Figure 1.41.

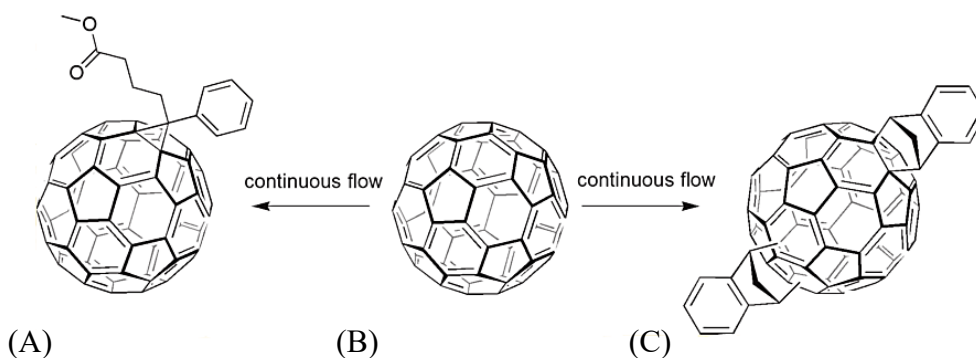


Figure 1.41. (A) IC₆₀BA, (B) C₆₀ and (C) PC₆₀BM

The primary advantage of continuous flow chemistry as discussed by Hartman et al. is the potential for improved reaction yield, which is of significant benefit for a large-scale materials production [113].

1.7.1 The Physics of flow chemistry

T. Shinbrot et al. have shown that transient effects can cause trace material concentration in flow chemistry leading to potential blockages in the fluid. They focussed on numerical simulations of laminar flow in a stirred tank and suggested that sensitivity to density fluctuations affects the fluid control. To date, much effort has been dedicated to study localisation of particles in volume preserving flows. Two assumptions on the mechanism of this localisation were considered. Of importance, the first is that massive or large particles follow different, usually nonconservative, trajectories from an ambient flow. Secondly, these particles can be concentrated by subsurface currents and rise until they are at the boundary of a flow. Therefore, the physical properties of these blockages and the sensitivity to density fluctuations has been determined [126].

To resolve the current challenges in flow chemistry a fundamental understanding of particle mixing is required. A detailed characterisation of the mixing behaviour including the transport of mass, momentum and heat has been considered by Bothe et al. The mixing behaviour of a solution flow in a T-shaped micro-reactor with rectangular cross sections was investigated; for the description of the mixing quality [125] and from their observations it has been shown that an increase of the contact area is of key importance. Increasing contact area can be achieved mechanically (Figure 1.42) or hydrodynamically [125][126][23].

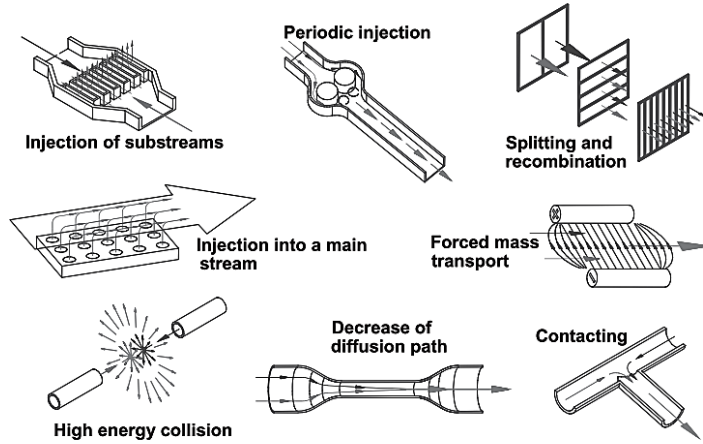


Figure 1.42. Micromixing principles schemes for flow chemistry application [23].

To calculate the mixing quality Bothe et al. derived equation 1.5 represented below:

$$\varphi(V) = \frac{1}{|V|} \int_V \|\nabla f\| dV \quad \text{with } f = \frac{c}{c_{max}}$$

Equation 1.5 [125]

where $|V|$ denotes the volume content of the spatial region V and $\|\nabla f\|$ is the (Euclidean) length of the gradient of the normalised concentration. An analogous measure can be applied to a cross section instead of a volume, in which case V has to be replaced by the appropriate areal region. For a segregated species distribution, the quantity φ exactly gives the specific contact area, or respectively the specific contact length, if applied to a cross section. Therefore, this implementation of specific contact area can be simply evaluated by this equation [125].

In more details, the polymer physics has been discussed by Michael Rubinstein et al. [133] who demonstrates the summary of mixtures in terms of thermodynamics. Two major parts of free energy of mixing exists, i.e. entropic and energetic parts that can be calculated by the following equations 1.6 and 1.7 [133] respectively as represented below:

$$-\frac{T\Delta S_{mix}}{V} = kT \left[\frac{\varphi}{v_A} \ln \varphi + \frac{1-\varphi}{v_B} \ln(1-\varphi) \right]$$

Equation 1.6 [133]

$$\frac{\Delta U_{mix}}{V} = kT \frac{c}{v_0} \varphi(1-\varphi)$$

Equation 1.7 [133]

Where, $-\Delta S_{mix}$ translational entropy of mixing; v_A – volume of A chain; v_B – volume of B chain; v_0 – volume of a lattice site; c - Flory interaction parameter

$$c = A + \frac{B}{T}$$

As a result, very few polymer mixtures are truly miscible, since only some polymers have soluble side chains and mostly only low molecular weight liquids are miscible.

Hartman et al. summarised all criteria which determine flow suitability, in particular; flow chemistry instrumentation, design of the elements, significance of the shutdown process and compatibility with the upscaling of flow and batch methods in order to make a decision guide for replacement batch system by flow chemistry [113].

In essence, there are four types of the reaction synthesis suitable for conversion to implementation by flow methods:

- Type I is the continuous way of product synthesis, by introduction of reagents A and B into the column to form A-B, where any unreacted A or B by-products are disposed.
- Type II reactions introduce reagent B to the column as a supported reagent; overreaction may occur due to the excess of reagent B substrate consuming A.
- Type III reactions have reagents A and B react together in the presence of a homogeneous type catalyst, which is eluted from a product as a contaminant.
- Type IV is the same reagent mixture in the column as Type III, however the catalyst used is heterogeneous and embedded in the flow column and therefore no separation of the catalyst from the product is required.

According to green and sustainable chemistry, the choice of flow system will favour type III and IV systems, as homogeneous or heterogeneous catalyst synthesis can result in less energy consumption and pollution in comparison to synthesis without catalysts. The best contamination free product can potentially result from the Type IV synthesis method (if by-products can be minimised); therefore, this method is potentially advantageous over another type III method [109], Figure 1.43.

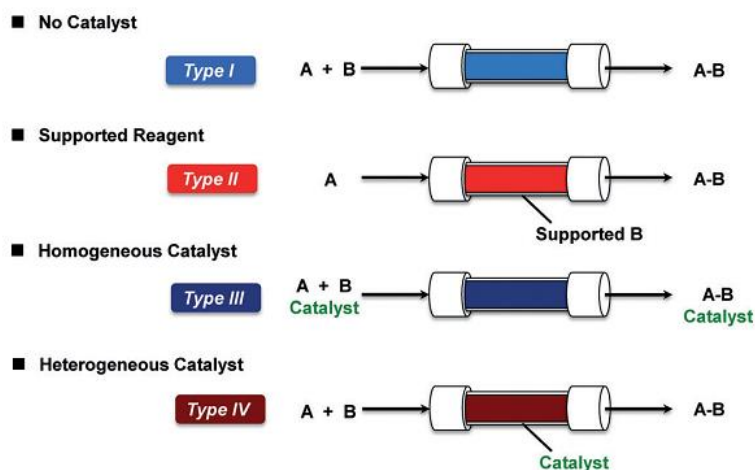


Figure 1.43. Flow method reaction types [109]

According to a literature survey with the possible flow chemistry reaction methods and different apparatus used, in Chapter 6 it has been investigated which of these methods are the most efficient for the large scale OE materials synthesis application. The methods were developed to improve both material cost and reaction yield, in order to allow commercially viable synthesis.

1.8 Summary

This overview has outlined the effective way towards large area OPV module commercialisation by incorporating economically viable, highly efficient, active layer materials into solar modules. It included an investigation on the currently available scale up production methods to achieve inexpensive material production. The synthesis of benchmark materials has been considered on a mass scale, and more importantly, compared to the synthesis of PDCBT polymer and ITIC small molecular compounds for potential

introduction into OPV devices on small scale, nanoparticle devices and large scale printed modules. Much more understanding and optimisation of experimental work for component material synthesis upscale and effective printing/processing of these materials is required to realise the development of new high-performance materials in OPV devices. The systematic study to establish operative large scale production methods by batch or flow chemistry and their cost control is a yet relatively unexplored area of solar research. Almost no work has been conducted in this respect, with the existing work focusing on a small-scale device manufacturing only. One of the vital key factors for the most efficient large scale devices' mass manufacturing is cost-effective utilisation of organic photovoltaic materials.

Consequently, this thesis aims to uncover relationships between the synthesis and cost of flow or batch reactions of selected high performance materials and address any upscale issues, as well as, to examine device physics and more importantly investigate both performance improvements and fabrication cost reductions.

References

- [1] Lai, T.H., Tsang, S.W., Manders, J.R., Chen, S. and So, F., 2013. Properties of interlayer for organic photovoltaics. *Materials Today*, 16(11), pp.424-432.
- [2] Po, R. and Roncali, J., 2016. Beyond efficiency: scalability of molecular donor materials for organic photovoltaics. *Journal of Materials Chemistry C*, 4(17), pp.3677-3685.
- [3] Parida, B., Iniyar, S. and Goic, R., 2011. A review of solar photovoltaic technologies. *Renewable and sustainable energy reviews*, 15(3), pp.1625-1636.
- [4] Ganesamoorthy, R., Sathiyar, G. and Sakthivel, P., 2017. Fullerene based acceptors for efficient bulk heterojunction organic solar cell applications. *Solar Energy Materials and Solar Cells*, 161, pp.102-148.
- [5] Peng, H., Sun, X., Weng, W. and Fang, X., 2016. *Polymer materials for energy and electronic applications*. Academic Press.
- [6] Canziani, O.F. and Parry, M.L., 2007. Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC).
- [7] Griffith, M.J., Cooling, N.A., Vaughan, B., Elkington, D.C., Hart, A.S., Lyons, A.G., Quereschi, S., Belcher, W.J. and Dastoor, P.C., 2015. Combining printing, coating, and vacuum deposition on the roll-to-roll scale: a hybrid organic photovoltaics fabrication. *IEEE Journal of Selected Topics in Quantum Electronics*, 22(1), pp.112-125.
- [8] Cooling, N.A., Barnes, E.F., Almyahi, F., Feron, K., Al-Mudhaffer, M.F., Al-Ahmad, A., Vaughan, B., Andersen, T.R., Griffith, M.J., Hart, A.S. and Lyons, A.G., 2016. A low-cost mixed fullerene acceptor blend for printed electronics. *Journal of Materials Chemistry A*, 4(26), pp.10274-10281.
- [9] Australian Energy Regulator, "State of the Energy Market," 2015.
- [10] IRENA Renewable Power Generation Costs, Report ISBN:978-92-9260-452-3, 2021
- [11] Chiang, C.K., Fincher Jr, C.R., Park, Y.W., Heeger, A.J., Shirakawa, H., Louis, E.J., Gau, S.C. and MacDiarmid, A.G., 1977. Electrical conductivity in doped polyacetylene. *Physical review letters*, 39(17), p.1098.

- [12] Fidanovski, K. and Mawad, D., 2019. Conjugated polymers in bioelectronics: addressing the interface challenge. *Advanced Healthcare Materials*, 8(10), p.1900053.
- [13] Breyer, C., Gerlach, A., Mueller, J., Behacker, H. and Milner, A., 2009, September. Grid-parity analysis for EU and US regions and market segments–Dynamics of grid-parity and dependence on solar irradiance, local electricity prices and PV progress ratio. In *24th European Photovoltaic Solar Energy Conference, Hamburg, Germany* (pp. 21-25).
- [14] Tang, C.W., 1986. Two-layer organic photovoltaic cell. *Applied physics letters*, 48(2), pp.183-185.
- [15] Tress, W., 2011. Device physics of organic solar cells, pp.1123-1147
- [16] Liu, Q., Jiang, Y., Jin, K., Qin, J., Xu, J., Li, W., Xiong, J., Liu, J., Xiao, Z., Sun, K. and Yang, S., 2020. 18% Efficiency organic solar cells. *Science Bulletin*, 65(4), pp.272-275.
- [17] Liu, F., Zhou, L., Liu, W., Zhou, Z., Yue, Q., Zheng, W., Sun, R., Liu, W., Xu, S., Fan, H. and Feng, L., 2021. Organic solar cells with 18% efficiency enabled by an alloy acceptor: a two-in-one strategy. *Advanced Materials*, 33(27), p.2100830.
- [18] Nilsson, S., Bernasik, A., Budkowski, A. and Moons, E., 2007. Morphology and phase segregation of spin-casted films of polyfluorene/PCBM blends. *Macromolecules*, 40(23), pp.8291-8301.
- [19] Benanti, T.L. and Venkataraman, D., 2006. Organic solar cells: An overview focusing on active layer morphology. *Photosynthesis research*, 87(1), pp.73-81
- [20] Daneshazarian, R., Cuce, E., Cuce, P.M. and Sher, F., 2018. Concentrating photovoltaic thermal (CPVT) collectors and systems: Theory, performance assessment and applications. *Renewable and Sustainable Energy Reviews*, 81, pp.473-492.
- [21] Scharber, M.C. and Sariciftci, N.S., 2013. Efficiency of bulk-heterojunction organic solar cells. *Progress in polymer science*, 38(12), pp.1929-1940.
- [22] Xu, C., Zhao, Z., Yang, K., Niu, L., Ma, X., Zhou, Z., Zhang, X.L. and Zhang, F., 2022. Recent Progress on All-Small-Molecule Organic Photovoltaics. *Journal of Materials Chemistry A*.

- [23] Hessel, V., Löwe, H. and Schönfeld, F., 2005. Micromixers—a review on passive and active mixing principles. *Chemical engineering science*, 60(8-9), pp.2479-2501.
- [24] Rakib, M.I., Evans, S.P. and Clausen, P.D., 2020. Measured gust events in the urban environment, a comparison with the IEC standard. *Renewable Energy*, 146, pp.1134-1142.
- [25] Rossi, E., Carofiglio, T., Venturi, A., Ndobe, A., Muccini, M. and Maggini, M., 2011. Continuous-flow synthesis of an efficient methanofullerene acceptor for bulk-heterojunction solar cells. *Energy & Environmental Science*, 4(3), pp.725-727.
- [26] Pirotte, G., Kesters, J., Verstappen, P., Govaerts, S., Manca, J., Lutsen, L., Vanderzande, D. and Maes, W., 2015. Continuous Flow Polymer Synthesis toward Reproducible Large-Scale Production for Efficient Bulk Heterojunction Organic Solar Cells. *ChemSusChem*, 8(19), pp.3228-3233.
- [27] Zhang, M., Guo, X., Ma, W., Ade, H. and Hou, J., 2014. A polythiophene derivative with superior properties for practical application in polymer solar cells. *Advanced Materials*, 26(33), pp.5880-5885.
- [28] Aqoma, H., Park, S., Park, H.Y., Hadmojo, W.T., Oh, S.H., Nho, S., Kim, D.H., Seo, J., Park, S., Ryu, D.Y. and Cho, S., 2018. 11% Organic Photovoltaic Devices Based on PTB7-Th: PC71BM Photoactive Layers and Irradiation-Assisted ZnO Electron Transport Layers. *Advanced Science*, 5(7), p.1700858.
- [28] Zhao, K., Wang, Q., Xu, B., Zhao, W., Liu, X., Yang, B., Sun, M. and Hou, J., 2016. Efficient fullerene-based and fullerene-free polymer solar cells using two wide band gap thiophene-thiazolothiazole-based photovoltaic materials. *Journal of Materials Chemistry A*, 4(24), pp.9511-9518.
- [29] Pan, Q.Q., Li, S.B., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2018. Exploring more effective polymer donors for the famous non-fullerene acceptor ITIC in organic solar cells by increasing electron-withdrawing ability. *Organic Electronics*, 53, pp.308-314.
- [30] Wadsworth, A., Moser, M., Marks, A., Little, M.S., Gasparini, N., Brabec, C.J., Baran, D. and McCulloch, I., 2019. Critical review of the molecular design progress in non-fullerene electron acceptors towards commercially viable organic solar cells. *Chemical Society Reviews*, 48(6), pp.1596-1625.
- [31] Nielsen, T.D., Cruickshank, C., Foged, S., Thorsen, J. and Krebs, F.C., 2010. Business, market and intellectual property analysis of polymer solar cells. *Solar Energy Materials and Solar Cells*, 94(10), pp.1553-1571.

- [32] Nitschke, P., Jarzabek, B., Vasylieva, M., Godzierz, M., Janeczek, H., Musioł, M. and Domiński, A., 2021. The effect of alkyl substitution of novel imines on their supramolecular organization, towards photovoltaic applications. *Polymers*, 13(7), p.1043.
- [33] Chow, T.T., 2010. A review on photovoltaic/thermal hybrid solar technology. *Applied energy*, 87(2), pp.365-379.
- [34] Esfahani, S.N., Asghari, S. and Rashid-Nadimi, S., 2017. A numerical model for soldering process in silicon solar cells. *Solar Energy*, 148, pp.49-56.
- [35] Carlson, D.E. and Wronski, C.R., 1976. Amorphous silicon solar cell. *Applied Physics Letters*, 28(11), pp.671-673.
- [36] Shah, A., Torres, P., Tscharnner, R., Wyrsh, N. and Keppner, H., 1999. Photovoltaic technology: the case for thin-film solar cells. *science*, 285(5428), pp.692-698.
- [37] Bergmann, R.B., 1999. Crystalline Si thin-film solar cells: a review. *Applied physics A*, 69(2), pp.187-194.
- [38] Gevorgyan, S.A., Espinosa, N., Ciammaruchi, L., Roth, B., Livi, F., Tsopanidis, S., Züfle, S., Queirós, S., Gregori, A., Benatto, G.A.D.R. and Corazza, M., 2016. Baselines for lifetime of organic solar cells. *Advanced Energy Materials*, 6(22), p.1600910.
- [39] Brabec, C.J., 2004. Organic photovoltaics: technology and market. *Solar energy materials and solar cells*, 83(2-3), pp.273-292.
- [40] Burroughes, J.H., Jones, C.A. and Friend, R.H., 1988. New semiconductor device physics in polymer diodes and transistors. *nature*, 335(6186), pp.137-141.
- [41] Garnier, F., Hajlaoui, R., Yassar, A. and Srivastava, P., 1994. All-polymer field-effect transistor realized by printing techniques. *Science*, 265(5179), pp.1684-1686.
- [42] Someya, T., Kato, Y., Sekitani, T., Iba, S., Noguchi, Y., Murase, Y., Kawaguchi, H. and Sakurai, T., 2005. Conformable, flexible, large-area networks of pressure and thermal sensors with organic transistor active matrixes. *Proceedings of the National Academy of Sciences*, 102(35), pp.12321-12325.
- [43] Mitridis, S., 2008. Determination of lattice site location of impurities in compound semiconductors, by transmission electron microscopy. *Physics of Advanced Materials Winter School 2008*, (2008), 1, 17.

- [44] Shaheen, S.E., Ginley, D.S. and Jabbour, G.E., 2005. Organic-based photovoltaics: toward low-cost power generation. *MRS bulletin*, 30(1), pp.10-19.
- [45] Dunlap Jr, W.C. and Watters, R.L., 1953. Direct measurement of the dielectric constants of silicon and germanium. *Physical Review*, 92(6), p.1396.
- [46] Yan, C., Barlow, S., Wang, Z., Yan, H., Jen, A.K.Y., Marder, S.R. and Zhan, X., 2018. Non-fullerene acceptors for organic solar cells. *Nature Reviews Materials*, 3(3), pp.1-19.
- [47] Tang, C.W., 1986. Two-layer organic photovoltaic cell. *Applied physics letters*, 48(2), pp.183-185.
- [48] Sariciftci, N.S., Smilowitz, L., Heeger, A.J. and Wudl, F., 1992. Photoinduced electron transfer from a conducting polymer to buckminsterfullerene. *Science*, 258(5087), pp.1474-1476.
- [49] Yu, G., Gao, J., Hummelen, J.C., Wudl, F. and Heeger, A.J., 1995. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science*, 270(5243), pp.1789-1791.
- [50] Hamam, K.J.T., 2013. Organic Solar Cells Based on High Dielectric Constant Materials: An Approach to Increase Efficiency.
- [51] Coakley, K.M. and McGehee, M.D., 2004. Conjugated polymer photovoltaic cells. *Chemistry of materials*, 16(23), pp.4533-4542.
- [52] Penza, M., Cozzi, S., Tagliente, M.A., Mirengi, L., Martucci, C. and Quirini, A., 1999. Characterization of transparent and conductive electrodes of indium tin oxide thin films by sequential reactive evaporation. *thin solid Films*, 349(1-2), pp.71-77.
- [53] C. J. Mulligan, 2013, *Towards Production Scale-Up of Organic Photovoltaics*, PhD Thesis, The University of Newcastle, Newcastle.
- [54] Marathe, D.M., Tarkas, H.S., Mahajan, M.S., Ghosh, S.S., Khadayate, R.S. and Sali, J.V., 2016. Poly 3-Hexylthiophene: Single Wall Carbon Nanotube Active Layer by Dual Feed Ultrasonic Spray Method for Solar Cell Application. *Journal of Nanoelectronics and Optoelectronics*, 11(1), pp.12-17.
- [55] Su'ait, M.S., Rahman, M.Y.A. and Ahmad, A., 2015. Review on polymer electrolyte in dye-sensitized solar cells (DSSCs). *Solar Energy*, 115, pp.452-470.

- [56] Hoppe, H. and Sariciftci, N.S., 2004. Organic solar cells: An overview. *Journal of materials research*, 19(7), pp.1924-1945.
- [57] Janssen, R.A. and Nelson, J., 2013. Factors limiting device efficiency in organic photovoltaics. *Advanced Materials*, 25(13), pp.1847-1858.
- [58] Holliday, S., Li, Y. and Luscombe, C.K., 2017. Recent advances in high performance donor-acceptor polymers for organic photovoltaics. *Progress in Polymer Science*, 70, pp.34-51.
- [59] Mihailetschi, V.D., 2005. Device physics of organic bulk heterojunction solar cells. *University of Groningen, The Netherlands*.
- [60] Johansson, D.M., Srdanov, G., Yu, G., Theander, M., Inganäs, O. and Andersson, M.R., 2000. Synthesis and characterization of highly soluble phenyl-substituted poly (p-phenylenevinylenes). *Macromolecules*, 33(7), pp.2525-2529.
- [61] Shaheen, S.E., Brabec, C.J., Sariciftci, N.S., Padinger, F., Fromherz, T. and Hummelen, J.C., 2001. 2.5% efficient organic plastic solar cells. *Applied physics letters*, 78(6), pp.841-843.
- [62] Wang, H.J., Chen, C.P. and Jeng, R.J., 2014. Polythiophenes comprising conjugated pendants for polymer solar cells: a review. *Materials*, 7(4), pp.2411-2439.
- [63] Bundgaard, E. and Krebs, F.C., 2007. Low band gap polymers for organic photovoltaics. *Solar Energy Materials and Solar Cells*, 91(11), pp.954-985.
- [64] Kadem, B., Hassan, A. and Cranton, W., 2016. Efficient P3HT: PCBM bulk heterojunction organic solar cells; effect of post deposition thermal treatment. *Journal of Materials Science: Materials in Electronics*, 27(7), pp.7038-7048.
- [65] Glenis, S., Tourillon, G. and Garnier, F., 1986. Influence of the doping on the photovoltaic properties of thin films of poly-3-methylthiophene. *Thin Solid Films*, 139(3), pp.221-231.
- [66] Mehmood, U., Al-Ahmed, A. and Hussein, I.A., 2016. Review on recent advances in polythiophene based photovoltaic devices. *Renewable and Sustainable Energy Reviews*, 57, pp.550-561.
- [67] McCullough, R.D., 1998. The chemistry of conducting polythiophenes. *Advanced materials*, 10(2), pp.93-116.

- [68] M. G. Wilson, 2014, *Preparation of Regioregular Poly(3-hexylthiophene) and its Precursor Monomer, 2,5-dibromo-3-hexylthiophene, Using Low Pressure Flow Synthesis Techniques*, PhD Thesis, The University of Newcastle, Newcastle.
- [69] N. A. Cooling, 2013, *Ternary Porphyrinoid: Polymer: Fullerene Bulk Heterojunction Organic Solar Cells*, PhD Thesis, The University of Newcastle, Newcastle.
- [70] Sariciftci, N.S., Smilowitz, L., Heeger, A.J. and Wudl, F., 1993. Semiconducting polymers (as donors) and buckminsterfullerene (as acceptor): photoinduced electron transfer and heterojunction devices. *Synthetic Metals*, 59(3), pp.333-352.
- [71] Venkatraman, M., 1995. United States Patent (12)(10) Patent N0.: US 6,549,660 B1 Lipson et al.(45) Date of Patent: Apr. 15, 2003. *Evaluation*, 17(7), pp.729-736.
- [72] Kroon, J.M., Veenstra, S.C., Slooff, L.H., Verhees, W.J.H., Koetse, M.M., Sweelssen, J., Schoo, H.F.M., Beek, W.J.E., Wienk, M.M., Janssen, R.A.J. and Yang, X., 2005, June. Polymer based photovoltaics: novel concepts, materials and state-of-the art efficiencies. In *Presented at the 20th European Photovoltaic Solar Energy Conference and Exhibition* (Vol. 6, p. 10).
- [73] Lenes, M., Wetzelaer, G.J.A., Kooistra, F.B., Veenstra, S.C., Hummelen, J.C. and Blom, P.W., 2008. Fullerene bisadducts for enhanced open-circuit voltages and efficiencies in polymer solar cells. *Advanced Materials*, 20(11), pp.2116-2119.
- [74] Schroeder, B.C., Li, Z., Brady, M.A., Faria, G.C., Ashraf, R.S., Takacs, C.J., Cowart, J.S., Duong, D.T., Chiu, K.H., Tan, C.H. and Cabral, J.T., 2014. Enhancing Fullerene-Based Solar Cell Lifetimes by Addition of a Fullerene Dumbbell. *Angewandte Chemie*, 126(47), pp.13084-13089.
- [75] Larson, B.W., Whitaker, J.B., Wang, X.B., Popov, A.A., Rumbles, G., Kopidakis, N., Strauss, S.H. and Boltalina, O.V., 2013. Electron affinity of phenyl-C61-butyric acid methyl ester (PCBM). *The Journal of Physical Chemistry C*, 117(29), pp.14958-14964.
- [76] Chen, Z., Cai, P., Chen, J., Liu, X., Zhang, L., Lan, L., Peng, J., Ma, Y. and Cao, Y., 2014. Low band-gap conjugated polymers with strong interchain aggregation and very high hole mobility towards highly efficient thick-film polymer solar cells. *Advanced materials*, 26(16), pp.2586-2591.
- [77] Osedach, T.P., Andrew, T.L. and Bulović, V., 2013. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy & Environmental*

Science, 6(3), pp.711-718.

- [78] Qin, Y., Uddin, M.A., Chen, Y., Jang, B., Zhao, K., Zheng, Z., Yu, R., Shin, T.J., Woo, H.Y. and Hou, J., 2016. Highly Efficient Fullerene-Free Polymer Solar Cells Fabricated with Polythiophene Derivative. *Advanced Materials*, 28(42), pp.9416-9422.
- [79] Zhang, H., Li, S., Xu, B., Yao, H., Yang, B., & Hou, J. (2016). Fullerene-free polymer solar cell based on a polythiophene derivative with an unprecedented energy loss of less than 0.5 eV. *Journal of Materials Chemistry A*, 4(46), 18043-18049.
- [80] Waters, Richard Huw Robert, (2015), *Characterisation and lifetime studies of CPDT- and BT-based photovoltaic cells*, Bangor University (United Kingdom).
- [81] Liang, Y., Wu, Y., Feng, D., Tsai, S.T., Son, H.J., Li, G. and Yu, L., 2009. Development of new semiconducting polymers for high performance solar cells. *Journal of the American Chemical Society*, 131(1), pp.56-57.
- [82] Zheng, Y.Q., Potscavage Jr, W.J., Komino, T., Hirade, M., Adachi, J. and Adachi, C., 2013. Highly efficient bulk heterojunction photovoltaic cells based on C70 and tetraphenyldibenzoperiflanthene. *Applied Physics Letters*, 102(14), p.60.
- [83] Mulligan, C.J., Bilen, C., Zhou, X., Belcher, W.J. and Dastoor, P.C., 2015. Levelised cost of electricity for organic photovoltaics. *Solar energy materials and solar cells*, 133, pp.26-31.
- [84] Parlak, E.A., 2012. The blend ratio effect on the photovoltaic performance and stability of poly (3-hexylthiophene):[6, 6]-phenyl-C61 butyric acid methyl ester (PCBM) and poly (3-octylthiophene): PCBM solar cells. *Solar energy materials and solar cells*, 100, pp.174-184.
- [85] Bin, H., Zhang, Z.G., Gao, L., Chen, S., Zhong, L., Xue, L., Yang, C. and Li, Y., 2016. Non-fullerene polymer solar cells based on alkylthio and fluorine substituted 2D-conjugated polymers reach 9.5% efficiency. *Journal of the American Chemical Society*, 138(13), pp.4657-4664.
- [86] W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, and F. Gao, "Fullerene-Free Polymer Solar Cells with over 11 % Efficiency and Excellent Thermal Stability," pp. 4734–4739, 2016.
- [87] Sharma, V., Singh, V., Arora, M., Arora, S. and Tandon, R.P., 2015. Influence of donor–acceptor materials on the photovoltaic parameters of conjugated

polymer/fullerene solar cells. *Journal of Materials Science: Materials in Electronics*, 26(8), pp.6212-6217.

- [88] Lin, Y., Wang, J., Zhang, Z.G., Bai, H., Li, Y., Zhu, D. and Zhan, X., 2015. An electron acceptor challenging fullerenes for efficient polymer solar cells. *Advanced materials*, 27(7), pp.1170-1174.
- [89] M. Zhang, X. Guo, W. Ma, and H. Ade, "A Polythiophene Derivative with Superior Properties for Practical Application in Polymer Solar Cells," 2014.
- [90] Mo, D., Wang, H., Chen, H., Qu, S., Chao, P., Yang, Z., Tian, L., Su, Y.A., Gao, Y., Yang, B. and Chen, W., 2017. Chlorination of low-band-gap polymers: toward high-performance polymer solar cells. *Chemistry of Materials*, 29(7), pp.2819-2830.
- [91] C. Chen, S. Chan, T. Chao, C. Ting, and B. Ko, "Derivatives with Broadened Absorption Spectra for Use in High-Performance Bulk-Heterojunction Polymer Solar Cells," no. 12, pp. 12828–12833, 2008.
- [92] Ma, Y., Chen, S.C., Wang, Z., Ma, W., Wang, J., Yin, Z., Tang, C., Cai, D. and Zheng, Q., 2017. Indacenodithiophene-based wide bandgap copolymers for high performance single-junction and tandem polymer solar cells. *Nano Energy*, 33, pp.313-324.
- [93] Coppo, P. and Turner, M.L., 2005. Cyclopentadithiophene based electroactive materials. *Journal of Materials Chemistry*, 15(11), pp.1123-1133.
- [94] Wang, T.L., Yang, C.H., Shieh, Y.T., Chen, Y.C., Ho, T.H. and Chen, C.H., 2012. An extremely low bandgap donor–acceptor copolymer for panchromatic solar cells. *Solar energy materials and solar cells*, 107, pp.298-306.
- [95] Wienk, M.M., Kroon, J.M., Verhees, W.J., Knol, J., Hummelen, J.C., Van Hal, P.A. and Janssen, R.A., 2003. Efficient methano [70] fullerene/MDMO-PPV bulk heterojunction photovoltaic cells. *Angewandte Chemie*, 115(29), pp.3493-3497.
- [96] Dupont, S.R., Oliver, M., Krebs, F.C. and Dauskardt, R.H., 2012. Interlayer adhesion in roll-to-roll processed flexible inverted polymer solar cells. *Solar Energy Materials and Solar Cells*, 97, pp.171-175.
- [97] Wadsworth, A., Moser, M., Marks, A., Little, M.S., Gasparini, N., Brabec, C.J., Baran, D. and McCulloch, I., 2019. Critical review of the molecular design progress in non-fullerene electron acceptors towards commercially viable organic solar cells. *Chemical Society Reviews*, 48(6), pp.1596-1625.

- [98] Su, W., Fan, Q., Guo, X., Meng, X., Bi, Z., Ma, W., Zhang, M. and Li, Y., 2017. Two compatible nonfullerene acceptors with similar structures as alloy for efficient ternary polymer solar cells. *Nano Energy*, 38, pp.510-517.
- [99] Lin, Y., Zhao, F., Wu, Y., Chen, K., Xia, Y., Li, G., Prasad, S.K., Zhu, J., Huo, L., Bin, H. and Zhang, Z.G., 2017. Mapping Polymer Donors toward High-Efficiency Fullerene Free Organic Solar Cells. *Advanced materials*, 29(3), p.1604155.
- [100] Pan, Q.Q., Li, S.B., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2018. Exploring more effective polymer donors for the famous non-fullerene acceptor ITIC in organic solar cells by increasing electron-withdrawing ability. *Organic Electronics*, 53, pp.308-314.
- [101] Li, S., Ye, L., Zhao, W., Zhang, S., Mukherjee, S., Ade, H. and Hou, J., 2016. Energy-level modulation of small-molecule electron acceptors to achieve over 12% efficiency in polymer solar cells. *Advanced materials*, 28(42), pp.9423-9429.
- [102] Lin, Y., Zhao, F., He, Q., Huo, L., Wu, Y., Parker, T.C., Ma, W., Sun, Y., Wang, C., Zhu, D. and Heeger, A.J., 2016. High-performance electron acceptor with thienyl side chains for organic photovoltaics. *Journal of the American Chemical Society*, 138(14), pp.4955-4961.
- [103] Zheng, Z., Awartani, O.M., Gautam, B., Liu, D., Qin, Y., Li, W., Bataller, A., Gundogdu, K., Ade, H. and Hou, J., 2017. Efficient charge transfer and fine-tuned energy level alignment in a THF-processed fullerene-free organic solar cell with 11.3% efficiency. *Advanced Materials*, 29(5), p.1604241.
- [104] Zhao, W., Qian, D., Zhang, S., Li, S., Inganäs, O., Gao, F. and Hou, J., 2016. Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability. *Advanced materials*, 28(23), pp.4734-4739.
- [105] Pan, Q.Q., Li, S.B., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2018. Exploring more effective polymer donors for the famous non-fullerene acceptor ITIC in organic solar cells by increasing electron-withdrawing ability. *Organic Electronics*, 53, pp.308-314.
- [106] Kim, Y., Choulis, S.A., Nelson, J., Bradley, D.D., Cook, S. and Durrant, J.R., 2005. Device annealing effect in organic solar cells with blends of regioregular poly (3-hexylthiophene) and soluble fullerene. *Applied Physics Letters*, 86(6), p.063502.
- [107] Huang, Y., Kramer, E.J., Heeger, A.J. and Bazan, G.C., 2014. Bulk heterojunction solar cells: morphology and performance relationships. *Chemical reviews*, 114(14),

pp.7006-7043.

- [108] Ruderer, M.A., Guo, S., Meier, R., Chiang, H.Y., Körstgens, V., Wiedersich, J., Perlich, J., Roth, S.V. and Müller-Buschbaum, P., 2011. Solvent-induced morphology in polymer-based systems for organic photovoltaics. *Advanced Functional Materials*, 21(17), pp.3382-3391.
- [109] Kobayashi, S., 2016. Flow “fine” synthesis: high yielding and selective organic synthesis by flow methods. *Chemistry–An Asian Journal*, 11(4), pp.425-436.
- [110] Seyler, H., Jones, D.J., Holmes, A.B. and Wong, W.W., 2012. Continuous flow synthesis of conjugated polymers. *Chemical Communications*, 48(10), pp.1598-1600.
- [111] Seyler, H., Subbiah, J., Jones, D. J., Holmes, A. B., & Wong, W. W. (2013). Controlled synthesis of poly (3-hexylthiophene) in continuous flow. *Beilstein journal of organic chemistry*, 9(1), 1492-1500.
- [112] Kumar, A., Hasan, J., Majji, A., Avhale, A., Gopinathan, S., Sharma, P., Tarange, D., Bajpai, R. and Kumar, A., 2014. Continuous-flow synthesis of regioregular poly (3-hexylthiophene): ultrafast polymerization with high throughput and low polydispersity index. *Journal of Flow Chemistry*, 4(4), pp.206-210.
- [113] M. Trojanowicz, “Flow chemistry vs. flow analysis,” *Talanta*, vol. 146, pp. 621–640, Jan. 2016.
- [114] Seyler, H., Jones, D.J., Holmes, A.B. and Wong, W.W., 2012. Continuous flow synthesis of conjugated polymers. *Chemical Communications*, 48(10), pp.1598-1600.
- [115] Bannock, J.H., Krishnadasan, S.H., Nightingale, A.M., Yau, C.P., Khaw, K., Burkitt, D., Halls, J.J., Heeney, M. and de Mello, J.C., 2013. Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Advanced Functional Materials*, 23(17), pp.2123-2129.
- [116] Bannock, J.H., Krishnadasan, S.H., Nightingale, A.M., Yau, C.P., Khaw, K., Burkitt, D., Halls, J.J., Heeney, M. and de Mello, J.C., 2013. Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Advanced Functional Materials*, 23(17), pp.2123-2129.
- [117] Pashkova, A. and Greiner, L., 2011. Towards Small-Scale Continuous Chemical Production: Technology Gaps and Challenges. *Chemie Ingenieur Technik*, 83(9), pp.1337-1342.

- [118] Wiles, C. and Watts, P., 2008. Continuous flow reactors, a tool for the modern synthetic chemist. *European journal of organic chemistry*, 2008(10), pp.1655-1671.
- [119] Myers, R.M., Fitzpatrick, D.E., Turner, R.M. and Ley, S.V., 2014. Flow chemistry meets advanced functional materials. *Chemistry–A European Journal*, 20(39), pp.12348-12366.
- [120] Helgesen, M., 2016. Flow synthesis-the answer to reproducible high-performance conjugated polymers on the scale that R2R processing demands. In *Global Organic Photovoltaic Conference 2016: Global Organic Photovoltaic Conference*.
- [121] Grenier, F., Aïch, B.R., Lai, Y.Y., Guérette, M., Holmes, A.B., Tao, Y., Wong, W.W. and Leclerc, M., 2015. Electroactive and photoactive poly [isoindigo-alt-EDOT] synthesized using direct (hetero) arylation polymerization in batch and in continuous flow. *Chemistry of Materials*, 27(6), pp.2137-2143.
- [122] Helgesen, M., Carlé, J.E., dos Reis Benatto, G.A., Søndergaard, R.R., Jørgensen, M., Bundgaard, E. and Krebs, F.C., 2015. Making Ends Meet: Flow Synthesis as the Answer to Reproducible High-Performance Conjugated Polymers on the Scale that Roll-to-Roll Processing Demands. *Advanced Energy Materials*, 5(9), p.1401996.
- [123] Rossetti, I. and Compagnoni, M., 2016. Chemical reaction engineering, process design and scale-up issues at the frontier of synthesis: Flow chemistry. *Chemical Engineering Journal*, 296, pp.56-70.
- [124] Ingham, R.J., 2014. *Control tools for flow chemistry processing and their application to the synthesis of bromodomain inhibitors* (Doctoral dissertation, University of Cambridge).
- [125] Bothe, D., Stemich, C. and Warnecke, H.J., 2006. Fluid mixing in a T-shaped micro-mixer. *Chemical Engineering Science*, 61(9), pp.2950-2958.
- [126] Shinbrot, T., Alvarez, M.M., Zalc, J.M. and Muzzio, F.J., 2001. Attraction of minute particles to invariant regions of volume preserving flows by transients. *Physical Review Letters*, 86(7), p.1207.
- [127] Shinbrot, T., Alvarez, M.M., Zalc, J.M. and Muzzio, F.J., 2001. Attraction of minute particles to invariant regions of volume preserving flows by transients. *Physical Review Letters*, 86(7), p.1207.
- [128] Pirotte, G., Kesters, J., Verstappen, P., Govaerts, S., Manca, J., Lutsen, L., and Maes, W. (2015). Continuous Flow Polymer Synthesis toward Reproducible Large-Scale

Production for Efficient Bulk Heterojunction Organic Solar Cells. *ChemSusChem*, 8(19), 3228-3233.

- [129] Bannock, J.H., Xu, W., Baïssas, T., Heeney, M. and de Mello, J.C., 2016. Rapid flow-based synthesis of poly (3-hexylthiophene) using 2-methyltetrahydrofuran as a bio-derived reaction solvent. *European Polymer Journal*, 80, pp.240-246.
- [130] Seyler, H., Subbiah, J., Jones, D.J., Holmes, A.B. and Wong, W.W., 2013. Controlled synthesis of poly (3-hexylthiophene) in continuous flow. *Beilstein journal of organic chemistry*, 9(1), pp.1492-1500.
- [131] Kumar, A., Hasan, J., Majji, A., Avhale, A., Gopinathan, S., Sharma, P., and Kumar, A. (2014). Continuous-flow synthesis of regioregular poly (3-hexylthiophene): ultrafast polymerization with high throughput and low polydispersity index. *Journal of Flow Chemistry*, 4(4), 206-210.
- [132] Seyler, H., Wong, W. W., Jones, D. J., & Holmes, A. B. (2011). Continuous flow synthesis of fullerene derivatives. *The Journal of Organic Chemistry*, 76(9), 3551-3556.
- [133] M. Rubinstein and R. H. Colby, "Polymer physics." Oxford University Press New York, 2003.

Chapter 2: Experimental

2.1 Materials and reagents

All solvents were either A.R. or A.C.S grade and purchased from Sigma-Aldrich Inc. or Merck PTY Ltd., Australia. Thiophene-3-carboxylic acid and 5,5'-Dibromo-2,2'-bithiophene were purchased from Henan Tianfu Chemical Co., Ltd, China. Bromine ($\geq 99.99\%$, trace metals basis), N,N'-Dicyclohexylcarbodiimide/DCC (99%), N,N-Dimethylpyridin-4-amine/DMAP (ReagentPlus®, $\geq 99\%$), 2-Butyl-1-octanol, dichlorobis(triphenylphosphine)nickel(II) ($\text{NiCl}_2(\text{PPh}_3)_2$), triphenylphosphine (PPh_3), zinc powder (purum), potassium iodide (ACS reagent, $\geq 99.0\%$), trifluoroacetic acid (ReagentPlus®, 99%), N-Bromosuccinimide/NBS (ReagentPlus®, 99%), trimethyltin chloride solution (1.0 M in hexanes), n-Butyllithium solution (1.6 M in hexanes) and Palladium-tetrakis(triphenylphosphine)/ $\text{Pd}(\text{PPh}_3)_4$ (99%) were purchased from Sigma-Aldrich Inc., Australia. Thieno[3,2-b]thiophene was purchased from Hangzhou Sartort Chemical., Ltd, China. Diethyl 2,5-dibromoterephthalate was purchased from Zhejiang Arts & Crafts Imp. & Exp. CO., China. N-butyllithium 2.5M in hexane, zinc chloride (anhydrous, free-flowing, Redi-Dri™, reagent grade, $\geq 98\%$) and celite (filter aid, dried, untreated) were supplied by Sigma-Aldrich Inc., Australia. 1-bromo-4-hexylbenzene was purchased from Trylead Chemical Technology Co., Ltd. Acetic acid (glacial) and sulfuric acid (98%) were purchased from Chem-Supply Pty Ltd. Malononitrile ($\geq 99\%$) was purchased from Sigma-Aldrich Inc. Australia. 1-3-indandione (97%) reagent was supplied by Accel Pharmtech, LLC, United

States. Sodium Sulfate AR anhydrous powder was purchased from Chem-Supply Pty Ltd, Australia. Sodium thiosulfate AR was supplied by Bacto Laboratories Pty Ltd, Australia. 3,4-ethylenedioxythiophene (EDOT) was purchased from Yurui (Shanghai) Chemical Co., Ltd, China.

All further compounds required for polymers (P3HT, PDCBT), fullerenes (PCMB, ICx A) and small molecule (ITIC) synthesis were synthesised as described in chapters 4-6.

2.2 Characterisation methods and Equipment

Vilber Lourmat VL-6C 6W 254 nm Tube 12W UV UltraViolet Light CN-6 Darkroom UV indicator was used for performing thin layer chromatography (TLC) on Sigma-Aldrich aluminium backed sheets pre-coated with silica gel. Silica gel column chromatography was carried out using a 40 mm diameter column packed with silica gel grade 60, 70-230 mesh. An ISG DMP-100 melting point device was utilised for melting point determinations.

Chemical compounds were characterised by UV-vis and NMR spectroscopic methods. A Varian Cary 6000i UV-Vis-NIR spectrophotometer was used for recording the UV-vis spectra of compounds. The UV-vis spectra were measured of either a thin film deposited on quartz or a solution (concentration between 1×10^{-6} M and 5×10^{-6} M) with scanning range between 300 nm to 1100 nm, except where otherwise stated. ^1H NMR studies were performed using a 300 MHz Bruker Avance-300DPX NMR spectrometer with deuterated chloroform (CDCl_3) as solvent. Calibration against the residual ^1H solvent signal at δ H 7.26 ppm was used for all spectra.

2.2.1 Methodology for donor and acceptor materials selection and costing

As discussed in Chapter 1, the calculation of SC index plays a critical role in the material selection and affects material synthesis cost as well. Initially, by utilising published methods [1], [2], [3], we have assessed between 150 to 200 of the most highly efficient OPV materials. Analysis of key criteria narrowed down our selection to 7 of the best candidates (listed in the Table) with relatively simple synthesis routes (i.e. less than six number of synthetic steps (>6 steps increases the synthetic complexity [1])), economic viability and high efficiency.

First considered were donor materials which perform well in organic solar cells ranging in PCE from 5.3-7.64 % [2] [3], however no preference was observed for selection, due to their expensive and complex syntheses with SC indexes ranging between 75-81 (See Chapter 3 Table 3.1). Even though, a low SC index is attributed to PC₆₀BM and ICxA compounds, in terms of the efficiency and cost of production, these materials are less preferable in comparison to the ITIC small molecule acceptor and PC₇₁BM acceptors. This survey found that the most competitive and beneficial donor material based on the average SC index and an optimal cost per gram of \$48.89 is PDCBT, which achieves a maximum PCE efficiency of 10.16 % with the ITIC acceptor at a cost per gram of \$170.59. Thus, at gram scale, a total of \$219.48 for the donor/acceptor pair is achieved for the most cost efficient active layer materials to be incorporated in a solar cell device for R2R.

The developed method for chemical synthesis cost and cost breakdown (based on major chemical supplier quotes such as Solarmer Co., Sigma-Aldrich Co. and 1-Material Co.) is detailed in Chapter 3.

2.2.2 Synthetic methods

Two main chemical synthesis methods i.e. flow and batch synthesis are described in this chapter.

2.2.2.1 Flow chemistry

This method provides potential for development of material upscale as a well-established technique in large quantity production. However, currently existing work is focusing only on a laboratory scale (using microreactors). This thesis examines the optimisation of this method to achieve the scale up goal.

Based on the literature survey [4–17], there are two most effective continuous flow chemistry methods which have been applied in order to improve and upscale the flow synthesis of P3HT by the Grignard metathesis polymerisation method.

The first method I have adapted is an optimisation of a method developed by former COE PhD student Dr Mitchell Wilson, who was able to eliminate the poorly soluble neat Ni(dppp)Cl_2 initiator and instead used oligomer chains complexed to Ni in order to improve suitability for flow chemistry by improving catalyst solubility in organic solvents, Figure 2.1. rrP3HT yields of 32-55 % were achieved [4]. However, based on the previous investigations on optimisation of the flow system which is represented below in Figure 2.2, a few improvements were proposed to improve the synthesis:

1. Search for a better solvent for the Ni(dppp)Cl_2 and P3HT, to avoid blockages in the flow chemistry tubing.

2. Determination of P3HT solubility in THF during the flow reaction.
3. Determination of the Ni(dppp)Cl_2 solubility in THF and EDOT in particular
4. Scale up by increasing tubing diameter and achieve consistent flow rate control.

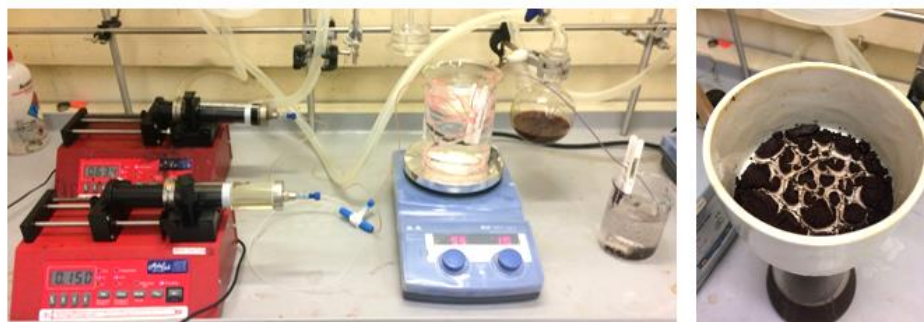


Figure 2.1. P3HT flow synthesis 0.5g scale. Mass recovered 0.305g (yield = 53 %)

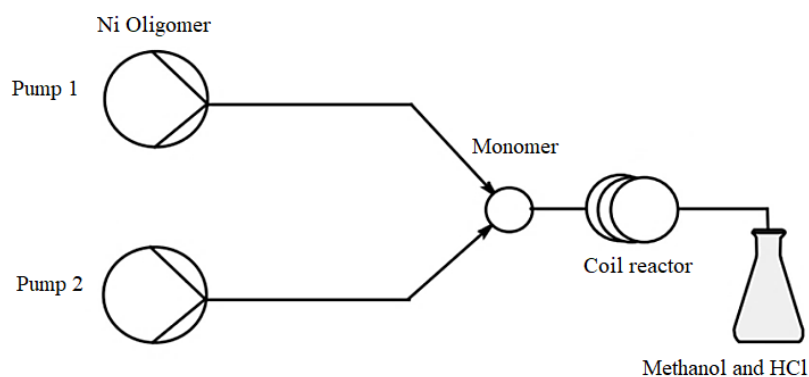


Figure 2.2. Flow system scheme for P3HT synthesis by introduction Ni-oligomer initiator [4]

In the second method, I have modified the procedure described by Kumar et al., where they achieved rapid P3HT flow synthesis [18] by using 3,4-ethylenedioxythiophene (EDOT) to

improve the solubility of Ni(dppp)Cl₂, as this catalyst has poor solubility in the traditional solvent THF. This method allows dissolution of the Ni(dppp)Cl₂ in order to perform flow chemistry without requiring the preforming of an oligomer solution [18]. Also, the introduction of EDOT in the catalyst solution increases its stability and it remains reactive for up to two weeks, as Kumar et. al report, whereas instability of the oligomer solution is observed over a few hours. This advantage increases the potential for scalability of the flow system.

To investigate the effect of EDOT in my standard P3HT polymer synthesis, successful batch synthesis experiments were performed. By simply adding a mixture of THF and EDOT solvents at the ratio of 1:10 to a batch reaction (standard batch reaction), this showed us that the polymerisation remained successful in the presence of EDOT, Table 2.1. The aim of this experiment was to check that EDOT does not hinder the reaction or cause other problems with a standard batch synthesis method, so that we can proceed with the flow chemistry optimisation. We proceeded with the soxlet purification of P3HT with methanol and hexane solvents. However the polymer ¹H-NMR showed that polymer was not as pure as the standard batch reactions. Therefore the polymer was further purified by reprecipitation in methanol from a chloroform solution and ¹H-NMR results improved.

Table 2.1. P3HT with EDOT and without EDOT batch synthesis results.

	Actual Yield	Theoretical yield	Expected yield
P3HT with EDOT	0.346 g (69.2 %)	~ 0.5 g (100 %)	64 %
P3HT w/o EDOT	0.705 g (70.5 %)	~1 g (100 %)	64 %

With optimal batch conditions determined, an attempt to modify the flow system for the two methods described above was made by introducing identical monomer and catalyst concentrations, where the catalyst solution concentration is exchanged with equimolar oligomer solution. This variation to the suggested concentrations reported in Kumar et.al [5] paper, performed well with high yield, which can be further optimised by variation of other parameters in the flow system and the use of larger vessels will enable future mass production. Optimisation of the existing flow chemistry setup with the goal of improving reaction yield was undertaken considering the improvements above.

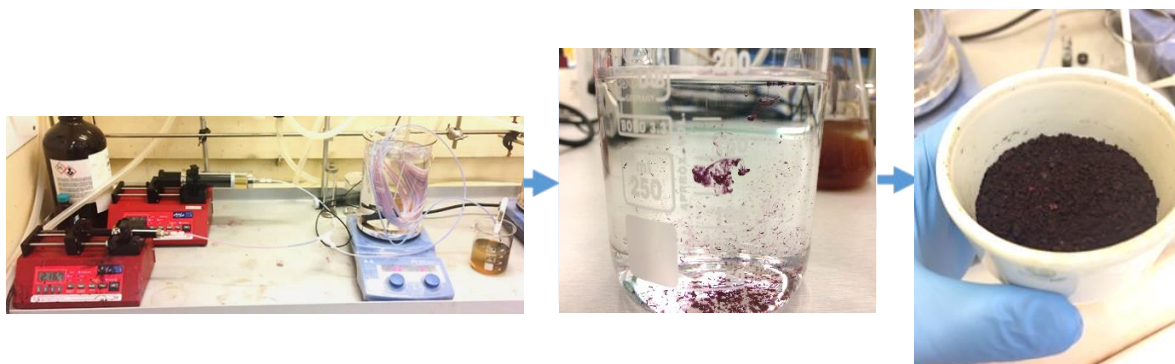


Figure 2.3. P3HT5KS flow synthesis with Ni catalyst solution without preinitiation, quenching in acidified methanol and vacuum filtration. Yield: 1.0 g (56 %)

In Figure 2.3 shown above, an upscaled tubing inner diameter of 1.5mm² rather than 0.8mm² was introduced, which allows better free flowing of particulates (P3HT can precipitate in the tube as molecular weight increases) and reduces blockages. In order to achieve higher yield for the flow chemistry polymerisation reactions, the flow reaction monomer and catalyst solution parameters such as concentration, pumping flow rates, temperature, mixing control and the residence time and their variation have been studied. In order to increase the

throughput of the polymerisation reaction, we firstly introduced larger diameter tubing, which improved the flow of particulates at temperatures above 50 °C, however blockages were formed in the tubes at the temperatures below that range (35-40 °C) as a result of more efficient polymerisation reaction (i.e better mixing in the narrower tubing). Therefore, in this reaction a temperature of 38 °C degrees was applied, giving a purified yield of 1.0 g (56 %). Fabricated bulk heterojunction device data for devices prepared from this material is compared to that for standard bulk batch prepared P3HT in Table 2.2. These results show that the flow chemistry prepared P3HT preforms as well as (or slightly better than) batch prepared P3HT, showing that flow chemistry does provide an attractive method for P3HT synthesis.

Table 2.2. Bulk heterojunction OPV devices performance (P3HT3KS:PC₆₀BM and reference P3HT20K:PC₆₀BM blends). The *I*-*V* characteristics is represented for masked device average of 6 solar cells. Devices were annealed at 140 °C temperature for 4 min.

Material	PCE (%)	V _{OC} (V)	J _{SC}	Fill Factor
P3HT(P3HT3KS):PC ₆₀ BM	2.79±0.37	0.56±0.01	7.9±0.38	0.62±0.08
P3HT(20K):PC ₆₀ BM	2.47±0.25	0.55±0	6.65±0.67	0.67±0.01

2.2.2.2 Batch chemistry

2.2.2.2.1 Benchmark material production

Traditional batch chemistry reactions for the synthesis of benchmark materials was performed at large scale (approximately 100 g) to provide a benchmark comparison for the

flow chemistry prepared materials. Large scale synthesis of P3HT by Grignard metathesis (GRIM) method followed by purification by soxhlet extraction was performed successfully and BHJ devices were fabricated from the synthesised batch material. Fullerene acceptor molecules such as PCBM and ICx_A, and also conductive polymer PEDOT:PSS were also successfully synthesised by literature methods for use in device synthesis, with test devices provide similar device performance as previous batches made in the COE group. The details of these synthesised materials are introduced in Chapter 6 Section 6.2.1.

2.2.2.2.2 PDCBT and ITIC synthesis

Polymer and small molecule used in this study were prepared by the following methods. Where preparing compounds that were previously published/prepared, spectra were compared with existing literature spectra to confirm identity. Synthesis routes for those two compounds are represented in Fig 2.4 and Fig 2.5 below [19]–[21]:

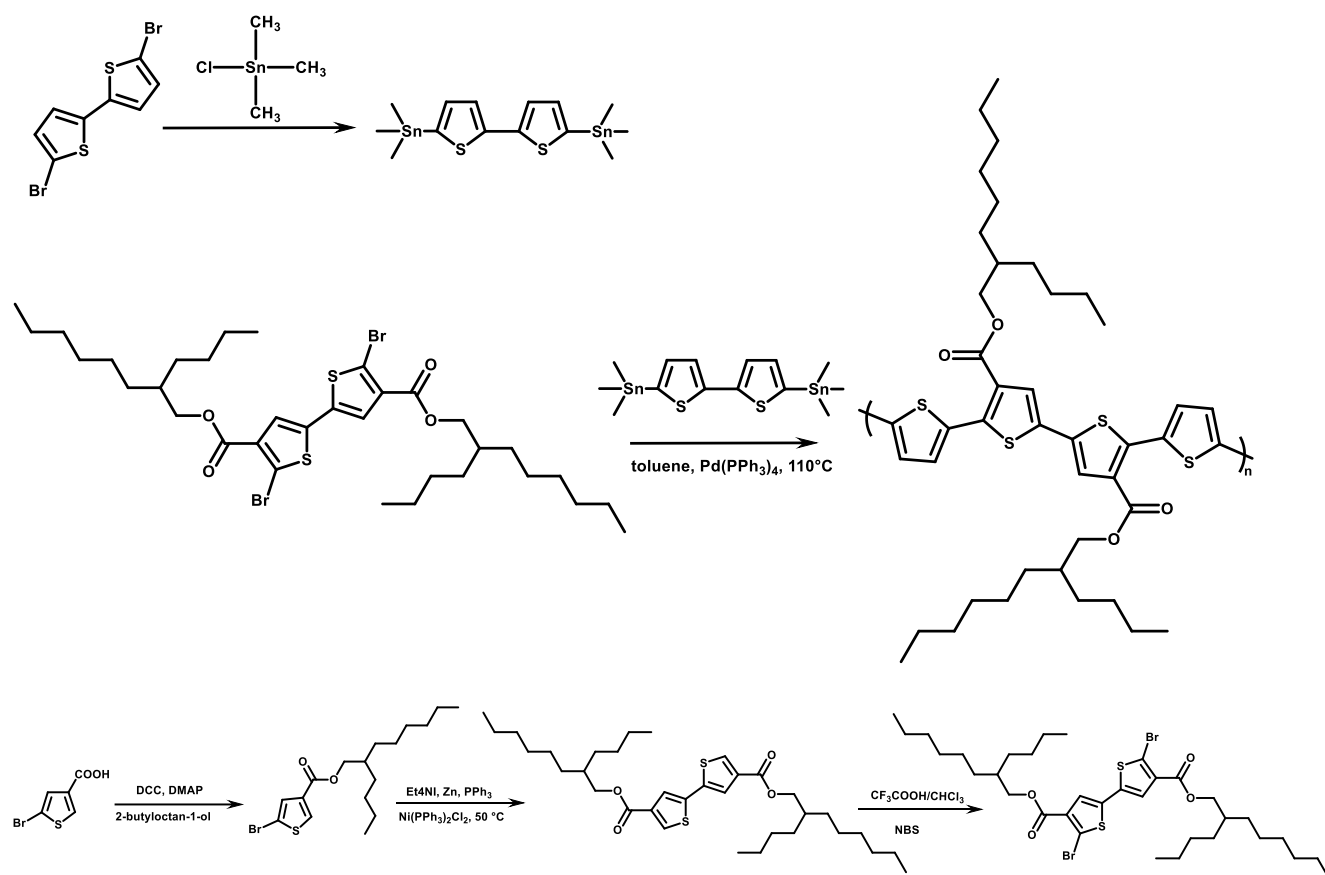
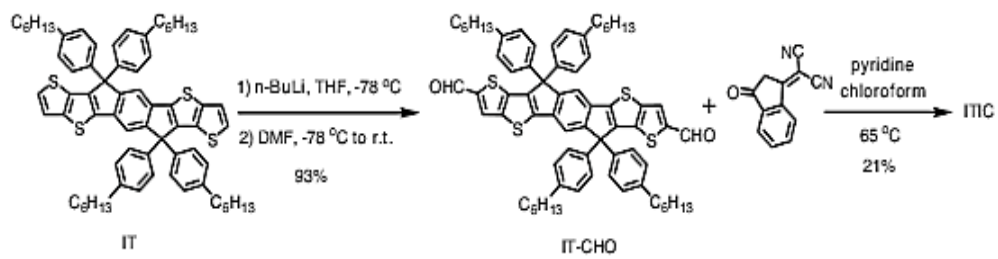


Figure 2.4 Synthesis of PDCBT [21]



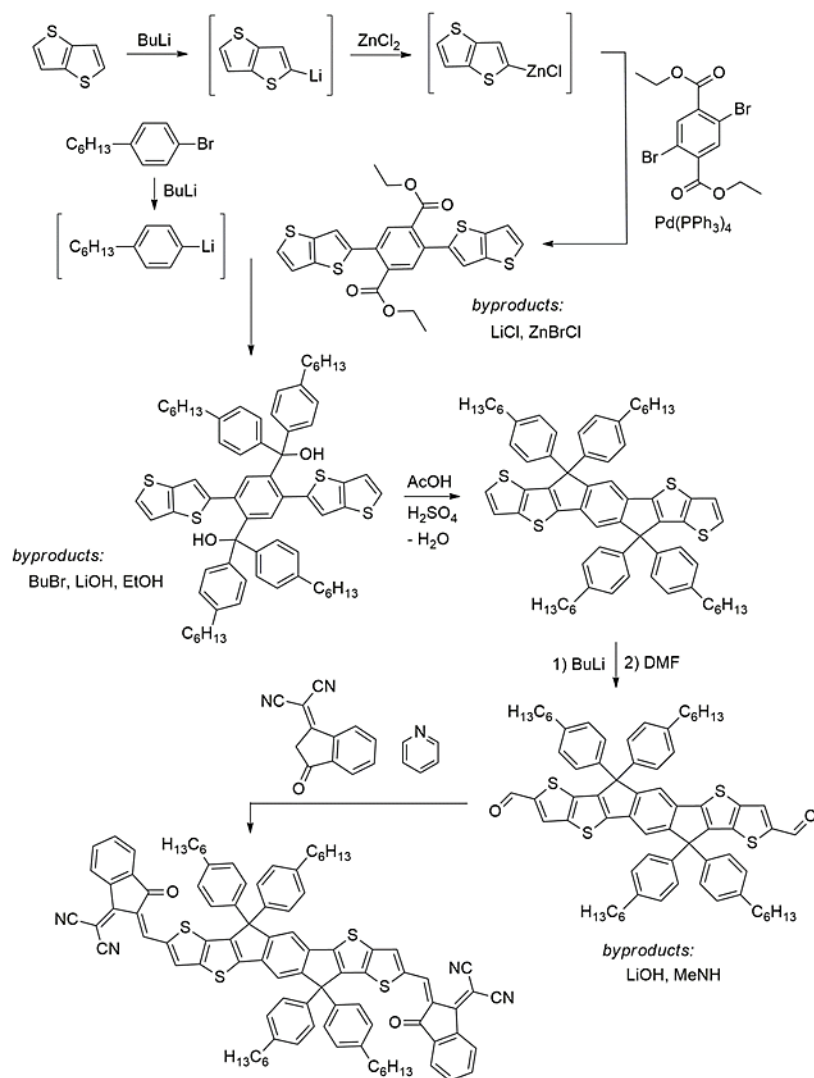


Figure 2.5 Synthesis of ITIC [19]

2.3 Small- and Large-scale organic photovoltaic device fabrication

To fabricate BHJ devices, a standard fabrication procedure has been followed. Firstly, small 5 mm^2 devices ITO substrates were cleaned in acetone and isopropanol solvents for 5 min and then dried by house nitrogen, followed by ozone treatment for 10-15 minutes. The next fabrication step is PEDOT:PSS layer deposition (approximately 65 nm), and deposition of

the mixed P3HT:PCBM active layer with an optimised film thickness of 100-120 nm from common solvent (chlorobenzene) by spin coating of the solutions onto the substrate. To complete solar cell fabrication, electrode materials (20 nm of calcium and ~90 nm of aluminium) were vacuum evaporated onto the active layer, and devices were tested using an AM 1.5 IV data recorder with the light intensity calibrated to 100 mW cm⁻² and by EQE measurements.

To carry out fabrication of organic photovoltaic devices, further testing in a clean room facility within the Centre for Organic Electronics at the University of Newcastle was used. The construction of this facility was completed in April 2008, and the air quality certified to Class 1000 Standard (<1000 particles per cubic foot of air). This enabled device manufacturing under controlled atmospheric conditions, minimising the damage that can occur to cells due to dust and other debris during fabrication process.

Materials: For the electrode application in OPV device Indium Tin Oxide (ITO) pre-patterned microscope slides ($R_s = 15 \Omega/\text{sq}$) were purchased from Xinyan Technology Ltd and glass microscope ITO coated slides ($R_s = 8\text{-}12 \Omega/\text{sq}$) were supplied by Livingstone International Pty Ltd. For OPV device encapsulation Delo Katiobond UV-curing barrier epoxy resin (LP655, Delo Industrial Adhesives, Germany) was used.

Reagents: Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₀BM) fullerene acceptors were synthesised in-house at the University of Newcastle as reported elsewhere in this thesis. FBT-Th₄ and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₀BM) were purchased from 1-Material Co. (China). Poly(3,4-ethylenedioxythiophene)-

poly(styrenesulfonate) (PEDOT:PSS) was purchased from H.C. Starck as Clevios P VP Al 4083, with a solid content of 1.3 – 1.7 % by weight, and a PEDOT:PSS ratio of 1:6 by weight, and kept under 5 °C in a refrigerator until used for deposition of conductive layer in device manufacturing.

HPLC grade (99.8%) chlorobenzene, ethanol, isopropanol and acetone solvents were all supplied by Sigma Aldrich for device fabrication and cleaning process.

2.3.1 ITO substrates cleaning

ITO substrates were washed with Milli-Q water and detergent under ultrasonication for 10 minutes. Then the process was repeated using acetone and isopropanol solvents respectfully. Finally, the ITO slides were mechanically cleaned for 10 minutes using ozone treatment.

2.3.2 Active layer solution preparation

2.3.2.1 Organic-based solution

In this thesis, photoactive layer materials were prepared from P3HT, FBT-Th₄(1,4) and PDCBT donors and PC₆₀BM or PC₇₀BM acceptor materials at 1:2 ratio for FBT-Th₄(1,4):PC₆₀BM and PDCBT:PC₇₀BM with the reference P3HT:PC₆₀BM device of 1:0.8 material ratio. These organic-based active layer solutions were spin coated from chlorobenzene solvent using a Laurell WS-400A-6NPP/LITE spin coater at concentrations of 30 mg/mL for FBT-Th₄(1,4):PC₆₀BM and PDCBT:PC₇₀BM and 36 mg/mL for P3HT:PC₆₀BM, respectively. The mixtures were sonified for 30-60 minutes in ultrasonic

bath heated up to 60°C temperature to ensure formation of a homogeneous solution. Devices were fabricated on the same day as solutions were prepared.

2.3.2.2 Aqueous Nanoparticle dispersions

The Landfester mini-emulsion process was applied for nanoparticle synthesis using Hielscher ultrasound booster horns UIP400S (400W, 24kHz). Resulting nanoparticle inks were centrifuged with water solvent through polyethersulfone (PES; cutoff 10 kDa MWCO) by using ultrafiltration tubes (Vivaproducts)

2.3.3 Spin coating

A Laurell WS-400A-6NPP/LITE spin coater was used for the deposition of conductive PEDOT:PSS and active layers onto ITO/glass substrates. The process of spin coating includes placing and securing the substrate onto the chuck of the spin-coater by applying vacuum. Then, to achieve uniform thin film, a few drops of PEDOT:PSS solution were placed onto the glass. This substrate was spun at a fixed speed of 4000 rpm for 60 seconds and the final film thickness was approximately 65 nm. In order to remove any residual water, the substrates were then heated on a hotplate, under nitrogen at 120 °C for 15 mins. Once devices were cooled, the active layer solution was deposited usually at 1500 rpm – 2000 rpm for 30-60 seconds under nitrogen atmosphere to achieve a photoactive layer thickness of 100 ± 10 nm. The active layer solution's film thickness was controlled by altering concentration, changing acceleration rate or adjusting the spin-speed of the spin coater.

2.3.4 Ca/Al evaporation

The cathode of the OPV was formed from a thin layer of calcium (20 nm) and aluminium (95-110 nm) using an Angstrom Amod thermal evaporator. The rate of Ca and Al deposition through a mask was 0.2 Å/S and 2 Å/S, respectively, and was monitored by a quartz crystal microbalance throughout the evaporation process.

2.3.5 Large scale R2R OPV device fabrication

A Solar-1 Coater from Grafisk Maskinfabrik, developed by Department of Energy Conversion (DTU), was utilised in large scale solar cells production (as shown in Figure 2.6) [22]. Large scale PTE substrates were coated with silver grid, PEDOT:PSS, active layer, zinc oxide, and sputtered aluminium layers to form a traditional printing OPV architecture.



Figure 2.6 Solar-1 Coater at the University of Newcastle, Newcastle Institute for Energy and Resources (NIER)

2.4 Device testing

2.4.1 Solar simulator. I-V characteristics

In order to define the OPV device performance, a Newport Class A solar simulator was used for testing I-V characteristics of the solar cells. The instrument records data to determine the voltage, current, fill factor and power conversion efficiency (PCE) of the devices. An AM 1.5 spectrum filter simulator, a Keithley 2400 (a source meter used for testing both masked

devices (active area is 0.038 cm^{-2}) and unmasked devices (0.05 cm^{-2}) and a silicon reference diode with a KG5 filter for calibration light intensity to 100 Mw cm^{-2} were used to record the devices performances.

2.4.2 External quantum efficiency measurements

As described in Chapter 1, external quantum efficiency defines the incident photons conversation to electrons ratio inside the OPV device as a function of wavelength. The photosensitive device generates current as the wavelength of illuminating light is changed and this data is analysed in a Labview program. The instrument comprises a quartz tungsten-halogen lamp, dual gating monochromator, chopper, fibre bundle, apertures, lenses, sample holder and silico and germanium diodes (for the purpose of reference diodes current calibration).

2.4.3 Ultra-violet-visible spectroscopy

A high-performance Varian Cary 6000i UV-Vis-NIR spectrophotometer is an ultimate tool for measurement of transmission and reflection spectra of materials. In order to avoid any noise with wavelength below 350 nm all thin films samples were spun onto a quartz substrate. 2 Light sources and 2 photodetectors are used in the operation of the spectrometer and each of these are used in these spectral range for these measurements. Across 175-350 nm a deuterium lamp is used for illumination, while a tungsten lamp is used for the wavelengths higher than 350 nm. Within wavelength range of 175-800 nm a silicon photo detector is employed, and lead sulphide (PbS) detector used in the near infrared (800-1800 nm). To measure transmittance, the spectrophotometer was adjusted to use a narrow band of 1 nm and

a reduced beam height was employed for all measurements to improve the signal to noise ratio. All measurements began with a baseline correction at 100% transmission (chamber empty) and 0% transmission (light beam blocked with Teflon insert) in order to account for baseline effects.

2.4.4 Profilometry

Profilometry permits accurate thickness measurements of OPV's devices. A Bruker's DektakXT™ Stylus Profiler permitted measurements of the electron and hole transport layer of organic solar cells with 1 mm resolution and highest vertical range of 1200 μm .

2.5 Optical microscopy

Films of 110-130 nm thickness were deposited onto glass substrates from chlorobenzene and chloroform solvents. A Zeiss Axioplan2 optical microscope aided imaging of devices using an Olympus DP70 CCD camera, with images processed by Olympus DP Controller version 2.1.1.183 software.

2.6 Atomic force microscopy

The atomic force microscope (AFM) used in this study was an Asylum Research Cypher Scanning Probe Microscope and operated in AC mode. Samples were prepared by spin coating onto a pre-cleaned glass silica slide (1 cm $\times$ 1 cm) then dried on a hot plate at 150 $^{\circ}\text{C}$ for 15 min.

2.7 Dynamic Light Scattering

In order to detect nanoparticle size, from particles of a few nanometers in size up to micrometers in diameter, the light scattering (DLS) technique was applied using a Zetzsizer Nano ZS (Malvern instruments) with a 633 nm laser. To determine the average particle size in suspension, 5 μ L of nanoparticle ink (30 mg/mL) was diluted with water and 2 mL of this solution was filled in a plastic cuvette for DLS measurements at 25 °C temperature.

2.8 Scanning Electron Microscopy

To achieve high resolution imaging of active particles on the nanometer scale, scanning electron microscopy was utilised in this thesis. The key principle of SEM is to raster focused electron beams onto the photoactive surface to capture images from the backscattered and secondary electrons.

Sample preparation for the SEM process involves conductive silicon substrates with nanoparticle ink (diluted with water 1:10 ratio) deposited at 2000 RPM/min with acceleration of 112 rpm/s. Measurement of the SEM images for the nanoparticle study was conducted by Dr. Natalie Holmes. Particle nanoscale morphology was studied by using Zeiss Sigma ZP field emission FESEM instrument, the accelerating voltages were 1-3 kV and instrument magnifications setting up to 400k.

2.9 Scanning Transmission X-ray Microscopy

Scanning transmission X-ray microscopy (STXM), is a sub-micron scale microscopic synchrotron-based technique which offers chemical contrast for a range of materials including organic semiconductors. It enables quantitative investigation and characterisation of chemical composition of multi-component films. The STXM samples studied for this thesis were fabricated by depositing 2.5 μL of NP inks of P3HT:ICx A and PDCBT:ITIC onto low stress silicon nitride (Si_3N_4) window membrane substrates with silicon dioxide coating (purchased from Norcada, Canada). The silicon nitride window dimensions were 250 x 250 μm^2 , membrane thickness of 15 nm, silicon frame dimensions of 5 x 5 mm^2 . Spin coating conditions were as follows: 3000 rpm, low acceleration of 112 rpm/s, 1 min. The measurements were conducted by Dr Natalie Holmes, Dr Matthew Barr and Dr Adam Fahy at the Advanced Light Source synchrotron, beamline 5.3.2.2 Polymer STXM.

2.10 Methods of production cost reduction and scale up reaction safety

Scale-up reaction (> 100 g) purification may cause many safety issues not normally encountered during smaller scale (< 10 g) work. For safety, simplification of the work up and reduction of cost, chromatography, in particular, needs to be replaced by different purification method in mass production. The fire and respiratory hazards of the large amounts of flammable organic solvents used in the silica gel column work up, make this technique much less safe and viable in large scale purification. Also, the size of specialised glassware (e.g., columns) can make it difficult for handling and still may not give efficient separation of eluting bands, making it necessary to repeat chromatography procedures. Therefore,

crystallisations, extractions, triturations, distillations and washes are used whenever possible to minimise solvent usage and reduce cost and risk.

As an example, in this work, successful simplification of ITIC small molecule starting material work up has been achieved. The main issue encountered during column purifications, was low solubility of crude, that required large quantities of solvent (> 2 L to clean up only small amounts (< 50 mg) of crude. This requirement increases the cost drastically when considering the scaling up goal. Therefore, in the step 1 reaction, recrystallisation as a method of inexpensive work up procedure was performed instead of silica gel column chromatography (Figure 2.7 (A) – (C)).

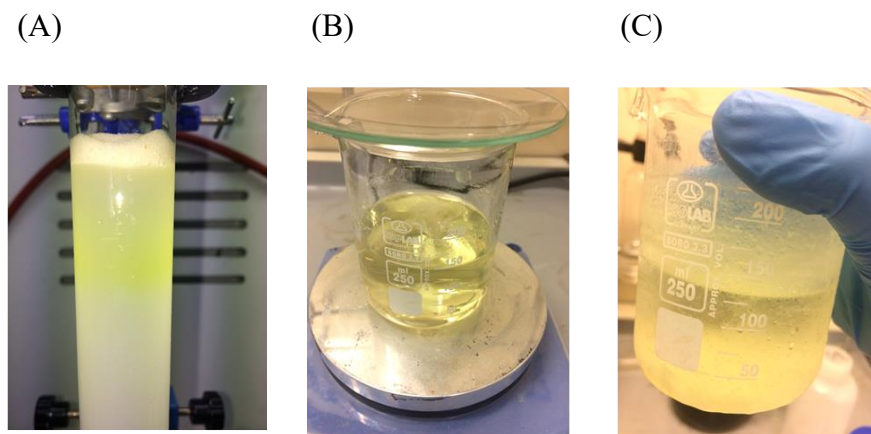


Figure 2.7 (A) silica gel column purification of starting material; (B) and (C) recrystallization of starting material from (1:1) hexane:ethyl acetate solvent ratio

Another method for impurity removal is multiple washes of aqueous solutions (e.g., 5% NaHCO_3 , 1M citric acid, 5% brine, 1M NaOH) with analysis (via TLC or more sophisticated chromatography) of both the wash and the organic phases. Additionally, reactions that occur

in a hydrophilic medium (e.g., acetone, ethanol) makes a precipitation technique ideal for purification by slow addition of water. These synthesis modifications for ITIC compound are described in more details in Chapter 4.

Consequently, we should use reagents that can make workups and purifications cleaner and easier for substantial industrial development of material synthesis. These changes can lead to cleaner reactions, less intensive purifications, lower flammable solvent usage, lower fire hazard, and less expenditure of time. Ultimately, efficiency and safety will be improved successfully.

References

- [1] Osedach, T.P., Andrew, T.L. and Bulović, V., 2013. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy & Environmental Science*, 6(3), pp.711-718.
- [2] Liang, Y., Wu, Y., Feng, D., Tsai, S. T., Son, H. J., Li, G., and Yu, L. (2009). Development of new semiconducting polymers for high performance solar cells. *Journal of the American Chemical Society*, 131(1), 56-57.
- [3] Chen, Z., Cai, P., Chen, J., Liu, X., Zhang, L., Lan, L., and Cao, Y. (2014). Low band-gap conjugated polymers with strong interchain aggregation and very high hole mobility towards highly efficient thick-film polymer solar cells. *Advanced materials*, 26(16), 2586-2591.
- [4] M. G. Wilson, 2014, *Preparation of Regioregular Poly(3-hexylthiophene) and its Precursor Monomer, 2,5-dibromo-3-hexylthiophene, Using Low Pressure Flow Synthesis Techniques*, PhD Thesis, The University of Newcastle, Newcastle.
- [5] Kumar, A., Hasan, J., Majji, A., Avhale, A., Gopinathan, S., Sharma, P., and Kumar, A. (2014). Continuous-flow synthesis of regioregular poly (3-hexylthiophene):

ultrafast polymerization with high throughput and low polydispersity index. *Journal of Flow Chemistry*, 4(4), 206-210.

- [6] Wiles, C., and Watts, P. (2008). Continuous flow reactors, a tool for the modern synthetic chemist. *European journal of organic chemistry*, 2008(10), 1655-1671.
- [7] Rossi, E., Carofiglio, T., Venturi, A., Ndobe, A., Muccini, M., and Maggini, M. (2011). Continuous-flow synthesis of an efficient methanofullerene acceptor for bulk-heterojunction solar cells. *Energy and Environmental Science*, 4(3), 725-727.
- [8] Helgesen, M., Carlé, J. E., dos Reis Benatto, G. A., Søndergaard, R. R., Jørgensen, M., Bundgaard, E., and Krebs, F. C. (2015). Making Ends Meet: Flow Synthesis as the Answer to Reproducible High-Performance Conjugated Polymers on the Scale that Roll-to-Roll Processing Demands. *Advanced Energy Materials*, 5(9), 1401996.
- [9] Pirotte, G., Kesters, J., Verstappen, P., Govaerts, S., Manca, J., Lutsen, L., and Maes, W. (2015). Continuous Flow Polymer Synthesis toward Reproducible Large-Scale Production for Efficient Bulk Heterojunction Organic Solar Cells. *ChemSusChem*, 8(19), 3228-3233.
- [10] Bannock, J. H., Xu, W., Baïssas, T., Heeney, M., and de Mello, J. C. (2016). Rapid flow-based synthesis of poly (3-hexylthiophene) using 2-methyltetrahydrofuran as a bio-derived reaction solvent. *European Polymer Journal*, 80, 240-246.
- [11] Pirotte, G., Kesters, J., Verstappen, P., Govaerts, S., Manca, J., Lutsen, L., and Maes, W. (2015). Continuous Flow Polymer Synthesis toward Reproducible Large-Scale Production for Efficient Bulk Heterojunction Organic Solar Cells. *ChemSusChem*, 8(19), 3228-3233.
- [12] Seyler, H., Wong, W. W., Jones, D. J., and Holmes, A. B. (2011). Continuous flow synthesis of fullerene derivatives. *The Journal of Organic Chemistry*, 76(9), 3551-3556.
- [13] Grenier, F., Aïch, B. R., Lai, Y. Y., Guérette, M., Holmes, A. B., Tao, Y., and Leclerc, M. (2015). Electroactive and photoactive poly [isoindigo-alt-EDOT] synthesized using direct (hetero) arylation polymerization in batch and in continuous flow. *Chemistry of Materials*, 27(6), 2137-2143.
- [14] Seyler, H., Wong, W. W., Jones, D. J., and Holmes, A. B. (2011). Continuous flow synthesis of fullerene derivatives. *The Journal of Organic Chemistry*, 76(9), 3551-3556.

- [15] Myers, R. M., Fitzpatrick, D. E., Turner, R. M., and Ley, S. V. (2014). Flow chemistry meets advanced functional materials. *Chemistry—A European Journal*, 20(39), 12348-12366.
- [16] Seyler, H., Subbiah, J., Jones, D. J., Holmes, A. B., and Wong, W. W. (2013). Controlled synthesis of poly (3-hexylthiophene) in continuous flow. *Beilstein journal of organic chemistry*, 9(1), 1492-1500.
- [17] Bannock, J. H., Krishnadasan, S. H., Nightingale, A. M., Yau, C. P., Khaw, K., Burkitt, D., and de Mello, J. C. (2013). Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Advanced Functional Materials*, 23(17), 2123-2129.
- [18] Kumar, A., Hasan, J., Majji, A., Avhale, A., Gopinathan, S., Sharma, P., and Kumar, A. (2014). Continuous-flow synthesis of regioregular poly (3-hexylthiophene): ultrafast polymerization with high throughput and low polydispersity index. *Journal of Flow Chemistry*, 4(4), 206-210.
- [19] Xu, Y. X., Chueh, C. C., Yip, H. L., Ding, F. Z., Li, Y. X., Li, C. Z., and Jen, A. K. Y. (2012). Improved charge transport and absorption coefficient in indacenodithieno [3, 2-b] thiophene-based ladder-type polymer leading to highly efficient polymer solar cells. *Advanced materials*, 24(47), 6356-6361.
- [20] Lin, Y., Wang, J., Zhang, Z. G., Bai, H., Li, Y., Zhu, D., and Zhan, X. (2015). An electron acceptor challenging fullerenes for efficient polymer solar cells. *Advanced materials*, 27(7), 1170-1174.
- [21] Zhang, M., Guo, X., Ma, W., Ade, H., and Hou, J. (2014). A polythiophene derivative with superior properties for practical application in polymer solar cells. *Advanced Materials*, 26(33), 5880-5885.
- [22] Andersen, T. R., Almyahi, F., Cooling, N. A., Elkington, D., Wiggins, L., Fahy, A., and Dastoor, P. C. (2016). Comparison of inorganic electron transport layers in fully roll-to-roll coated/printed organic photovoltaics in normal geometry. *Journal of Materials Chemistry A*, 4(41), 15986-15996.

Chapter 3: Costing and device materials

Sections of the work introduced in this chapter has been published in the following paper:

Alaa Y. Al-Ahmad, Furqan Almyahi, Mohammed F. Al-Mudhaffer, Matthew Griffith, Wenqing Liu, Shuixing Li, **Kamilla Sivunova**, Daniel Elkington, Nathan A. Cooling, Krishna Feron, Minmin Shi, Warwick Belcher, Hongzheng Chen, Paul Dastoor and Thomas R. Andersen “A nuanced approach for assessing OPV materials for large scale applications”, Sustainable Energy Fuels, 2019, DOI: 10.1039/c9se01149h

3.1 Introduction

One of the key factors in scaling up OPV materials is the synthesis cost. In general, highly efficient materials directly correlate with the most expensive photoactive layers and the most complex syntheses. These compounds are typically non-scalable, or extremely difficult to synthesise at scale and include compounds such as: PC₇₀BM [1], FBT-Th₄(1,4), PTB1 etc., and are therefore unsuitable for industrial solar cell production [2]. In order to achieve the best performance a wide range of factors including architecture, materials system, thickness of active layer (~150 nm) [3] and printing methods must be optimised. Addressing these issues, whilst minimising the number of purification steps in the synthesis, simplifying synthesis and reducing waste products and solvents, is essential to establish an achievable and affordable high performing device fabrication.

Handling large scale process in a laboratory is another important aspect to be considered. Neglecting the safety rules correlates to risk to staff, environmental pollution, and large volumes of toxic by-products (which must be minimised or eliminated during the synthesis). According to up-to-date research in the area [3]–[5], three major parameters have been identified for achieving successful commercialisation; performance, stability, and cost. In addition, processability of materials and printability is also a significant consideration for safe up-scale manufacture.

The main objective of this chapter is production cost - the most essential OPV parameter for commercializing and circumventing the escalation of the levelised cost of generated electricity. This factor has traditionally been neglected in previous research [6] and still remains largely unexplored and generally unjustified in literature that claims potential low-cost technology focusing on production cost [6]–[9]. The majority of up-to-date publications are focused on the high-performance achievement, considering this as the most valuable parameter for the best device operation. Recent performance studies of OPV devices focus on achieving donor-acceptor systems with high efficiency such as the PM6 and 2,7-bis(3-dicyanomethylene-2Z-methylene-indan-1-one)-4,4,9,9-tetrahexyl-4,9-dihydro-sindaceno[1,2-b:5,6-b']-dithiophene (IDIC) system which exhibit much higher efficiencies (11.9%) [10] but with correspondingly more complex and expensive synthesis than benchmark P3HT, ICxAs, PCBM materials. Currently, active layer improvements result in OPV efficiencies of 16.4% [11], however it is challenging to determine the commercialization potential of such devices with unknown synthesis cost and stability factors.

As a first step to explaining the perceived importance of the cost, lifetime and performance of OPV in the research community, a survey based on the key words efficiency, lifetime and cost was conducted for organic solar cells since 1956 in the Web of Science database and the resultant number of publications found is shown in Figure 3.1. The number of papers in search results for efficiency was 5,188 and for lifetime and cost, 583 and 454 respectively. This data outlines the factors that govern the cost of manufacture (COM) in large-scale manufactured devices and gives some idea of the research effort being applied in each area. Efficiency of materials and devices is by far the most dominant criteria in terms of research interest. However, for each parameter, cost, efficiency, and longevity OPV technology must make improvements to achieve commercialisation, in particular, lowering the cost of materials that can be processed from acceptable solvents using inks formulated at scale. In this Chapter we will analyse the current literature, identifying high performance OPV donor and acceptor materials which are suitable for large scale, inexpensive synthesis and will therefore be suitable for the commercialisation of OPV.

A theoretical exploration of OPV parameters (1956-2020)

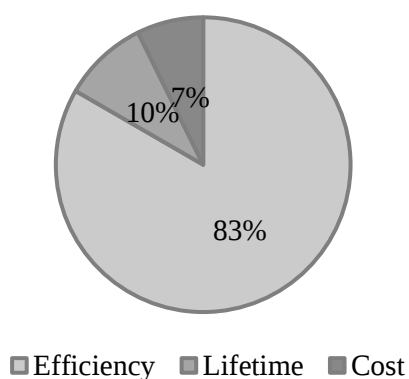


Figure 3.1 Significant triplet of photovoltaic parameters chart

3.2 Costing of materials and devices

Material cost per gram calculations are tabulated in this section for recently developed donor materials and fullerene and non-fullerene acceptors SF(DPPB)₄, PCBM, ITIC, IC_xA (selected based on a literature review[1], [5]-[30], [33]-[45], [51]-[57], [101]-[109], [111], [119]-[134], [151]-[160], [171]-[174], due to their high performance in organic solar cells) versus benchmark donor and acceptor materials, according to published procedures [3], [12]-[22] and the literature synthetic methods for these reagents [23]-[26]. Synthetic reports have been linearly adjusted and upscaled to 100 g of final product. Estimations of the volumes of workup solvents and silica gel required for all synthetic steps were based on published methods [27]. We assume that for each 2.5 g of crude 1 L of solvent and 200 g of silica gel with a density equal to 0.5 g/mL is required for a 20 cm long x 5 cm diameter column purification. All price sources from suppliers used for material synthesis analysis and the device manufacture are introduced in the previous Chapter 2, as a reference.

3.2.1 Investigation of synthesis cost for donor materials

In this section, we examine and compare the commercialisation potential of the newly developed PDCBT polymer based on device performance, stability, and cost in comparison with benchmark materials. This material has been selected after a careful review of high efficient newly developed donor materials in the organic photovoltaics literature [1], [2], [5]-[20], [31]-[40], [51]-[60], [101]-[110], [111]-[140], [151]-[160], [171]-[174].

A materials selection method used for materials selection was presented by Riccardo Po et al. in 2016 who utilised a synthetic complexity index (SC) for assessment of potential donor

photoactive materials [2]. In this calculation the number of synthetic steps (NSS), the reaction yield for each step (RY), the number of separate purification/isolation procedures for intermediate compounds (number of unit operations, NUO) required for each step (e.g. the number of column chromatography steps (NCC)), as well as the materials safety (number of hazardous chemicals, NHC) are all considered in the calculation of SC as detailed in Equation 1 below.

We have based our selection of viable materials for OPV applications, in part, upon this calculation. Taking into accordance that the SC index of materials represents the complexity for synthesis and scale up of materials, it should not exceed index value of 70 [10] due to high material costs and complex synthesis of the materials with > 70 index value [10], [16], [17], [19]–[21], [44], [46], [104], [127], [129], [132]. Accordingly, in order to preselect suitable donor and acceptor materials for upscale and R2R printing, we have performed SC calculations for the synthesis of several promising high efficient donor and acceptor photoactive materials using their published synthesis routes [16], [17], [19]–[21], [44], [46], [104], [127], [129], [132], as well as some lower performance (and lower cost) materials for comparison, and presented the SC analysis in the table below (Table 3.1). As examples, the calculations for SC indices of PDCBT and ITIC are presented with explanation.

$$SC = 35 \times NSS/NSS_{max} + 25 \times \log RY / \log RY_{max} + 15 \times NUO/NUO_{max} \\ + 15 \times NCC/NCC_{max} + 10 \times NHC/NHC_{max}$$

Equation 3.1. The synthetic complex index (SC) calculation [10]

Having summarised the calculated SC indices and the maximum PCE as reported in the literature (as shown in the Table 3.2) of devices using selected material combinations, several material combinations were selected for further analysis.

After careful analysis of each of recently developed materials (>250 compounds), in accordance with the literature reported performances in binary structured organic solar cells [5], [10], [11], [32], [165]–[174][1]–[16], [18]–[175], we have chosen those that appear viable to upscale economically and summarised the selected materials for further investigation. For each donor acceptor material system with high performance, we observed that the SC numbers varying between 58-83. This demonstrates the complexity of high efficiency (7.64-18.22 %) [21] [174] [43] [129] [172] [22] [116] materials and the expensive costs of their purification and synthesis. Highlighted drawbacks of these materials varied from the donor to acceptor blend, therefore having estimated the cost and compensating for their performance in OPVs and searching for a reasonable SC index and figure of merit (FOM) of materials (see section 3.3.2), the most advantageous selection resulted in PDCBT and ITIC donor-acceptor compounds. The active layer morphology of this system allows high efficiencies of up to 10.16 % [116] in devices and synthesis complexity is lower compared to the other candidates (66 for PDCBT and 64 for ITIC). To emphasise, the main criteria chosen is the costing and simplicity of PDCBT and ITIC materials synthesis routes. Step by step synthetic costing has been assessed in detail for these materials and the analysis is presented and summarised in Table 3.3 below. Synthesis routes and purification methods were examined, successfully adjusted and reported in the Chapter 4 of this thesis.

Table 3.1. Summary of SC index selected potential donors (FBT-Th4(1,4), PDCBT, PTB1, P3HT, D18, DTBT, DR3TSBDT, PPDT2FBT (FBT)) and acceptors (ITIC, SF(DPPB)₄, e-PPMF, PC₆₁BM, PC₇₁BM, ICxA, BTP-4F(Y6)) materials [2]

Compounds	NSS	RY	NUO	NCC	NHC	SC
DR3TSBDT [2]	18	12.7	28	9	69	89
FBT-Th ₄ (1,4)	8	79.4	7	4	38	75
PDCBT	6	81.0	5	3	27	66
ITIC	5	64.6	5	4	24	64
SF(DPPB) ₄	7	80.0	7	6	29	52
PTB1	4	85	8	2	28	63
P3HT	3	80.0	1	0	9	51
e-PPMF [172]	8	42.0	12	6	28	73
PC ₆₁ BM	2	62.5	2	1	6	48
PC ₇₁ BM	2	90	2	1	6	52
ICxA	1	85.11	1	0	5	47
DTBT [32]	3	84.0	5	2	20	58
BTP-4F (Y6) [174]	10	64.0	14	6	35	83
PBDB-T-2F (PM6) [171]	9	60	13	4	22	75
PPDT2FBT (FBT)	4	80	9	2	30	63

Table 3.2. Summary of maximum PCE (%) for various donor and acceptor material blend solar cells

Donors ¹	Acceptors ²	PCE (%)
DTBT	BTP-4F (Y6)	18.22 [32]
PBDB-T-2F	BTP-4F (Y6)	15.7 [174]
DR3TSBDT	PC ₇₁ BM	9.95 [129]
PPDT2FBT	e-PPMF	8.11 [172]
FBT-Th ₄ (1,4)	PC ₇₁ BM	7.64 [21]
PDCBT	PC ₇₁ BM, PC ₆₁ BM	7.2 [19]
PDCBT	ITIC	10.16 [116]
P3HT	PC ₆₁ BM	3.9 [27]
P3HT	ICXA	3.37 [16]
PTB1	PC ₇₁ BM, PC ₆₁ BM	5.3 [130]
P3HT	SF(DPPB) ₄	3.22 [3]

3.2.2 Selecting the best candidates for low cost OPV production

After a detailed analysis of synthetic route (number of steps), number of expensive purifications, reaction yields, device performance and overall synthesis costs, in order to complete the initial preselection of material systems and justify the choice of PDCBT and ITIC compounds, a figure of merit calculation is introduced. A simple figure of merit (FOM) was calculated to rank material combinations in terms of viability and is presented in the following equation:

$$FOM = \frac{\eta}{\left(\omega_D \times \frac{SC_D}{100}\right) + \left(\omega_A \times \frac{SC_A}{100}\right)}$$

Equation 3.2 A figure of merit (FOM) calculation

where η is the maximum reported efficiency of the material combination and ω_D and ω_A and SC_D and SC_A are the mass fraction of the donor and acceptor materials in the device active layer and the synthetic complexities of the donor and acceptor materials, divided by the maximum SC index of 100 for the highest complex material respectively.

Table 3.3. FOM for various donor and acceptor combinations

Donors ¹	Acceptors ²	D/A	PCE _{max} (%)	FOM
DTBT	BTP-4F (Y6)	1:1.6	18.22 [32]	9.55
PBDB-T-2F (PM6)	BTP-4F (Y6)	1:1.2	15.7 [174]	8.99
DR3TSBDT	PC ₇₁ BM	1:0.8	9.95 [129]	7.62
PPDT2FBT	<i>e</i> -PPMF	1:1.5	8.11 [172]	4.70
FBT-Th₄(1,4)	PC ₇₁ BM	1:2	7.64 [21]	4.27
PDCBT	PC ₇₁ BM	1:1	7.2 [19]	6.10
PDCBT	PC ₆₁ BM	1:1	6.3 [19]	5.53

PDCBT	ITIC	1:1	10.16 [116]	7.82
P3HT	PC ₆₁ BM	1:0.8	3.63 [14]	4.06
P3HT	IC _x A	1:0.8	3.90 [16]	4.40
PTB1	PC ₇₁ BM	1:1.2	5.3 [130]	4.23
PTB1	PC ₆₁ BM	1:1	4.76 [130]	4.29
P3HT	SF(DPPB) ₄	2:1	3.22 [3]	2.09

The highest values of FOM are shown in Table 3.3 from 7.62-9.55 are for the highest performing material blends such as DTBT:BTP-4F, PBDB-T-2F:BTP-4F, DR3TSBDT:PC₇₁BM, which contain donor and acceptor materials with expensive synthesis and high complexity (SC). In contrast, P3HT is cheap, relatively stable, but only demonstrates low to medium efficiency with PCBM (PCE of around 3 %). However, active layer materials such as PDCBT and ITIC exhibit much higher efficiency of up to 10.2 %, whilst retaining a relatively simple synthesis and therefore appear much more effective for upscaled commercialisation. Based on the calculation (summarised in Table 3.3) P3HT:PC₆₁BM gives a FOM of 4.06, whilst PDCBT:ITIC gives a value of 7.82 – almost double the value and therefore more viable towards the goal of high performing materials which are easily scaled up. Also, the less expensive synthesis and moderate SC index numbers is a major reason for the selection of these materials instead of higher performing materials.

From a purely theoretical perspective, after investigating donor materials and performing comparative studies for the best candidate, PDCBT as a high-performing donor polymer and ITIC as a small molecule acceptor were chosen as the material combination for this study.

The PDCBT structure is similar to P3HT which contains a hexyl group, whereas this group is substituted by the alkoxycarbonyl in PDCBT. The change makes a huge impact on the polymer electronic structure, in terms of improving the lower molecular orbitals (LMOs), planarity and the hole mobility for better charge separation in a PDCBT device. These changes also lead to better electron transfer in the device and results in the PDCBT system having higher performance compared to P3HT system [156]. Due to the material morphology the polymer blends well with the ITIC small molecular compound resulting in high efficiency solar cells.

As it has been demonstrated herein, PDCBT and ITIC materials have the potential to be a more viable donor-acceptor system than P3HT and ICxA for the application of large scale OSCs, based on the systems lower cost per unit long-term efficiency. This factor combined with a similar overall module cost illuminates the potential of these materials as a future active layer for OSC.

Table 3.4 below presents the full costing of PDCBT at a 100 g scale of production. Initial syntheses will be (often much) more expensive, because, for example, it is necessary to buy a 100 g bottle of reagent when only maybe 15 g is used per batch. Obviously in practicality the remainder will be used in subsequent syntheses and thus the additional cost is not lost. Additionally, the cost of waste disposal at $\text{kg solid} + \text{liquid waste} \times \10.84 should be considered (also the need to add $\sim \$641$ transport and environmental fee).

Table 3.4 Costing of PDCBT at a 100 g scale of production

Material	AUD/kg or AUD/L	Amount required for synthesis of 100 g	Price for 100 g
step 1			
thiophene-3-carboxylic acid	1,272	96.87 g	123.26
acetic acid	7.20	0.68 L	4.88
bromine	1,340	0.04 L	57.40
step 2			
5-bromothiophene-3-carboxylic acid (step 1 product)	-	92.91 g	-
DCC	790	54.12 g	42.76
DMAP	4,440	14.43 g	64.08
CH ₂ Cl ₂	5.00	2.26 L	11.28
2-butyloctan-1-ol	509	166.88 g	84.94
step 3			
2-butyloctyl 5-bromothiophene-3-carboxylate (step 2 product)	-	144.33 g	-
Ni(PPh ₃) ₂ Cl ₂	4,980	37.95 g	189.01
PPh ₃	140	30.47 g	4.26
Zn powder	288	56.13 g	16.17
KI	720	2.14 g	1.54
DMF	12	5.67 L	70.19
step 4			
bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate (step 3 product)	-	171.06 g	-
CH ₂ Cl ₂	7.20	1.45 L	10.44
trifluoroacetic acid	692	0.29 L	200.63
N-bromosuccinimide	308	108.73 g	33.49
step 5			
5,5'-dibromo-2,2'-bithiophene	308	57.62 g	17.74
THF anhydrous	100	4.09 L	408.62
n-butyllithium 2.5M in hexane	855	0.17 L	145.34
trimethyltin chloride 1M in hexanes	2,930	0.46 L	1,352.90

step 6			
bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (step 4 product)	-	130.47 g	-
5,5'-bis(trimethylstannyl)-2,2'-bithiophene (step 5 product)	-	85.81 g	-
toluene anhydrous	52.00	5.81 L	299.42
Pd(PPh ₃) ₄	5,408	10.47 g	56.59
Sum of reactants			3,194.93
work-up			
water	-almost no cost		
CH ₂ Cl ₂	5.00	61.1 L	238.65
Na ₂ SO ₄	37	0.4 kg	14.72
silica gel	10.2	49.2 kg	501.10
n-hexane	8.25	180.9 L	1,492.62
dichloromethane	5.00	65.2 L	326.04
ethyl acetate	7.80	34.2 L	266.85
brine	0		
methanol	2.75	119.3 L	328.02
Sum of work-up			3,183.00
The total sum for reactants and work-up			6,377.93

The weights and volumes of reagents and solvents are quantified exactly as in the relevant paper experimental section and have been scaled up (i.e. amounts x "scaling factor") to an isolated yield of 100 g based on reported synthetic yields. Then the best materials prices from the prepared costing spreadsheet have been incorporated and scaled accordingly. Quotes were obtained for reactants from a wide range of commercial sources and the cheapest in each case has been applied. The listed cost is for the actual amount of reagent used in the reaction, e.g. if a 100 g bottle cost \$100 and only 20 g is used, the applied cost is \$20. For

purification, the assumptions of Osedach et al. (2013) [132] to estimate factors such as solvent and silica use have been applied. To conclude from the cost analysis, the top 5 major cost items per g isolated of reagent in the synthesis are THF anhydrous, trifluoroacetic acid for HPLC ($\geq 99.0\%$), trimethyltin chloride solution 1.0 M in hexanes, 2-butyl-1-octanol and DCC and these items drastically impact cost effectiveness. In order to eliminate the costs and find potential source of a cost saving, investigating alternative chemicals for the updated synthesis and purification methods modifications is further described in Chapter 4.

The estimated total cost of PDCBT was found to be \$63.78 per g (at a 100 g of product scale) divided into a cost of \$31.95 per g for chemicals and materials involved in the reaction and a cost of \$31.83 per g for materials and chemicals consumed during workup/purification. As a comparison the commercial cost of PDCBT per g is \$2,775.12 from Brilliant Matters (Canada) (a factor of x44).

3.2.3 Investigation of the synthesis cost for acceptor materials

After surveying contemporary photovoltaic materials, based on the tabulated SC and device performance in the Table 3.1 and 3.2 in the previous section, the selected acceptor for further investigation was ITIC as part of a PDCBT:ITIC active layer for OPV. The same methodology was applied as for PDCBT and in this case, the cost of ITIC acceptor was calculated as \$225 per g on a 100 g batch scale, with the cost of purification on the 100 g scale have been calculated to be \$97.70/g (Table 3.5). Comparing the costs from Ossila Ltd (UK) suppliers commercial price for ITIC is \$3,350.00 per g (a factor of x15).

Table 3.5 Costing of ITIC at a 100 g scale of production

Material	AUD/kg or AUD/L	Amount required for synthesis of 100 g	Price for 100 g
step 1			
thieno[3,2-b]thiophene	5,408	224.78 g	1,215.57
THF anhydrous	100	10.68 L	1,067.82
n-butyllithium 2.5M in hexane	855	0.66 L	566.05
ZnCl ₂ anhydrous	355	218.37 g	77.52
diethyl 2,5-dibromoterephthalate	1,934	243.46 g	470.89
Pd(PPh ₃) ₄	5,408	36.84 g	199.23
step 2			
2,5-dithieno[3,2-b]thien-2-yl-, 1,4-diethyl ester (step 1 product)		264.82 g	
1-bromo-4-hexylbenzene	912	615.70 g	561.72
THF anhydrous	100	13.24 L	1,324.08
n-butyllithium 2.5M in hexane	855	1.02 L	871.71
acetic acid	7.20	13.24 L	95.33
H ₂ SO ₄	7.52	0.26 L	1.99
step 3			
IT (step 2 product)		350.88 g	
THF anhydrous	100	43.86 L	4,386.00
n-butyllithium 2.5M in hexane	855	0.33 L	285.00
DMF anhydrous	155	0.07 L	10.88
step 4			
malononitrile	340	367.10 g	124.81
1,3-indandione	2,010.46	406.03 g	816.32
anhydrous sodium acetate	104	30.85 g	30.85
ethanol	3.00	13.91 L	13.91
step 5			
IT-CHO (step 3 product)		350.88 g	
1,1-dicyanomethylene-3-indanone		489.47 g	
CH ₂ Cl ₂	7.20	87.72 L	631.58
pyridine	29.60	1.75 L	51.93
Sum of reactants			12,772.34
work-up			
water	-almost no cost		
acetic acid	7.20	23.20 L	166.86
brine	-almost no cost		
MgSO ₄ anhydrous	27	0.4 kg	10.06
celite	46	2.7 kg	123.87
ethyl acetate	7.80	209.8 L	1,636.47
silica gel	10.2	136.99 kg	1,394.48
petroleum ether	7.20	342.47 L	2,465.79
CH ₂ Cl ₂	7.20	175.4 L	1,263.17

Na ₂ SO ₄	37	0.86 kg	11.81
dichloromethane	5.00	342.47 L	1,712.36
methanol	2.75	350.9 L	964.91
Sum of work-up			9,769.75
The total sum for reactants and work-up			22,542.09

It is clear from the calculations that anhydrous THF is a major contributor to synthetic cost and that chromatography (silica gel and associated solvents) is the major cost contributor to workup. Expensive solvents increase the purification costs as well as the hazardous criteria of the synthesis, this identifies the target for savings in order to achieve production of highly effective materials safely and at low cost. A detailed investigation of ITIC synthesis simplification with cost reduction is introduced in Chapter 4.

3.2.4 Breakdown of device costing with incorporated selected materials versus benchmark photoactive layer compounds

Manufacture cost, especially the material cost plays an essential role in determining success and industrial feasibility of OPVs [29]. For the calculation of the cost of PDCBT and ITIC, on semi-commercial scale we decided to base the costing on the synthesis of 100 g product. This costing was based on the published route of synthesis [16], [17], [19]–[21], [44], [46], [104], [127], [129], [132], prices were sourced from various vendors as specified in previous Chapter 2. The estimated total cost of PDCBT polymer was found to be \$63.78 per g (at a 100 g of product scale) and the cost of the ITIC compound used in this work is \$225.42 per g on a 100 g batch scale.

However, to fully assess whether these price differences have a significant impact on the cost of completed OPV we calculate the material price for 1 m² of fabricated OPV prepared with the geometry Ag/PH1000/Active layer/ZnO/Al for different modules comparison. As shown in Figure 3.2, the module cost breakdown is material cost, production capital cost and production operating cost. Production capital cost identifies the equipment (R2R printers, electrical deposition, encapsulation and stirred tanks) and start -up equipment is pumps, electrical systems, land and civil works and engineering construction costs. Production Operating cost includes labour, utilities, maintenance, taxes/insurance, rent and production rate.

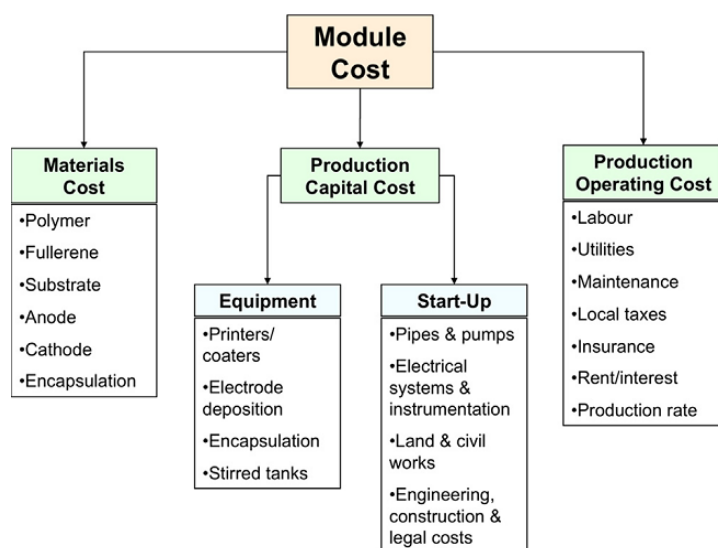


Figure 3.2. Module cost breakdown for OPV modules [176]

In order to determine the price of one square metre module we collected the material costs scaled to one square meter (assuming a coverage of 75 % except for substrate, UV-epoxy, silver grid and aluminium, where the coverage is 200 %, 100 %, 20 % and 100 %, respectively).

respectively (substrate is needed front and back, UV-epoxy is sleeve coated covering the entire width, silver is printed in grid pattern, and aluminium is deposited through a shadow mask meaning that the usage is full width even though the covering on the substrate is only 75 %)). Therefore, we assume the active layer contains equal parts donor:acceptor and has a density of 1 g/cm³. So, a 1 nm layer = 1 mg/m². The active layer is 150 nm at 75 % coverage and therefore equates to 112.5 mg/m². Then module cost = \$9.02 + active layer material cost. In summary, the module cost = \$9.02 + (combined active layer material \$ per gram)/2 x 0.1125. A cost breakdown for each layer in the P3HT:ICxA as an example of module costing method is demonstrated in Table 3.6.

Table 3.6. Module cost breakdown for P3HT:ICxA OPV panel

Material	Cost of	Price	Unit	Coverage	Layer	Amount/	Price m ²
silver	\$2400/L	\$41.96	cm ³	20%	200	0.039	\$1.65
PEDOT:PS	\$585/L	\$41.66	cm ³	75%	200	0.150	\$5.18
P3HT	\$8.55/g	\$8.55	g	75%	100	0.075	\$0.64
ICxA	\$15.14/g	\$15.14	g	75%	100	0.075	\$1.14
ZnO	\$1.96/g	\$11.00	cm ³	75%	30	0.023	\$0.25
aluminium	\$300/g	\$3.00	cm ³	75%	200	0.150	\$0.45
							total \$10.38

The calculated price per square meter for each material system (P3HT:ICxA, P3HT:SF(DPPB)₄, PDCBT:PCBM, PDCBT:ITIC) is shown in Table 3.7 below. From this table it can be seen that the cost of one square meter of OSC module based on different acceptor units have the following trend P3HT:ICxA < P3HT:SF(DPPB)₄ < PDCBT:PCBM < PDCBT:ITIC with a cost of \$10.38, \$18.20, \$19.38 and \$30.29, respectively. Whereas the cost difference for PDCBT and ITIC donor-acceptor materials are in the order of 3-fold from

P3HT:PCBM system, this price difference for 1 m² is more than compensated for by the 3-fold improvement in device performance of the newly developed materials blend. We can also determine a \$/W value for each module by considering the efficiency of the material combinations in the active layers. Assuming P3HT:ICxA performing at 3% efficiency, kW generated per 100 m² will be 1.0 kW at 1.04 \$/W. 6 hours of direct sunlight per day for 365 days/year = 2190 hours, therefore at 10 W/m² generates 21.90 kW/m² in a year. At 20 c/kWh the energy generated per 1 year lifetime will cost \$ 4.20.

Table 3.7. Cost effectiveness calculation for OSC devices with the four different active layers.

Blend	Lab PCE	\$/g	\$/g	Cost/m ²	kW/100m ²	\$/W
P3HT:ICxA	3.0 % [177]	\$9.30	\$15.14	\$10.38	1.0 kW	\$1.04
P3HT:SF(DPPB) ₄	3.2 % [3]	\$9.30	\$64.19	\$18.20	2.1 kW	\$0.63
PDCBT:PCBM	6.1 % [178]	\$63.78	\$61.23	\$19.38	2.1 kW	\$0.72
PDCBT:ITIC	10.7 % [116]	\$63.78	\$225.42	\$30.29	3.6 kW	\$0.59

A trend of module cost increase with the more expensive active layer materials combination is introduced in Table 3.8. It is observed with the cost of active layer materials at \$10, \$25, and \$50 per gram, the module cost per m² is at reasonable price and allows us to consider highly efficient materials with relatively simple synthesis for a scale up. To confirm the data analysis, the PDCBT and ITIC blend is in total \$ 144.6 is at ~ \$ 17 per m² suggesting its viability on a large-scale production.

Table 3.8. Material cost of active layer versus module cost

Combined active layer	Module cost / m ²
\$ 10	\$ 9.58
\$ 25	\$ 10.42
\$ 50	\$ 11.83
\$ 100	\$ 14.64
\$ 150	\$ 17.45
\$ 300	\$ 25.89
\$ 500	\$ 37.14
\$ 1000	\$ 65.27
\$ 2000	\$ 122.52
\$ 5000	\$ 290.27

Referring to the data demonstrated above for materials synthesis (SC index), synthesis costing, FOM and module cost, we can conclude and justify our selection of PDCBT :ITIC that these are clearly the materials system of choice. Therefore, they were chosen for further study and consideration for synthesis scale-up as discussed in later Chapter 4, and their device fabrication and optimisation work in Chapter 5.

3.3 Conclusion

In this chapter, a particular case study based on cost analysis of active layer materials to enable commercially viable economic modeling of the levelised cost of electricity for OPVs has been conducted. We can conclude that the analysis requires a trade-off among those three key factors - cost, efficiency and lifetime [179][175] and optimisation is a challenge to encompass the triplet. To significantly accelerate up-scale development, in this Chapter, costing studies were fully assessed step by step for analysis and calculation of synthesis cost of recently emerging high-performance materials (PDCBT, ITIC etc.) that were considered viable. In addition, cost of device fabrication for these materials, are presented. In conclusion, cost comparison with benchmark photoactive materials based on reported literature reviews

(P3HT, PCBM, ICx A, ICBA etc.) [16][3][180] is introduced, allowing us to directly compare the industrial viability of OSCs.

References

- [1] S. A. Lopez, B. Sanchez-Lengeling, J. de Goes Soares, and A. Aspuru-Guzik, “Design Principles and Top Non-Fullerene Acceptor Candidates for Organic Photovoltaics,” *Joule*, vol. 1, no. 4, pp. 857–870, 2017.
- [2] Po, R., & Roncali, J. (2016). Beyond efficiency: scalability of molecular donor materials for organic photovoltaics. *Journal of Materials Chemistry C*, 4(17), 3677-3685.
- [3] Al-Ahmad, A.Y., Almayhi, F., Al-Mudhaffer, M.F., Griffith, M.J., Liu, W., Li, S., Sivunova, K., Elkington, D., Cooling, N.A., Feron, K. and Shi, M., 2020. A nuanced approach for assessing OPV materials for large scale applications. *Sustainable Energy & Fuels*, 4(2), pp.940-949.
- [4] Cooling, N.A., Barnes, E.F., Almyahi, F., Feron, K., Al-Mudhaffer, M.F., Al-Ahmad, A., Vaughan, B., Andersen, T.R., Griffith, M.J., Hart, A.S. and Lyons, A.G., 2016. A low-cost mixed fullerene acceptor blend for printed electronics. *Journal of Materials Chemistry A*, 4(26), pp.10274-10281.
- [5] Gambhir, A., Sandwell, P. and Nelson, J., 2016. The future costs of OPV—A bottom-up model of material and manufacturing costs with uncertainty analysis. *Solar Energy Materials and Solar Cells*, 156, pp.49-58.
- [6] Liu, Z., Jiang, W., Li, W., Hong, L., Lei, T., Mi, D., Peng, R., Ouyang, X. and Ge, Z., 2017. Reducible fabrication cost for P3HT-based organic solar cells by using one-step synthesized novel fullerene derivative. *Solar Energy Materials and Solar Cells*, 159, pp.172-178.
- [7] Sun, C., Pan, F., Bin, H., Zhang, J., Xue, L., Qiu, B., Wei, Z., Zhang, Z.G. and Li, Y., 2018. A low cost and high performance polymer donor material for polymer solar cells. *Nature communications*, 9(1), pp.1-10.

- [8] Cai, M., Wu, Y., Chen, H., Yang, X., Qiang, Y. and Han, L., 2017. Cost-performance analysis of perovskite solar modules. *Advanced Science*, 4(1), p.1600269.
- [9] Cooling, N.A., Barnes, E.F., Almyahi, F., Feron, K., Al-Mudhaffer, M.F., Al-Ahmad, A., Vaughan, B., Andersen, T.R., Griffith, M.J., Hart, A.S. and Lyons, A.G., 2016. A low-cost mixed fullerene acceptor blend for printed electronics. *Journal of Materials Chemistry A*, 4(26), pp.10274-10281.
- [10] Fan, Q., Wang, Y., Zhang, M., Wu, B., Guo, X., Jiang, Y., Li, W., Guo, B., Ye, C., Su, W. and Fang, J., 2018. High-performance as-cast nonfullerene polymer solar cells with thicker active layer and large area exceeding 11% power conversion efficiency. *Advanced Materials*, 30(6), p.1704546.
- [11] Sun, H., Liu, T., Yu, J., Lau, T.K., Zhang, G., Zhang, Y., Su, M., Tang, Y., Ma, R., Liu, B. and Liang, J., 2019. A monothiophene unit incorporating both fluoro and ester substitution enabling high-performance donor polymers for non-fullerene solar cells with 16.4% efficiency. *Energy & Environmental Science*, 12(11), pp.3328-3337.
- [12] Li, S., Liu, W., Shi, M., Mai, J., Lau, T.K., Wan, J., Lu, X., Li, C.Z. and Chen, H., 2016. A spirobifluorene and diketopyrrolopyrrole moieties based non-fullerene acceptor for efficient and thermally stable polymer solar cells with high open-circuit voltage. *Energy & Environmental Science*, 9(2), pp.604-610.
- [13] Chen, Z., Cai, P., Chen, J., Liu, X., Zhang, L., Lan, L., Peng, J., Ma, Y. and Cao, Y., 2014. Low band-gap conjugated polymers with strong interchain aggregation and very high hole mobility towards highly efficient thick-film polymer solar cells. *Advanced materials*, 26(16), pp.2586-2591.
- [14] Ma, Y., Chen, S.C., Wang, Z., Ma, W., Wang, J., Yin, Z., Tang, C., Cai, D. and Zheng, Q., 2017. Indacenodithiophene-based wide bandgap copolymers for high performance single-junction and tandem polymer solar cells. *Nano Energy*, 33, pp.313-324.
- [15] Hummelen, J.C., Knight, B.W., LePeq, F., Wudl, F., Yao, J. and Wilkins, C.L., 1995. Preparation and characterization of fulleroid and methanofullerene derivatives. *The Journal of Organic Chemistry*, 60(3), pp.532-538.
- [16] Cooling, N.A., Barnes, E.F., Almyahi, F., Feron, K., Al-Mudhaffer, M.F., Al-Ahmad, A., Vaughan, B., Andersen, T.R., Griffith, M.J., Hart, A.S. and Lyons, A.G., 2016. A low-cost mixed fullerene acceptor blend for printed electronics. *Journal of Materials Chemistry A*, 4(26), pp.10274-10281.
- [17] Lin, Y., Wang, J., Zhang, Z.G., Bai, H., Li, Y., Zhu, D. and Zhan, X., 2015. An

electron acceptor challenging fullerenes for efficient polymer solar cells. *Advanced materials*, 27(7), pp.1170-1174.

- [18] Pan, Q.Q., Li, S.B., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2018. Exploring more effective polymer donors for the famous non-fullerene acceptor ITIC in organic solar cells by increasing electron-withdrawing ability. *Organic Electronics*, 53, pp.308-314.
- [19] Zhang, M., Guo, X., Ma, W., Ade, H. and Hou, J., 2014. A polythiophene derivative with superior properties for practical application in polymer solar cells. *Advanced Materials*, 26(33), pp.5880-5885.
- [20] Zhao, K., Wang, Q., Xu, B., Zhao, W., Liu, X., Yang, B., Sun, M. and Hou, J., 2016. Efficient fullerene-based and fullerene-free polymer solar cells using two wide band gap thiophene-thiazolothiazole-based photovoltaic materials. *Journal of Materials Chemistry A*, 4(24), pp.9511-9518.
- [21] Chen, Z., Cai, P., Chen, J., Liu, X., Zhang, L., Lan, L., Peng, J., Ma, Y. and Cao, Y., 2014. Low band-gap conjugated polymers with strong interchain aggregation and very high hole mobility towards highly efficient thick-film polymer solar cells. *Advanced materials*, 26(16), pp.2586-2591.
- [22] Kawashima, K., Osaka, I. and Takimiya, K., 2015. Effect of chalcogen atom on the properties of naphthobischalcogenadiazole-based π -conjugated polymers. *Chemistry of Materials*, 27(19), pp.6558-6570.
- [23] Pan, J.Y., Zuo, L.J., Hu, X.L., Fu, W.F., Chen, M.R., Fu, L., Gu, X., Shi, H.Q., Shi, M.M., Li, H.Y. and Chen, H.Z., 2013. Star-shaped D–A small molecules based on diketopyrrolopyrrole and triphenylamine for efficient solution-processed organic solar cells. *ACS Applied Materials & Interfaces*, 5(3), pp.972-980.
- [24] Sahu, D., Padhy, H., Patra, D., Huang, J.H., Chu, C.W. and Lin, H.C., 2010. Synthesis and characterization of novel low-bandgap triphenylamine-based conjugated polymers with main-chain donors and pendent acceptors for organic photovoltaics. *Journal of Polymer Science Part A: Polymer Chemistry*, 48(24), pp.5812-5823.
- [25] Huo, L., Hou, J., Chen, H.Y., Zhang, S., Jiang, Y., Chen, T.L. and Yang, Y., 2009. Bandgap and molecular level control of the low-bandgap polymers based on 3, 6-dithiophen-2-yl-2, 5-dihydropyrrolo [3, 4-c] pyrrole-1, 4-dione toward highly efficient polymer solar cells. *Macromolecules*, 42(17), pp.6564-6571.
- [26] Ma, S., Fu, Y., Ni, D., Mao, J., Xie, Z. and Tu, G., 2012. Spiro-fluorene based 3D donor towards efficient organic photovoltaics. *Chemical Communications*, 48(97),

pp.11847-11849.

- [27] Osedach, T.P., Andrew, T.L. and Bulović, V., 2013. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy & Environmental Science*, 6(3), pp.711-718.
- [28] Dupont, S.R., Oliver, M., Krebs, F.C. and Dauskardt, R.H., 2012. Interlayer adhesion in roll-to-roll processed flexible inverted polymer solar cells. *Solar Energy Materials and Solar Cells*, 97, pp.171-175.
- [29] Li, N., McCulloch, I. and Brabec, C.J., 2018. Analyzing the efficiency, stability and cost potential for fullerene-free organic photovoltaics in one figure of merit. *Energy & Environmental Science*, 11(6), pp.1355-1361.
- [30] Pappenfus, T.M., Almyahi, F., Cooling, N.A., Culver, E.W., Rasmussen, S.C. and Dastoor, P.C., 2018. Exploration of the Direct Arylation Polymerization Method for the Practical Application of Conjugated Materials: Synthetic Scale-Up, Solar Cell Performance, and Cost Analyses. *Macromolecular Chemistry and Physics*, 219(21), p.1800272.
- [31] Hou, J., Inganäs, O., Friend, R.H. and Gao, F., 2018. Organic solar cells based on non-fullerene acceptors. *Nature materials*, 17(2), pp.119-128.
- [32] Li, C., Zhou, J., Song, J., Xu, J., Zhang, H., Zhang, X., Guo, J., Zhu, L., Wei, D., Han, G. and Min, J., 2021. Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells. *Nature Energy*, 6(6), pp.605-613.
- [33] Hoppe, H. and Sariciftci, N.S., 2004. Organic solar cells: An overview. *Journal of materials research*, 19(7), pp.1924-1945.
- [34] M. G. Wilson, 2014, *Preparation of Regioregular Poly(3-hexylthiophene) and its Precursor Monomer, 2,5-dibromo-3-hexylthiophene, Using Low Pressure Flow Synthesis Techniques*, PhD Thesis, The University of Newcastle, Newcastle.
- [35] Benanti, T.L. and Venkataraman, D., 2006. Organic solar cells: An overview focusing on active layer morphology. *Photosynthesis research*, 87(1), pp.73-81.
- [36] Seyler, H., Jones, D.J., Holmes, A.B. and Wong, W.W., 2012. Continuous flow synthesis of conjugated polymers. *Chemical Communications*, 48(10), pp.1598-1600.
- [37] Gunes, S., Neugebauer, H. and Sariciftci, N.S., 2007. Conjugated polymer-based

organic solar cells. *Chemical reviews*, 107(4), pp.1324-1338.

- [38] Shaheen, S.E., Ginley, D.S. and Jabbour, G.E., 2005. Organic-based photovoltaics: toward low-cost power generation. *MRS bulletin*, 30(1), pp.10-19.
- [39] Hains, A.W., Liang, Z., Woodhouse, M.A. and Gregg, B.A., 2010. Molecular semiconductors in organic photovoltaic cells. *Chemical reviews*, 110(11), pp.6689-6735.
- [40] Rueff, J.M., Nierengarten, J.F., Gilliot, P., Demessence, A., Cregut, O., Drillon, M. and Rabu, P., 2004. Influence of magnetic ordering on the luminescence in a layered organic– inorganic OPV– Ni (II) compound. *Chemistry of materials*, 16(15), pp.2933-2937.
- [41] O'Rourke, P.J. and Bracco, F.V., 1979. Two scaling transformations for the numerical computation of multidimensional unsteady laminar flames. *Journal of Computational Physics*, 33(2), pp.185-203.
- [42] Charlette, F., Meneveau, C. and Veynante, D., 2002. A power-law flame wrinkling model for LES of premixed turbulent combustion Part I: non-dynamic formulation and initial tests. *Combustion and Flame*, 131(1-2), pp.159-180.
- [43] Osedach, T.P., Andrew, T.L. and Bulović, V., 2013. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy & Environmental Science*, 6(3), pp.711-718.
- [44] Zhao, W., Qian, D., Zhang, S., Li, S., Inganäs, O., Gao, F. and Hou, J., 2016. Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability. *Advanced materials*, 28(23), pp.4734-4739.
- [45] Mo, D., Wang, H., Chen, H., Qu, S., Chao, P., Yang, Z., Tian, L., Su, Y.A., Gao, Y., Yang, B. and Chen, W., 2017. Chlorination of low-band-gap polymers: toward high-performance polymer solar cells. *Chemistry of Materials*, 29(7), pp.2819-2830.
- [46] Zhang, H., Li, S., Xu, B., Yao, H., Yang, B. and Hou, J., 2016. Fullerene-free polymer solar cell based on a polythiophene derivative with an unprecedented energy loss of less than 0.5 eV. *Journal of Materials Chemistry A*, 4(46), pp.18043-18049.
- [47] Gevorgyan, S.A., Espinosa, N., Ciammaruchi, L., Roth, B., Livi, F., Tsopanidis, S., Züfle, S., Queirós, S., Gregori, A., Benatto, G.A.D.R. and Corazza, M., 2016. Baselines for lifetime of organic solar cells. *Advanced Energy Materials*, 6(22), p.1600910.

- [48] Yu, G., Gao, J., Hummelen, J.C., Wudl, F. and Heeger, A.J., 1995. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science*, 270(5243), pp.1789-1791.
- [49] Zhao, Y., Xu, G., Guo, X., Xia, Y., Cui, C., Zhang, M., Song, B., Li, Y. and Li, Y., 2015. Cooperative assembly of an active layer utilizing the synergistic effect of a functional fullerene triad as an acceptor for efficient P3HT-based PSCs. *Journal of Materials Chemistry A*, 3(35), pp.17991-18000.
- [50] Girotto, C., Cheyns, D., Aernouts, T., Banishoeib, F., Lutsen, L., Cleij, T.J., Vanderzande, D., Genoe, J., Poortmans, J. and Heremans, P., 2008. Bulk heterojunction organic solar cells based on soluble poly (thienylene vinylene) derivatives. *Organic electronics*, 9(5), pp.740-746.
- [51] C. Kamble and D. R. Mehta, "Organic Solar Technique using P3HT and PCBM as Promising Materials," vol. 3, no. 1, pp. 2024–2028, 2013.
- [52] Jung, B. and Theato, P., 2012. Chemical strategies for the synthesis of protein–polymer conjugates. *Bio-synthetic polymer conjugates*, pp.37-70.
- [53] Jung, J.W., Jo, J.W., Jung, E.H. and Jo, W.H., 2016. Recent progress in high efficiency polymer solar cells by rational design and energy level tuning of low bandgap copolymers with various electron-withdrawing units. *Organic Electronics*, 31, pp.149-170.
- [54] Yin, H., Geng, Y., Sun, G.Y. and Su, Z.M., 2017. Theoretical design of perylene diimide dimers with different linkers and bridged positions as promising non-fullerene acceptors for organic photovoltaic cells. *The Journal of Physical Chemistry C*, 121(4), pp.2125-2134.
- [55] Bundgaard, E. and Krebs, F.C., 2007. Low band gap polymers for organic photovoltaics. *Solar Energy Materials and Solar Cells*, 91(11), pp.954-985.
- [56] Ganesamoorthy, R., Sathiyam, G. and Sakthivel, P., 2017. Fullerene based acceptors for efficient bulk heterojunction organic solar cell applications. *Solar Energy Materials and Solar Cells*, 161, pp.102-148.
- [57] Parida, B., Iniyam, S. and Goic, R., 2011. A review of solar photovoltaic technologies. *Renewable and sustainable energy reviews*, 15(3), pp.1625-1636.
- [58] N. A. Cooling, 2013, *Ternary Porphyrinoid: Polymer: Fullerene Bulk Heterojunction Organic Solar Cells*, PhD Thesis, The University of Newcastle,

Newcastle.

- [59] Razykov, T.M., Ferekides, C.S., Morel, D., Stefanakos, E., Ullal, H.S. and Upadhyaya, H.M., 2011. Solar photovoltaic electricity: Current status and future prospects. *Solar energy*, 85(8), pp.1580-1608.
- [60] Branker, K., Pathak, M.J.M. and Pearce, J.M., 2011. A review of solar photovoltaic levelized cost of electricity. *Renewable and sustainable energy reviews*, 15(9), pp.4470-4482.
- [61] Singh, G.K., 2013. Solar power generation by PV (photovoltaic) technology: A review. *Energy*, 53, pp.1-13.
- [62] Halls, J.J.M., Walsh, C.A., Greenham, N.C., Marseglia, E.A., Friend, R.H., Moratti, S.C. and Holmes, A.B., 1995. Efficient photodiodes from interpenetrating polymer networks. *Nature*, 376(6540), pp.498-500.
- [63] Krebs, F.C., 2008. Polymer photovoltaics: a practical approach. SPIE-International Society for Optical Engineering, pp. 10-15.
- [64] E. Actuators, 2017. "Electrically Driving Sensors Based on Polymer", pp.150-169.
- [65] Yibowei, M.E., Adekoya, J.G., Adediran, A.A. and Adekomaya, O., 2021. Carbon-based nano-filler in polymeric composites for supercapacitor electrode materials: a review. *Environmental Science and Pollution Research*, 28(21), pp.26269-26279.
- [66] E. H. Based, "Energy Harvesting Based on Polymer," pp. 151–196, 2017.
- [67] Fragal, V.H., da Silva, E.P., Fragal, E.H., Pellá, M.C.G., Sequinel, T., Silva, R., Radmann, C.T., Mortola, V.B. and Gorup, L.F., 2022. 27 Carbon Nanostructures. *Energy from Waste: Production and Storage*, p.417.
- [68] Peng, H., Sun, X., Weng, W. and Fang, X., 2016. Polymer materials for energy and electronic applications. Academic Press, pp. 9–61.
- [69] Le, T.H., Kim, Y. and Yoon, H., 2017. Electrical and electrochemical properties of conducting polymers. *Polymers*, 9(4), p.150.
- [70] Ci, J., Kang, H., Liu, C., He, A. and Liu, R., 2015. Protein resistance adsorption mechanism and applications of zwitterionic polymers. *Progress in Chemistry*, 27(9), p.1198.

- [71] Kilic, K.I., 2021. Molecular Modeling of Mechanically Reliable Hybrid Organosilicate Materials, Stanford University, pp. 107–149, 2017.
- [72] Yang, J., Liu, Y., Liu, S., Li, L., Zhang, C. and Liu, T., 2017. Conducting polymer composites: material synthesis and applications in electrochemical capacitive energy storage. *Materials Chemistry Frontiers*, 1(2), pp.251-268.
- [73] Peng, H., Sun, X., Weng, W. and Fang, X., 2016. Polymer materials for energy and electronic applications. Academic Press, pp. 243–285.
- [74] Peng, H., Sun, X., Weng, W. and Fang, X., 2016. Polymer materials for energy and electronic applications. Academic Press.
- [75] Lai, T.H., Tsang, S.W., Manders, J.R., Chen, S. and So, F., 2013. Properties of interlayer for organic photovoltaics. *Materials Today*, 16(11), pp.424-432.
- [76] International Energy Agency, 2016. World Energy Outlook: Executive Summary.
- [77] Zhang, S., Ye, L. and Hou, J., 2016. Breaking the 10% Efficiency Barrier in Organic Photovoltaics: Morphology and Device Optimization of Well-Known PBDTTT Polymers. *Advanced Energy Materials*, 6(11), p.1502529.
- [78] Tang, C.W., 1986. Two-layer organic photovoltaic cell. *Applied physics letters*, 48(2), pp.183-185.
- [79] Yu, G., Gao, J., Hummelen, J.C., Wudl, F. and Heeger, A.J., 1995. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science*, 270(5243), pp.1789-1791.
- [80] Nilsson, S., Bernasik, A., Budkowski, A. and Moons, E., 2007. Morphology and phase segregation of spin-casted films of polyfluorene/PCBM blends. *Macromolecules*, 40(23), pp.8291-8301.
- [81] Guerrero, A. and Garcia-Belmonte, G., 2017. Recent advances to understand morphology stability of organic photovoltaics. *Nano-micro letters*, 9(1), pp.1-16.
- [82] Bergmann, R.B., 1999. Crystalline Si thin-film solar cells: a review. *Applied physics A*, 69(2), pp.187-194.
- [83] Shah, A., Torres, P., Tscharnner, R., Wyrsh, N. and Keppner, H., 1999. Photovoltaic technology: the case for thin-film solar cells. *science*, 285(5428), pp.692-698.

- [84] Carlson, D.E. and Wronski, C.R., 1976. Amorphous silicon solar cell. *Applied Physics Letters*, 28(11), pp.671-673.
- [85] Hamed, W.A., Yahya, R., Bola, A.U.L. and Mahmud, H.N.M.E., 2013. Recent approaches to controlling the nanoscale morphology of polymer-based bulk-heterojunction solar cells. *Energies*, 6(11), pp.5847-5868.
- [86] Esfahani, S.N., Asghari, S. and Rashid-Nadimi, S., 2017. A numerical model for soldering process in silicon solar cells. *Solar Energy*, 148, pp.49-56.
- [87] Nicholson, P.G. and Castro, F.A., 2010. Organic photovoltaics: principles and techniques for nanometre scale characterization. *Nanotechnology*, 21(49), p.492001.
- [88] Zheng, Y. and Xue, J., 2010. Organic photovoltaic cells based on molecular donor-acceptor heterojunctions. *Polymer Reviews*, 50(4), pp.420-453.
- [89] Shaheen, S.E., Ginley, D.S. and Jabbour, G.E., 2005. Organic-based photovoltaics: toward low-cost power generation. *MRS bulletin*, 30(1), pp.10-19.
- [90] Benanti, T.L. and Venkataraman, D., 2006. Organic solar cells: An overview focusing on active layer morphology. *Photosynthesis research*, 87(1), pp.73-81.
- [91] Spanggaard, H. and Krebs, F.C., 2004. A brief history of the development of organic and polymeric photovoltaics. *Solar Energy Materials and Solar Cells*, 83(2-3), pp.125-146.
- [92] Garnier, F., Hajlaoui, R., Yassar, A. and Srivastava, P., 1994. All-polymer field-effect transistor realized by printing techniques. *Science*, 265(5179), pp.1684-1686.
- [93] Economopoulos, S.P., Itskos, G., Koutentis, P.A. and Choulis, S.A., 2014. Overview of polymer and copolymer materials for organic photovoltaics. *Organic Photovoltaics*, pp.1-26.
- [94] Burroughes, J.H., Jones, C.A. and Friend, R.H., 1988. New semiconductor device physics in polymer diodes and transistors. *nature*, 335(6186), pp.137-141.
- [95] Someya, T., Kato, Y., Sekitani, T., Iba, S., Noguchi, Y., Murase, Y., Kawaguchi, H. and Sakurai, T., 2005. Conformable, flexible, large-area networks of pressure and thermal sensors with organic transistor active matrixes. *Proceedings of the National Academy of Sciences*, 102(35), pp.121-125.

- [96] Sariciftci, N.S., Smilowitz, L., Heeger, A.J. and Wudl, F., 1992. Photoinduced electron transfer from a conducting polymer to buckminsterfullerene. *Science*, 258(5087), pp.1474-1476.
- [97] Kim, I., 2015. First-principles study on electronic and structural properties of Cu(In/Ga) Salloys for solar cells., pp.23-28.
- [98] Tang, C.W., 1986. Two-layer organic photovoltaic cell. *Applied physics letters*, 48(2), pp.183-185.
- [99] Coakley, K.M. and McGehee, M.D., 2004. Conjugated polymer photovoltaic cells. *Chemistry of materials*, 16(23), pp.4533-4542.
- [100] Parlak, E.A., 2012. The blend ratio effect on the photovoltaic performance and stability of poly (3-hexylthiophene):[6, 6]-phenyl-C61 butyric acid methyl ester (PCBM) and poly (3-octylthiophene): PCBM solar cells. *Solar energy materials and solar cells*, 100, pp.174-184.
- [101] Sharma, V., Singh, V., Arora, M., Arora, S. and Tandon, R.P., 2015. Influence of donor–acceptor materials on the photovoltaic parameters of conjugated polymer/fullerene solar cells. *Journal of Materials Science: Materials in Electronics*, 26(8), pp.6212-6217.
- [102] Helgesen, M., Bjerring, M., Nielsen, N.C. and Krebs, F.C., 2010. Influence of the annealing temperature on the photovoltaic performance and film morphology applying novel thermocleavable materials. *Chemistry of Materials*, 22(19), pp.5617-5624.
- [103] Kadem, B., Hassan, A. and Cranton, W., 2016. Efficient P3HT: PCBM bulk heterojunction organic solar cells; effect of post deposition thermal treatment. *Journal of Materials Science: Materials in Electronics*, 27(7), pp.7038-7048.
- [104] Bin, H., Zhang, Z.G., Gao, L., Chen, S., Zhong, L., Xue, L., Yang, C. and Li, Y., 2016. Non-fullerene polymer solar cells based on alkylthio and fluorine substituted 2D-conjugated polymers reach 9.5% efficiency. *Journal of the American Chemical Society*, 138(13), pp.4657-4664.
- [105] Suait, M.S., Rahman, M.Y.A. and Ahmad, A., 2015. Review on polymer electrolyte in dye-sensitized solar cells (DSSCs). *Solar Energy*, 115, pp.452-470.
- [106] Mihailetchi, V.D., 2005. Device physics of organic bulk heterojunction solar cells. *University of Groningen, The Netherlands*.

- [107] Glenis, S., Tourillon, G. and Garnier, F., 1986. Influence of the doping on the photovoltaic properties of thin films of poly-3-methylthiophene. *Thin Solid Films*, 139(3), pp.221-231.
- [108] Chidichimo, G. and Filippelli, L., 2010. Organic solar cells: problems and perspectives. *International Journal of Photoenergy*, 2010.
- [109] Shaheen, S.E., Brabec, C.J., Sariciftci, N.S., Padinger, F., Fromherz, T. and Hummelen, J.C., 2001. 2.5% efficient organic plastic solar cells. *Applied physics letters*, 78(6), pp.841-843.
- [110] McCullough, R.D., 1998. The chemistry of conducting polythiophenes. *Advanced materials*, 10(2), pp.93-116.
- [111] Johansson, D.M., Srdanov, G., Yu, G., Theander, M., Inganäs, O. and Andersson, M.R., 2000. Synthesis and characterization of highly soluble phenyl-substituted poly (p-phenylenevinylenes). *Macromolecules*, 33(7), pp.2525-2529.
- [112] Sariciftci, N.S., Smilowitz, L., Heeger, A.J. and Wudl, F., 1993. Semiconducting polymers (as donors) and buckminsterfullerene (as acceptor): photoinduced electron transfer and heterojunction devices. *Synthetic Metals*, 59(3), pp.333-352.
- [113] Kroon, J.M., Veenstra, S.C., Slooff, L.H., Verhees, W.J.H., Koetse, M.M., Sweelssen, J., Schoo, H.F.M., Beek, W.J.E., Wienk, M.M., Janssen, R.A.J. and Yang, X., 2005, June. Polymer based photovoltaics: novel concepts, materials and state-of-the art efficiencies. In *Presented at the 20th European Photovoltaic Solar Energy Conference and Exhibition* (Vol. 6, p. 10).
- [114] Deng, L.L., Xie, S.L., Yuan, C., Liu, R.F., Feng, J., Sun, L.C., Lu, X., Xie, S.Y., Huang, R.B. and Zheng, L.S., 2013. High LUMO energy level C60 (OCH3) 4 derivatives: Electronic acceptors for photovoltaic cells with higher open-circuit voltage. *Solar energy materials and solar cells*, 111, pp.193-199.
- [115] Benanti, T.L. and Venkataraman, D., 2006. Organic solar cells: An overview focusing on active layer morphology. *Photosynthesis research*, 87(1), pp.73-81.
- [116] Qin, Y., Uddin, M.A., Chen, Y., Jang, B., Zhao, K., Zheng, Z., Yu, R., Shin, T.J., Woo, H.Y. and Hou, J., 2016. Highly Efficient Fullerene-Free Polymer Solar Cells Fabricated with Polythiophene Derivative. *Advanced Materials*, 28(42), pp.9416-9422.
- [117] Penza, M., Cozzi, S., Tagliente, M.A., Mirengi, L., Martucci, C. and Quirini, A.,

1999. Characterization of transparent and conductive electrodes of indium tin oxide thin films by sequential reactive evaporation. *thin solid Films*, 349(1-2), pp.71-77.
- [118] Dang, M.T., Hirsch, L. and Wantz, G., 2011. P3HT: PCBM, best seller in polymer photovoltaic research, vol. 23, no. 31, pp. 3597–3602, 2011.
- [119] Liu, C., Wang, K., Gong, X. and Heeger, A.J., 2016. Low bandgap semiconducting polymers for polymeric photovoltaics. *Chemical Society Reviews*, 45(17), pp.4825-4846.
- [120] Wang, H.J., Chen, C.P. and Jeng, R.J., 2014. Polythiophenes comprising conjugated pendants for polymer solar cells: a review. *Materials*, 7(4), pp.2411-2439.
- [121] Bundgaard, E. and Krebs, F.C., 2007. Low band gap polymers for organic photovoltaics. *Solar Energy Materials and Solar Cells*, 91(11), pp.954-985.
- [122] Wang, T.L., Yang, C.H., Shieh, Y.T., Chen, Y.C., Ho, T.H. and Chen, C.H., 2012. An extremely low bandgap donor–acceptor copolymer for panchromatic solar cells. *Solar energy materials and solar cells*, 107, pp.298-306.
- [123] Holliday, S., Li, Y. and Luscombe, C.K., 2017. Recent advances in high performance donor-acceptor polymers for organic photovoltaics. *Progress in Polymer Science*, 70, pp.34-51.
- [124] C. J. Mulligan, 2013, *Towards Production Scale-Up of Organic Photovoltaics*, PhD Thesis, The University of Newcastle, Newcastle.
- [125] Padinger, F., Rittberger, R.S. and Sariciftci, N.S., 2003. Effects of postproduction treatment on plastic solar cells. *Advanced Functional Materials*, 13(1), pp.85-88.
- [126] Chen, C.P., Chan, S.H., Chao, T.C., Ting, C. and Ko, B.T., 2008. Low-bandgap poly (thiophene-phenylene-thiophene) derivatives with broaden absorption spectra for use in high-performance bulk-heterojunction polymer solar cells. *Journal of the American Chemical Society*, 130(38), pp.12828-12833.
- [127] Si, W., Zhang, X., Lu, S., Yasuda, T., Asao, N., Han, L., Yamamoto, Y. and Jin, T., 2015. Manganese powder promoted highly efficient and selective synthesis of fullerene mono-and biscycloadducts at room temperature. *Scientific reports*, 5(1), pp.1-8.
- [128] Zou, Y., Najari, A., Berrouard, P., Beaupré, S., Réda Aïch, B., Tao, Y. and Leclerc, M., 2010. A thieno [3, 4-c] pyrrole-4, 6-dione-based copolymer for efficient solar

cells. *Journal of the American Chemical Society*, 132(15), pp.5330-5331.

- [129] Kan, B., Zhang, Q., Li, M., Wan, X., Ni, W., Long, G., Wang, Y., Yang, X., Feng, H. and Chen, Y., 2014. Solution-processed organic solar cells based on dialkylthiol-substituted benzodithiophene unit with efficiency near 10%. *Journal of the American Chemical Society*, 136(44), pp.15529-15532.
- [130] Liang, Y., Wu, Y., Feng, D., Tsai, S.T., Son, H.J., Li, G. and Yu, L., 2009. Development of new semiconducting polymers for high performance solar cells. *Journal of the American Chemical Society*, 131(1), pp.56-57.
- [131] Liang, Y., Wu, Y., Feng, D., Tsai, S.T., Son, H.J., Li, G. and Yu, L., 2009. Development of new semiconducting polymers for high performance solar cells. *Journal of the American Chemical Society*, 131(1), pp.56-57.
- [132] Osedach, T.P., Andrew, T.L. and Bulović, V., 2013. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy & Environmental Science*, 6(3), pp.711-718.
- [133] Grenier, F., Aïch, B.R., Lai, Y.Y., Guérette, M., Holmes, A.B., Tao, Y., Wong, W.W. and Leclerc, M., 2015. Electroactive and photoactive poly [isoindigo-alt-EDOT] synthesized using direct (hetero) arylation polymerization in batch and in continuous flow. *Chemistry of Materials*, 27(6), pp.2137-2143.
- [134] Seyler, H., Jones, D.J., Holmes, A.B. and Wong, W.W., 2012. Continuous flow synthesis of conjugated polymers. *Chemical Communications*, 48(10), pp.1598-1600.
- [135] Kim, Y., Choulis, S.A., Nelson, J., Bradley, D.D., Cook, S. and Durrant, J.R., 2005. Device annealing effect in organic solar cells with blends of regioregular poly (3-hexylthiophene) and soluble fullerene. *Applied Physics Letters*, 86(6), p.063502.
- [136] Waters, R.H.R., 2015, *Characterisation and lifetime studies of CPDT-and BT-based photovoltaic cells*, Bangor University (United Kingdom).
- [137] Bannock, J.H., Krishnadasan, S.H., Nightingale, A.M., Yau, C.P., Khaw, K., Burkitt, D., Halls, J.J., Heeney, M. and de Mello, J.C., 2013. Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Advanced Functional Materials*, 23(17), pp.2123-2129.
- [138] Zheng, Y.Q., Potscavage Jr, W.J., Komino, T., Hirade, M., Adachi, J. and Adachi, C., 2013. Highly efficient bulk heterojunction photovoltaic cells based on C70 and tetraphenyldibenzoperiflanthene. *Applied Physics Letters*, 102(14), p.60.

- [139] Pashkova, A. and Greiner, L., 2011. Towards Small-Scale Continuous Chemical Production: Technology Gaps and Challenges. *Chemie Ingenieur Technik*, 83(9), pp.1337-1342.
- [140] Sahu, D., Tsai, C.H., Wei, H.Y., Ho, K.C., Chang, F.C. and Chu, C.W., 2012. Synthesis and applications of novel low bandgap star-burst molecules containing a triphenylamine core and dialkylated diketopyrrolopyrrole arms for organic photovoltaics. *Journal of Materials Chemistry*, 22(16), pp.7945-7953.
- [141] Xu, Y.X., Chueh, C.C., Yip, H.L., Ding, F.Z., Li, Y.X., Li, C.Z., Li, X., Chen, W.C. and Jen, A.K.Y., 2012. Improved charge transport and absorption coefficient in indacenodithieno [3, 2-b] thiophene-based ladder-type polymer leading to highly efficient polymer solar cells. *Advanced materials*, 24(47), pp.6356-6361.
- [142] Luo, H., Lai, J., Wang, C. and Chen, Q., 2018. Understanding the effects of the energy band alignment at the donor/acceptor interface on the open circuit voltage of organic photovoltaic devices. *Chemical Physics Letters*, 711, pp.113-117.
- [143] Tremolet de Villers, B.J., O'Hara, K.A., Ostrowski, D.P., Biddle, P.H., Shaheen, S.E., Chabinyk, M.L., Olson, D.C. and Kopidakis, N., 2016. Removal of residual diiodooctane improves photostability of high-performance organic solar cell polymers. *Chemistry of Materials*, 28(3), pp.876-884.
- [144] Wadsworth, A., Moser, M., Marks, A., Little, M.S., Gasparini, N., Brabec, C.J., Baran, D. and McCulloch, I., 2019. Critical review of the molecular design progress in non-fullerene electron acceptors towards commercially viable organic solar cells. *Chemical Society Reviews*, 48(6), pp.1596-1625.
- [145] Bundgaard, E., Livi, F., Hagemann, O., Carlé, J.E., Helgesen, M., Heckler, I.M., Zawacka, N.K., Angmo, D., Larsen-Olsen, T.T., dos Reis Benatto, G.A. and Roth, B., 2015. Matrix organization and merit factor evaluation as a method to address the challenge of finding a polymer material for roll coated polymer solar cells. *Advanced Energy Materials*, 5(10), p.1402186.
- [146] Mulligan, C.J., Wilson, M., Bryant, G., Vaughan, B., Zhou, X., Belcher, W.J. and Dastoor, P.C., 2014. A projection of commercial-scale organic photovoltaic module costs. *Solar Energy Materials and Solar Cells*, 120, pp.9-17.
- [147] Gao, H.L., Zhang, X.W., Meng, J.H., Yin, Z.G., Zhang, L.Q., Wu, J.L. and Liu, X., 2015. Enhanced efficiency in polymer solar cells via hydrogen plasma treatment of ZnO electron transport layers. *Journal of Materials Chemistry A*, 3(7), pp.3719-3725.

- [148] Griffith, M.J., Cooling, N.A., Vaughan, B., O'Donnell, K.M., Al-Mudhaffer, M.F., Al-Ahmad, A., Noori, M., Almyahi, F., Belcher, W.J. and Dastoor, P.C., 2015. Roll-to-Roll Sputter Coating of Aluminum Cathodes for Large-Scale Fabrication of Organic Photovoltaic Devices. *Energy Technology*, 3(4), pp.428-436.
- [149] Andersen, T.R., Almyahi, F., Cooling, N.A., Elkington, D., Wiggins, L., Fahy, A., Feron, K., Vaughan, B., Griffith, M.J., Mozer, A.J. and Sae-Kung, C., 2016. Comparison of inorganic electron transport layers in fully roll-to-roll coated/printed organic photovoltaics in normal geometry. *Journal of Materials Chemistry A*, 4(41), pp.15986-15996.
- [150] Aqoma, H., Park, S., Park, H.Y., Hadmojo, W.T., Oh, S.H., Nho, S., Kim, D.H., Seo, J., Park, S., Ryu, D.Y. and Cho, S., 2018. 11% Organic Photovoltaic Devices Based on PTB7-Th: PC71BM Photoactive Layers and Irradiation-Assisted ZnO Electron Transport Layers. *Advanced Science*, 5(7), p.1700858.
- [151] Scharber, M.C., 2016. On the efficiency limit of conjugated polymer: fullerene-based bulk heterojunction solar cells. *Advanced Materials*, 28(10), pp.1994-2001.
- [152] Nelson, J., 2011. Polymer: fullerene bulk heterojunction solar cells. *Materials today*, 14(10), pp.462-470.
- [153] Liu, Y., Zhao, J., Li, Z., Mu, C., Ma, W., Hu, H., Jiang, K., Lin, H., Ade, H. and Yan, H., 2014. Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells. *Nature communications*, 5(1), pp.1-8.
- [154] Wienk, M.M., Kroon, J.M., Verhees, W.J., Knol, J., Hummelen, J.C., Van Hal, P.A. and Janssen, R.A., 2003. Efficient methano [70] fullerene/MDMO-PPV bulk heterojunction photovoltaic cells. *Angewandte Chemie*, 115(29), pp.3493-3497.
- [155] Wadsworth, A., Moser, M., Marks, A., Little, M.S., Gasparini, N., Brabec, C.J., Baran, D. and McCulloch, I., 2019. Critical review of the molecular design progress in non-fullerene electron acceptors towards commercially viable organic solar cells. *Chemical Society Reviews*, 48(6), pp.1596-1625.
- [156] Pan, Q.Q., Zhao, Z.W., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2019. A theoretical exploration on why the replacement of hexyl group by alkoxycarbonyl in P3HT could greatly improve the performance of non-fullerene organic solar cell. *Journal of the Taiwan Institute of Chemical Engineers*, 100, pp.160-167.
- [157] Griffith, M.J., Cooling, N.A., Vaughan, B., Elkington, D.C., Hart, A.S., Lyons, A.G., Quereschi, S., Belcher, W.J. and Dastoor, P.C., 2015. Combining printing, coating, and

- vacuum deposition on the roll-to-roll scale: a hybrid organic photovoltaics fabrication. *IEEE Journal of Selected Topics in Quantum Electronics*, 22(1), pp.112-125.
- [158] Pankow, R.M., Ye, L. and Thompson, B.C., 2019. Influence of an ester directing-group on defect formation in the synthesis of conjugated polymers via direct arylation polymerization (DArP) using sustainable solvents. *Polymer Chemistry*, 10(33), pp.4561-4572.
- [159] Pankow, R.M. and Thompson, B.C., 2020. Approaches for improving the sustainability of conjugated polymer synthesis using direct arylation polymerization (DArP). *Polymer Chemistry*, 11(3), pp.630-640.
- [160] Li, Y., 2012. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. *Accounts of chemical research*, 45(5), pp.723-733.
- [161] Heuvel, R., Colberts, F.J., Li, J., Wienk, M.M. and Janssen, R.A., 2018. The effect of side-chain substitution on the aggregation and photovoltaic performance of diketopyrrolopyrrole-alt-dicarboxylic ester bithiophene polymers. *Journal of Materials Chemistry A*, 6(42), pp.20904-20915.
- [162] Hou, J., Inganäs, O., Friend, R.H. and Gao, F., 2018. Organic solar cells based on non-fullerene acceptors. *Nature materials*, 17(2), pp.119-128.
- [163] Li, N., McCulloch, I. and Brabec, C.J., 2018. Analyzing the efficiency, stability and cost potential for fullerene-free organic photovoltaics in one figure of merit. *Energy & Environmental Science*, 11(6), pp.1355-1361.
- [164] Welton, T., 2015. Solvents and sustainable chemistry. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 471(2183), p.20150502.
- [165] Xiao, L., He, B., Hu, Q., Maserati, L., Zhao, Y., Yang, B., Kolaczowski, M.A., Anderson, C.L., Borys, N.J., Klivansky, L.M. and Chen, T.L., 2018. Multiple roles of a non-fullerene acceptor contribute synergistically for high-efficiency ternary organic photovoltaics. *Joule*, 2(10), pp.2154-2166.
- [166] Sapsford, K.E., Berti, L. and Medintz, I.L., 2006. Materials for fluorescence resonance energy transfer analysis: beyond traditional donor-acceptor combinations. *Angewandte Chemie International Edition*, 45(28), pp.4562-4589.

- [167] Caron, S. ed., 2020. Practical synthetic organic chemistry: reactions, principles, and techniques. John Wiley & Sons, pp.205-211.
- [168] Pan, Q.Q., Li, S.B., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2018. Exploring more effective polymer donors for the famous non-fullerene acceptor ITIC in organic solar cells by increasing electron-withdrawing ability. *Organic Electronics*, 53, pp.308-314.
- [169] Colsmann, A., Röhm, H. and Sprau, C., 2020. Shining light on organic solar cells. *Solar RRI*, 4(6), p.2000015.
- [170] Huang, W., Jiang, Z., Fukuda, K., Jiao, X., McNeill, C.R., Yokota, T. and Someya, T., 2020. Efficient and mechanically robust ultraflexible organic solar cells based on mixed acceptors. *Joule*, 4(1), pp.128-141.
- [171] Zhang, S., Qin, Y., Zhu, J. and Hou, J., 2018. Over 14% efficiency in polymer solar cells enabled by a chlorinated polymer donor. *Advanced Materials*, 30(20), p.1800868.
- [172] Xiao, Z., Geng, X., He, D., Jia, X. and Ding, L., 2016. Development of isomer-free fullerene bisadducts for efficient polymer solar cells. *Energy & Environmental Science*, 9(6), pp.2114-2121.
- [173] Cui, Y., Yao, H., Zhang, J., Zhang, T., Wang, Y., Hong, L., Xian, K., Xu, B., Zhang, S., Peng, J. and Wei, Z., 2019. Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages. *Nature communications*, 10(1), pp.1-8.
- [174] Yuan, J., Zhang, Y., Zhou, L., Zhang, G., Yip, H.L., Lau, T.K., Lu, X., Zhu, C., Peng, H., Johnson, P.A. and Leclerc, M., 2019. Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core. *Joule*, 3(4), pp.1140-1151.
- [175] Gambhir, A., Sandwell, P. and Nelson, J., 2016. The future costs of OPV—A bottom-up model of material and manufacturing costs with uncertainty analysis. *Solar Energy Materials and Solar Cells*, 156, pp.49-58.
- [176] Mulligan, C.J., Bilen, C., Zhou, X., Belcher, W.J. and Dastoor, P.C., 2015. Levelised cost of electricity for organic photovoltaics. *Solar energy materials and solar cells*, 133, pp.26-31.
- [177] Al-Ahmad, A.Y., Almayhi, F., Al-Mudhaffer, M.F., Griffith, M.J., Liu, W., Li, S.,

- Sivunova, K., Elkington, D., Cooling, N.A., Feron, K. and Shi, M., 2020. A nuanced approach for assessing OPV materials for large scale applications. *Sustainable Energy & Fuels*, 4(2), pp.940-949.
- [178] Zhang, M., Guo, X., Ma, W., Ade, H. and Hou, J., 2014. A polythiophene derivative with superior properties for practical application in polymer solar cells. *Advanced Materials*, 26(33), pp.5880-5885.
- [179] Dastoor, P.C. and Belcher, W.J., 2019. How the West was Won? A History of Organic Photovoltaics. *Substantia*, 3(2), pp.99-110.
- [180] Griffith, M.J., Cooling, N.A., Vaughan, B., Elkington, D.C., Hart, A.S., Lyons, A.G., Quereschi, S., Belcher, W.J. and Dastoor, P.C., 2015. Combining printing, coating, and vacuum deposition on the roll-to-roll scale: a hybrid organic photovoltaics fabrication. *IEEE Journal of Selected Topics in Quantum Electronics*, 22(1), pp.112-125.

Chapter 4: PDCBT and ITIC synthesis and scale up

4.1 Overview

In this chapter, recently developed photoactive materials (PDCBT and ITIC) were successfully synthesised on a laboratory scale and assessed for a large-scale production. As well as, mass scale batches of benchmark materials (P3HT, PCBM, ICx_A, PEDOT:PSS) were synthesised and incorporated into devices for further investigation and direct comparison with devices fabricated from PDCBT and ITIC. A step by step up-scale assessment of the synthesis of PDCBT and ITIC is introduced. Production cost reduction methods in their syntheses are addressed and approach to achieve industrialisation of these materials is introduced.

4.2 Introduction

The successful scale up of high performing newly developed OPV materials in a cost-effective way has not been widely explored in the literature with only a few reports [1], [2]. Therefore, in this chapter we address this issue by investigating the scale up of materials identified in the previous chapter.

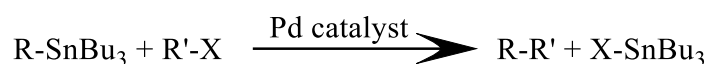
Published research on the selected materials synthesis, demonstrated only a small-scale synthesis and successful incorporation of the materials into small scale solar cells. This approach produces high efficiency devices (PCE_{max} of 17.3%) [3] with long term stability (about 10 years) [4][5] in organic solar cells. However, the approach and potential of these materials is limited by the small scale and massive upscaling is required for commercial solar module production. Therefore, in this study the challenges of upscaled production whilst obtaining high yields is addressed. In addition, suggestions are made as for future research to achieve cost effective, high performing modules on a large scale.

Miscibility of donor and acceptor materials for solar cells optimal morphology is one of the critical points for better device performance and stability. Consequently, device fabrication and characterisation are further investigated and introduced in this thesis for PDCBT donor and ITIC acceptor devices in the next chapter (Chapter 5) of this thesis.

For a successful PDCBT and ITIC donor/acceptor blend, it is important to consider energy levels, absorption, and charge mobility of the materials and blend. For an acceptor, aromatic fused ring electron acceptors typically exhibit high charge mobility due to conjugation in the fused rings with efficient interchain π - π overlaps. On the other hand, introducing electron withdrawing groups (amide, imide and cyano) may stabilise the LUMO level due to the π^* energy of the electron-withdrawing component [6], [7]. However, the main drawback of fused ring-based acceptors is the self-aggregation and planarity [6], which can be avoided by incorporating rigid out of plane rings into the structure. By utilising these concepts, the 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) molecule which has a bulky seven ring fused indacenodithieno[3,2-b]thiophene (IT) core, with 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (INCN) units, and four 4-hexylphenyl groups on its periphery, demonstrates low LUMO and HOMO levels, increased electron transfer ability and higher absorption. In addition, the four out-of-plane 4-hexylphenyl units off the IT main chain, decrease aggregation and improve film morphology in OPV devices [7]. Consequently, ITIC has great potential for high absorption, efficient electron transfer, good miscibility with donor materials (i.e. PDCBT).

4.3 PDCBT synthesis and scale up

The method to produce PDCBT is based upon Stille coupling, which is a common transformation used in organic chemistry. This coupling uses a suitable palladium catalyst to facilitate reaction between a suitable organotin compound (organostannane with a C-Sn bond) and an organic electrophile to form a new C-C σ -bond, as shown in the following Equation 4.1:



Equation 4.1 Stille coupling mechanism between organotin compound and an organic electrophile

In this process the reaction occurs between R and R' (coupling partners can be aryl or vinyl groups), where X can be a halogen (Cl, Br, or I) or a triflate (OTf). Hence, the product is a substituted biaryl system if the two partners groups are aryl groups, as is taken advantage of in the PDCBT polymerisation step of the two monomers. This reaction can be achieved in the presence of a catalyst such as $\text{Pd(PPh}_3)_4$, in which the palladium atom has an oxidation state zero [8].

Direct arylation polymerisation (DArP) is another appealing synthetic methodology developed by Robert M. Pankow et al. [9], [10], which exhibits production of PDCBT via C-H activation and allows reduction of the number of synthetic steps, toxic waste and reagents

during the synthesis (Figure 4.1). However, the yield of polymer production by this method is 59%, comparing to the Stille coupling mechanism which is more efficient yield of 76%.

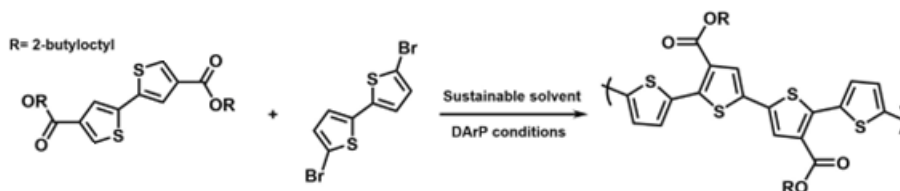


Figure 4.1 DArP using sustainable solvents to synthesise PDCBT polymer

Consequently, the standard method of Stille coupling was used in this work, due to higher yields during the synthesis. Improving the cost and sustainability of the polymerisation by replacing the solvent or metal catalyst to a green alternative is an important field for further research. The PDCBT polymer synthesis used in this study was based upon the literature method [11] as introduced in this chapter. Where preparing compounds ^1H -NMR spectra data was compared with published literature spectra to confirm chemical identity. A schematic of the synthetic route for PDCBT is presented in Figure 4.2 below [11] and step by step synthesis follows.

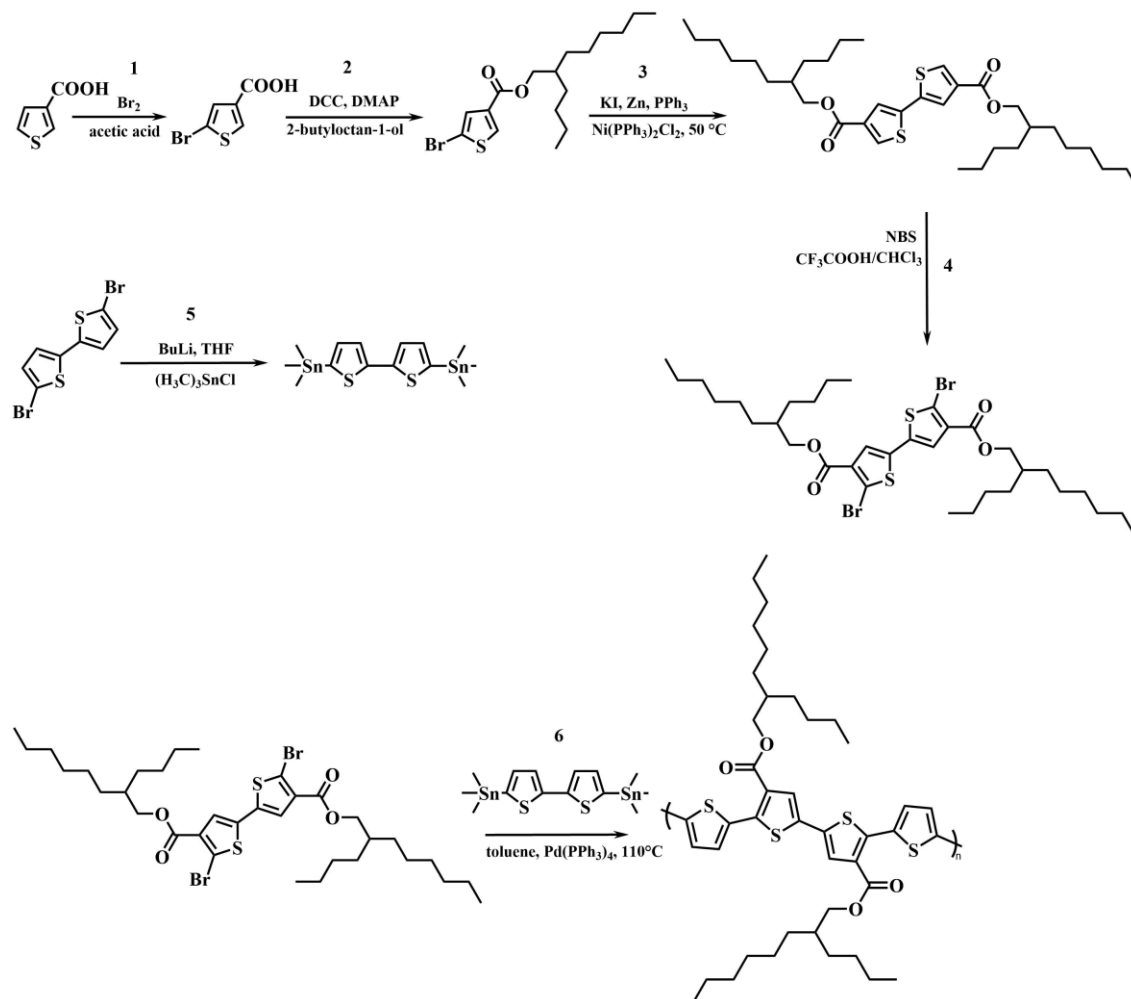


Figure 4.2 Synthesis of PDCBT by Stille coupling [11]: steps 1-4 are Bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (Monomer 1) synthesis. Step 1 yield 54%, step 2 yield 85%, step 3 yield 70%, step 4 yield 60%; step 5 is 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (Monomer 2) synthesis, step 5 yield 98%; step 6 is synthesis of PDCBT, yield 76%.

4.3.1 Bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (Monomer 1) production

4.3.1.1 5-bromothiophene-3-carboxylic acid (1) synthesis

A method to produce 5-bromothiophene-3-carboxylic acid was introduced by Ruurd Heuvel et al. [12]. The methods work up was effectively upgraded to improve the overall polymer synthesis. Instead of drying the material in a vacuum oven at 60 °C for 4 days to give the product, the compound was sublimed to give an essentially quantitative yield of pure product, which is fast and ideal for time-sensitive reactions. The process produced high purity white crystals and the reaction is represented in Figure 4.3 (2).

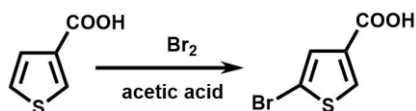


Figure 4.3 Synthesis of 5-bromothiophene-3-carboxylic acid

Bromine (5.3 mL, 103 mmol) as a solution in acetic acid (36 mL) was added at room temperature to a solution of thiophene-3-carboxylic acid (12 g, 94 mmol) in acetic acid (48 mL) over 25 minutes (illustrated in Figure 4.4 (A) and (B)). The resulting mixture was stirred for 6 days at room temperature. Once the reaction was completed, the resulting orange suspension was poured into 120 mL of ice-cold water to form voluminous white precipitate and isolated by vacuum filtration. The precipitate was re-suspended in ice cold water and isolated by vacuum filtration to give a white solid. The compound obtained, was sublimed at

144 °C to remove impurities to give a product as a white solid with a yield of 18.93 g (97 %).

^1H NMR (400 MHz, CDCl_3): δ 8.12 (d, 1H); 7.51 (d, 1H); m.p. = >141 °C

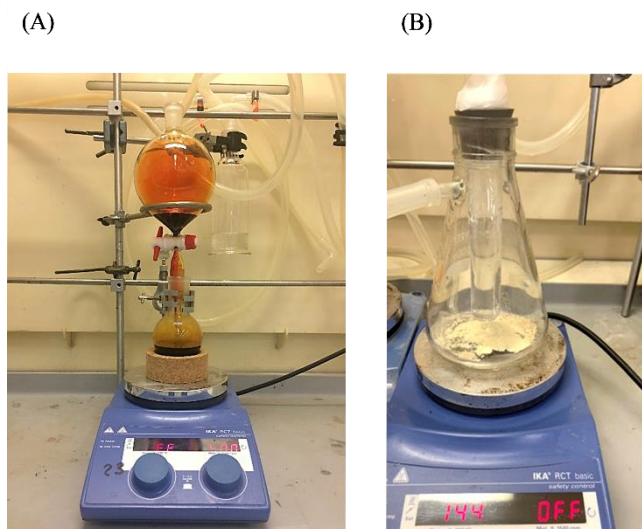


Figure 4.4 (A) Bromine addition to a thiophene-3-carboxylic acid and acetic acid reaction mixture; (B) Sublimation process of 5-bromothiophene-3-carboxylic acid

4.2.1.2 2-butyloctyl 5-bromothiophene-3-carboxylate (2) synthesis

The method follows the procedure of M. Zhang et. al (2014) [11]

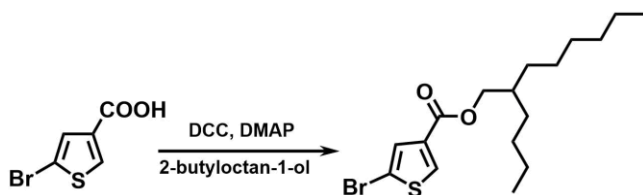


Figure 4.5 Synthesis of 2-butyloctyl 5-bromothiophene-3-carboxylate

In a 500 mL round-bottom flask with 250 mL of dichloromethane, the mixture of 5-bromothiophene-3-carboxylic acid (10.3 g, 50 mmol), DCC (6 g, 60 mmol) and DMAP (1.6 g, 17.5 mmol) was added. After dropwise addition of 2-butyloctan-1-ol (18.5 g, 100 mmol) via syringe, the mixture was left to stir for 40 h under N₂ atmosphere. The mixture was then diluted with 150 mL of DO water and extracted with DCM. After this acid-base wash with 0.1 M HCl and 0.1 M NaOH solutions was performed. The organic extracts were dried with anhydrous sodium sulphate and the solvent was removed, then it was purified by silica gel column chromatography using hexane/DCM (5:1) (Figure 4.6 (A) and (B)). Yielding pure colorless oil product of 2.3 g (12 %). ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, 1H); 7.45 (d, 1H), 4.18 (d, 2H), 1.70 (m, 1H), 1.32 (m, 16H), 0.88 (m, 6H); b.p. = >210 °C

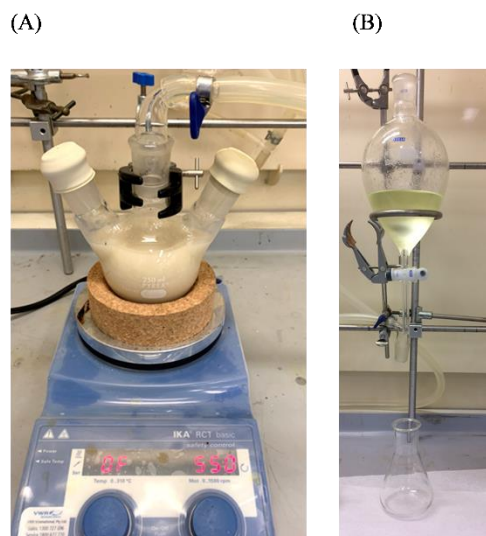


Figure 4.6 (A) Synthesis of 2-butyloctyl 5-bromothiophene-3-carboxylate; (B) Acid-base extraction of crude ester in polymer (PDCBT) production

As a result of the low yield, the purification procedure was investigated for this step. Due to low solubility of crude (0.005 g of crude per 10 mL of non-polar solvent), even small amounts of compound require large quantities of the solvent, which elevates the purification costs considering the scaling up goal. To improve yields from 12 % to 54 % of purified compound, vacuum distillation was used to decrease the costs of production. The schematic diagram of the vacuum distillation apparatus is illustrated in Figure 4.7 (A, B)

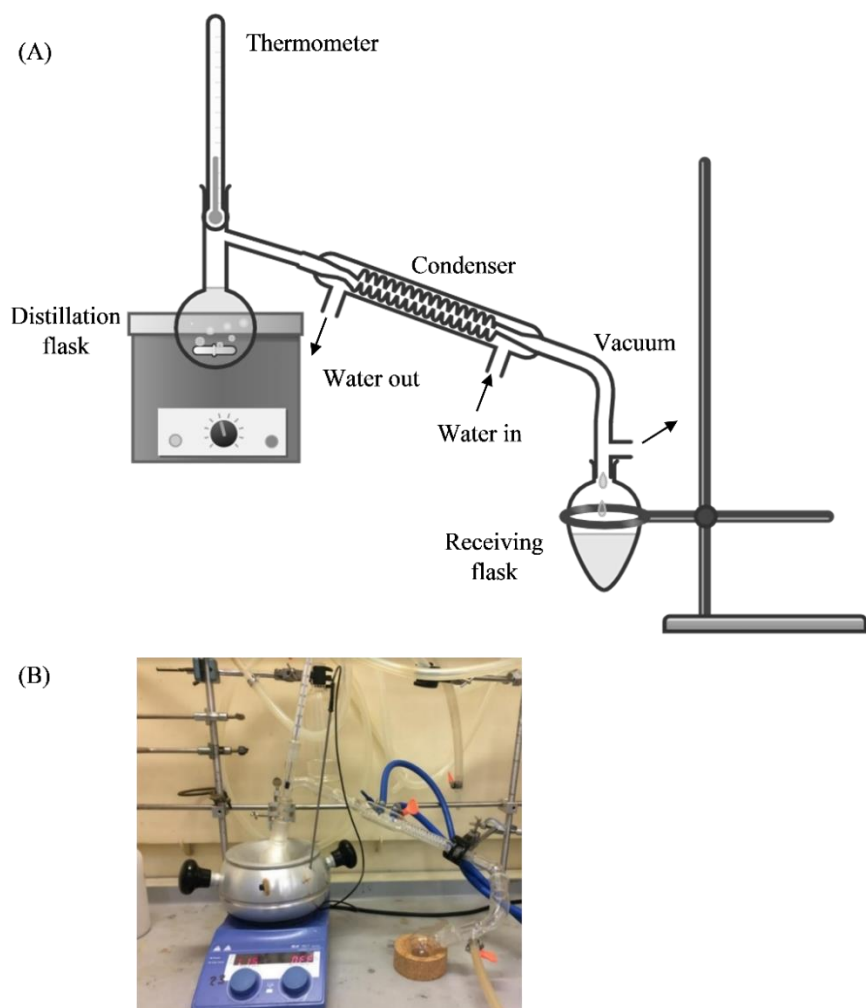


Figure 4.7 (A) Schematic of vacuum distillation apparatus; (B) vacuum distillation of the crude

Distillation method

To the mixture of 5-bromothiophene-3-carboxylic acid (5.58 g, 27 mmol), DCC (3.24 g, 32.4 mmol) and DMAP (0.86 g, 9.4 mmol) in a 250 mL round-bottom flask with 135 mL of CH_2Cl_2 was added 2-butyloctan-1-ol (9.98 g, 54 mmol). The resulting mixture was stirred for 40 hours under a nitrogen atmosphere and then diluted with 80 mL of water and extracted with dichloromethane. After removing the solvent and drying the organic extracts over sodium sulphate, the crude weight was 10 g.

The crude was loaded into a distillation flask (see Figure 4.5) to proceed with vacuum distillation purification. The synthesised ester product has a high boiling temperature of 210 °C and the residual alcohol contaminant has a boiling point of 145-149 °C. The main reason for the vacuum distillation is to prevent overheating of the liquid. Boiling commences when the vapor pressure of a liquid or solution equals the external pressure (the atmospheric pressure). Thus, if the applied pressure is reduced, the boiling point of the liquid decreases. So, the boiling temperature of the 2-butyloctan-1-ol has been reduced to 105 °C. After heating of the crude at this temperature for 3 hours, the alcohol was evaporated and collected in the receiving vessel, 3.7 g. The purified compound (6 g) contained 3.5 times lower content of contaminant alcohol according to the NMR results by integrating the individual peaks of the product and alcohol as presented in the crude (1:4), the Figure 4.8 (1) with the respective individual peaks integration characterisation after first distillation (1:0.96), shown in Figure 4.8 (2).

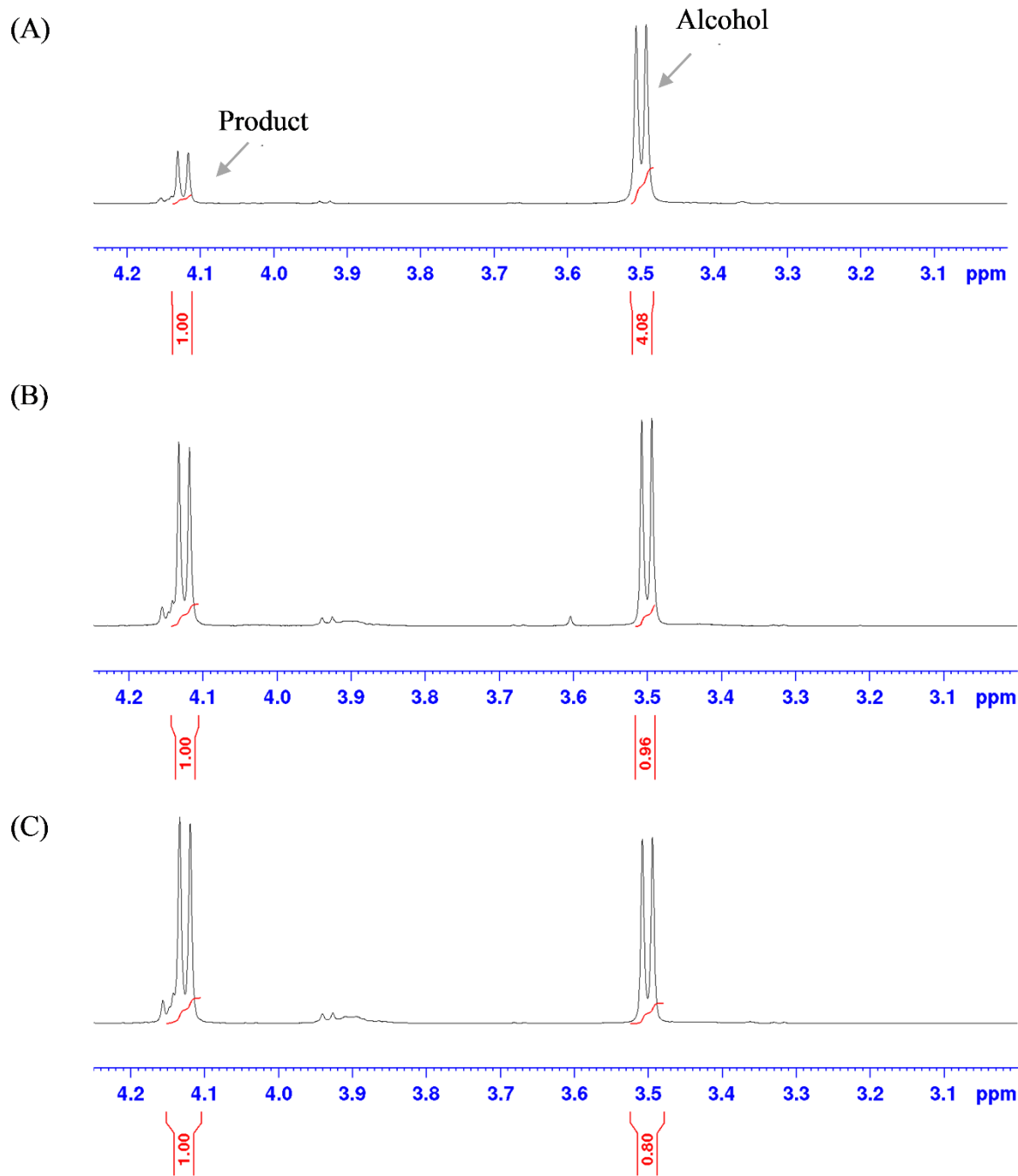
To improve the results, another distillation was applied to the distilled crude. The same procedure of vacuum distillation was used, yielding ester product (5.2 g), and the new NMR results show that product still contained residual alcohol (1:0.80) shown in Figure 4.8 (3). A third distillation process again reduced the contaminant to (1:0.76) according to the NMR analysis (Figure 4.8 (4)). 2-butyloctan-1-ol amounts collected from the distillation were 0.15 g and the product 4.8 g. A final distillation purification experiment led to the minimum obtained impurity in the ester to be (1:0.24) according to the Figure 4.8 (5).

The ester product collected was 4.04 g and trace 2-butyloctan-1-ol 0.08 g. Overall amount of the residual alcohol in 10 g of crude was 4.43 g and purified product 4.04 i.e. 40% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, 1H); 7.45 (d, 1H), 4.18 (d, 2H), 1.70 (m, 1H), 1.32 (m, 16H), 0.88 (m, 6H).

The main benefits of vacuum distillation that it leads to cleaner and less expensive purification with lower flammable solvent usage, fire hazard and it also can be applied for large amounts of crude material to be purified. However, there is a possibility that the heating during the distillation process leads to some de-esterification of the ester product and regeneration of alcohol due to trace amounts of water present.

Incorporating the distillation method into the synthesis has improved the overall yields up to 54 %. The mixture of 5-bromothiophene-3-carboxylic acid (0.52 g, 2.5 mmol), DCC (0.3 g, 3 mmol) and DMAP (0.08 g, 0.8 mmol) in a 50 mL round-bottom flask with 13 mL of dichloromethane was added 2-butyloctan-1-ol (0.93 g, 5 mmol). Resulting mixture was stirred for 40 hours under the nitrogen atmosphere and then it was diluted with 8 mL of water

and extracted with dichloromethane. After this acid-base wash with 0.1 M HCl and 0.1 M NaOH solutions was performed. The organic extracts were dried with anhydrous Na₂SO₄ and the solvent was removed. Then, crude was loaded into the 25 mL rbf with dry molecular sieves for distillation. Once, the vapor temperature reached 105 °C, the distillation process was stopped. The total distillation time was approximately 3.5 hours. After cooling down to room temperature, the crude was purified by silica gel column chromatography using hexane/DCM (5:1). Yielding pure colourless viscous oil 0.4 g (54 %). ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, 1H); 7.45 (d, 1H), 4.15 (d, 2H), 1.70 (m, 1H), 1.32 (m, 16H), 0.88 (m, 6H).



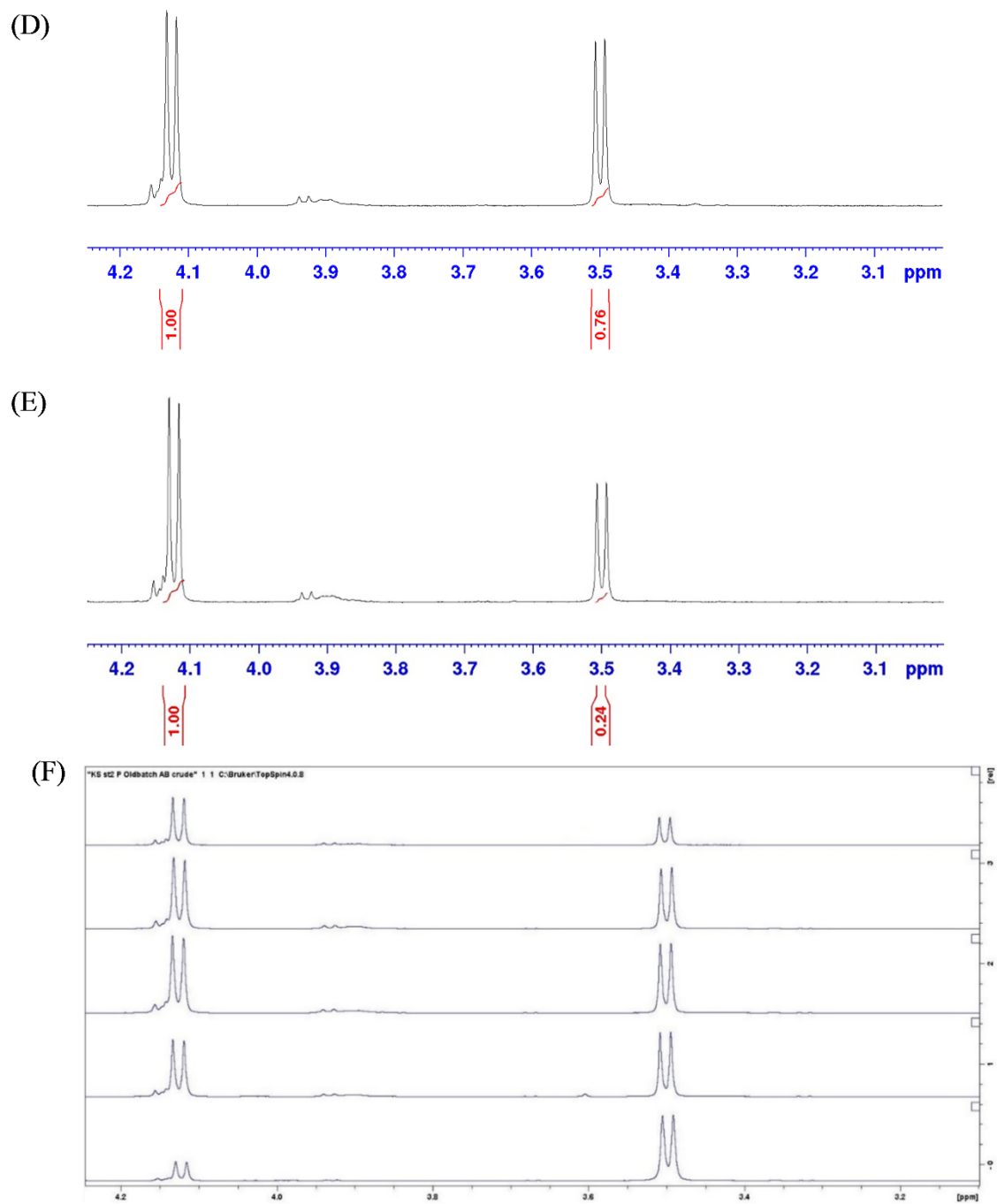


Figure 4.8 (A) Partial ^1H NMR spectra of 2-butyloctyl 5-bromothiophene-3-carboxylate, integration of the product peak at 4.15 ppm (d, 2H) and the alcohol peak at 3.5 ppm (d, 2H)

to 1:4.08 (B) first vacuum distillation of the crude (1:0.96); (C) second vacuum distillation (1:0.80); (D) third vacuum distillation (1:0.76); (E) forth vacuum distillation (1:0.24)

4.2.1.3 Bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate (3) synthesis

Method follows the procedure of M. Zhang et. al (2014) [11]

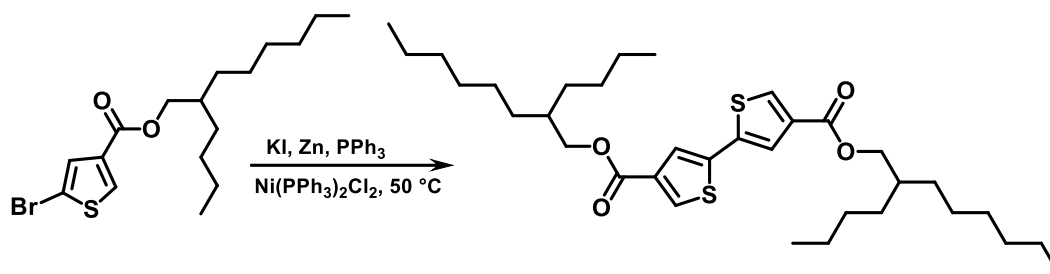


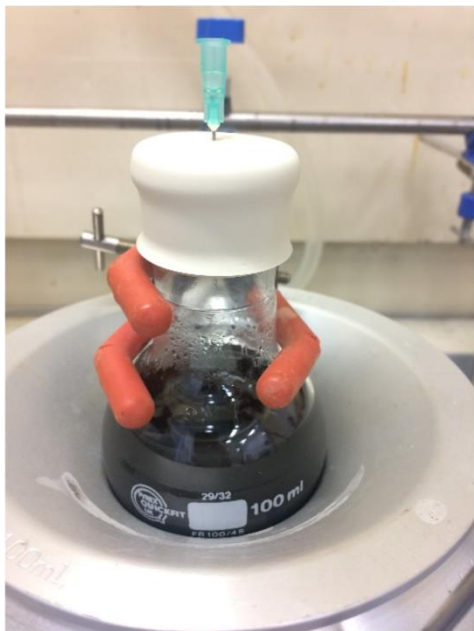
Figure 4.9 Synthesis of bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate

Following the literature procedure [11], synthesis of bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate (Figure 4.8 A, B, C) was performed on the following outlined scale.

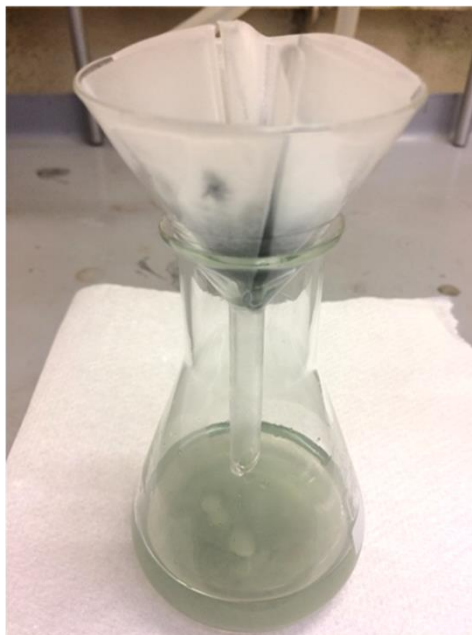
To a three-neck round bottom flask with the mixture of $\text{Ni(PPh}_3)_2\text{Cl}_2$ (1.11 g, 1.68 mmol), PPh_3 (0.89 g, 3.37 mmol), Zn powder (1.64 g, 25.3 mmol) and KI (0.06 g, 0.42 mmol) 156 mL of DMF was added under nitrogen atmosphere. The resulting mixture was quickly degassed and then stirred for 30 min at $50\text{ }^\circ\text{C}$. After addition of 2-butyloctyl 5-bromothiophene-3-carboxylate (4.22 g, 11.3 mmol) in DMF (9.4 mL), it was heated up to $80\text{ }^\circ\text{C}$ and stirred for 16 hours. The reaction then was cooled, sieved and extracted with ethyl acetate. Extracts were washed with brine, water and then purified by column chromatography using hexane/DCM (3:2) solvent ratio to afford the light-yellow oil (1.06 g, 16 % yield). ^1H

NMR (400 MHz, CDCl₃): δ 7.98 (d, 2H); 7.57 (d, 2H), 4.16 (d, 4H), 1.74 (m, 2H), 1.33 (m, 32H), 0.89 (t, 12H).

(A)



(B)



(C)

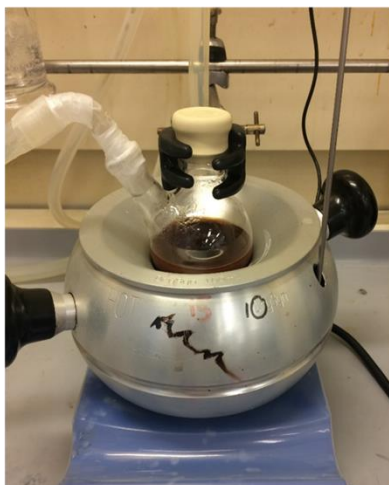


Figure 4.10 (A) synthesis of bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate; (B) sieving of filtrate during work up process; (C) colour progression from red to black upon addition of 2-butyloctyl 5-bromothiophene-3-carboxylate/compound (2)

Modified procedure

To modify the coupling method of the thiophenes and improve yields a new method is suggested, as described in reaction scheme (Figure 4.11) followed up with the improved experimental. In this experimental the amount of used zinc powder was reduced by 4 times to avoid additional filtration during work up process due to excess of unreacted zinc. Another adjustment made to the procedure was the reflux time used in the procedure. After careful analysis of starting materials and product formation by TLC method of spotting a mixture sample every 30 minutes, the reaction came to a completion at the time of 2.5 hours under reflux. As a result of these changes the improvement in yields was achieved from 16 % to 25 % yield.

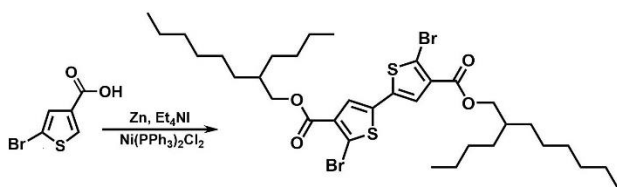


Figure 4.11 Bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate synthesis scheme

A mixture of $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ (0.293g, 0.45 mmol), Zn powder (0.440 g, 6.72 mmol) and Et_4NI (0.116 g, 0.45 mmol) tetramethylammonium iodide were added to a flask containing a stir bar, evacuated, and back-filled with nitrogen. Dry THF (11.20 mL) was added, and the

reaction mixture stirred at room temperature for 30 min. 5-bromothiophene-3-carboxylic acid (0.928 g, 4.48 mmol) was dissolved in THF (4.48 mL) and added to the flask via syringe. The resulting mixture was then heated at reflux (ca. 66 °C) with stirring for 2.5 hours. After cooling to room temperature, the mixture was filtered and washed with ethyl acetate. The filtrate was then washed with water, the organic phase dried with sodium sulfate, and the solvent was removed. Yield 290 mg, 25%. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, 2H); 7.57 (d, 2H), 4.17 (d, 4H), 1.76 (m, 2H), 1.33 (m, 32H), 0.89 (t, 12H).

4.2.1.4 Bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (4) (Monomer 1) synthesis

Method follows the procedure of M. Zhang et. al (2014) [11] Figure 4.12.

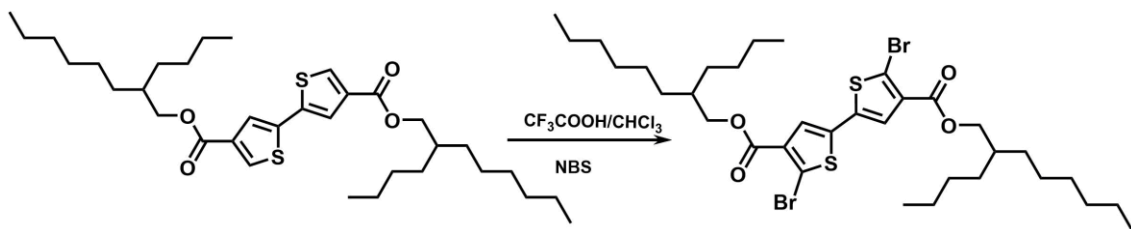


Figure 4.12 Bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate synthesis

This reaction method is consistent with the literature reports [11],[12]. To a 5 ml round bottom flask with a mixture of 2.5 mL of chloroform and 0.5 mL of trifluoroacetic acid, was added bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate (0.29 g, 0.5 mmol). NBS (0.19 g, 1.05 mmol) was added portion wise to the mixture as well, and it was then stirred for 1 hour in the dark. The extracts were washed with chloroform several times, dried and purification was performed by using column chromatography hexane/DCM (4:1). 0.190 g,

51 %. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, 2H), 7.35 (s, 2H), 4.22 (d, 4H), 1.75 (m, 2H), 1.38 (m, 32H), 0.89 (m, 12H).

4.3.2 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (Monomer 2) production

The 5,5'-bis(trimethylstannyl)-2,2'-bithiophene monomer synthesis for Stille polymerisation was prepared following the literature procedure of [13] (Figure 4.13).

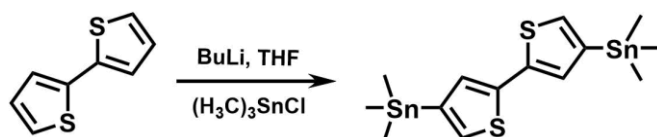


Figure 4.13 5,5'-bis(trimethylstannyl)-2,2'-bithiophene production (modified synthesis)

2,2'-bithiophene (0.036 g, 0.217 mmol) was added to a solution of anhydrous THF (5 mL). Mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and then, 0.208 g, 0.52 mmol of n-butyllithium (1.6 M in hexanes) was added slowly. It was left to stir for 2 hours. After addition of trimethyltin chloride in hexanes (0.57 mL, 0.565 mmol), the mixture was warmed up to room temperature and stirred for additional 2 hours under nitrogen atmosphere. The reaction mixture was dried to afford the crude which was taken to the next step without further purification. 0.90 g, 84 %. ^1H -NMR (400 MHz, CDCl_3): δ 7.27 (d, 2H), 7.09 (d, 2H), 0.39 (s, 18H).

4.3.2 Poly [5,5'- bis(2-butyloctyl) -(2,2'-bithiophene)-4,4'-dicarboxylate-alt- 5,5'-2,2'-bithiophene] (PDCBT) synthesis

For completing the polymer synthesis, the previously prepared monomers (bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene) (described in sections 4.2.1.4 and 4.2.2), were used for Stille polymerisation following literature procedure of M. Zhang et. al (2014) [11] Figure 4.14.

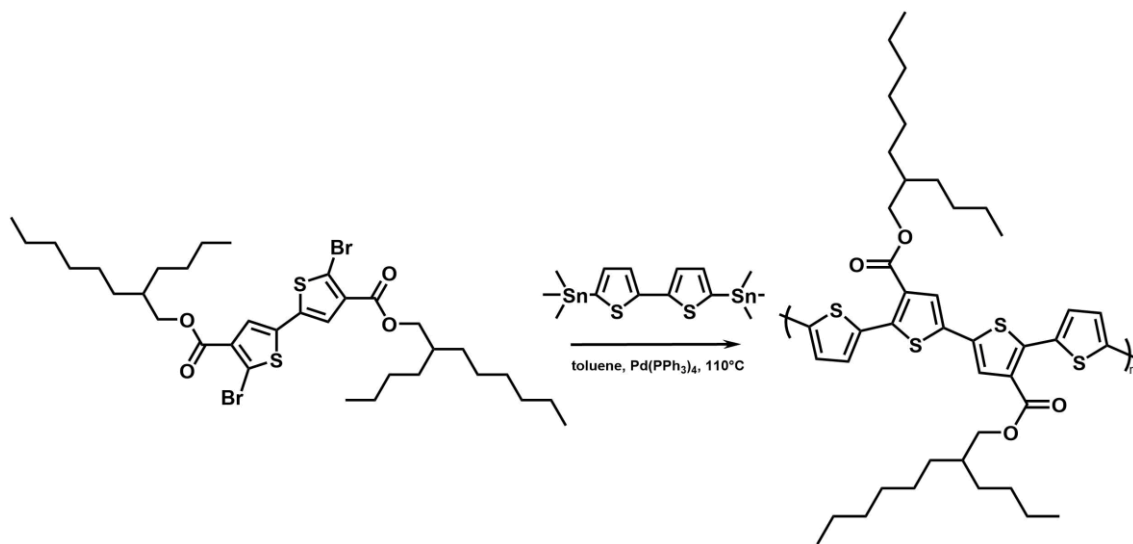


Figure 4.14 Poly [5,5'- bis(2-butyloctyl) -(2,2'-bithiophene)-4,4'-dicarboxylate-alt- 5,5'-2,2'-bithiophene] (PDCBT) synthesis.

To a 25 ml two-neck round bottom flask with 6 mL of toluene, was added bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (0.131 g, 0.2 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.086 g, 0.2 mmol). The mixture was degassed by nitrogen purge for 30 minutes. Then, Pd (PPh₃)₄ (0.011 g, 0.010 mmol) was added quickly, and the mixture was purged with nitrogen for another 20 minutes. After degassing completed,

it was refluxed over 16 hours. The reaction mixture was cooled down to room temperature, filtered into Soxhlet thimble with 120 mL of methanol and then purified by Soxhlet extraction (MeOH, hexanes, and CHCl₃). The polymer was dried under vacuum, after recovering it in a solid form from the chloroform fraction. 85 mg, 64 %. ¹H-NMR (400 MHz, CDCl₃): δ 7.58–7.45 (br, 4H), 7.19 (br, 2H), 4.21 (d, 4H), 1.75 (br, 2H), 1.30–1.28 (br, 32H), 0.89–0.86 (br, 12H) Figure 4.15.

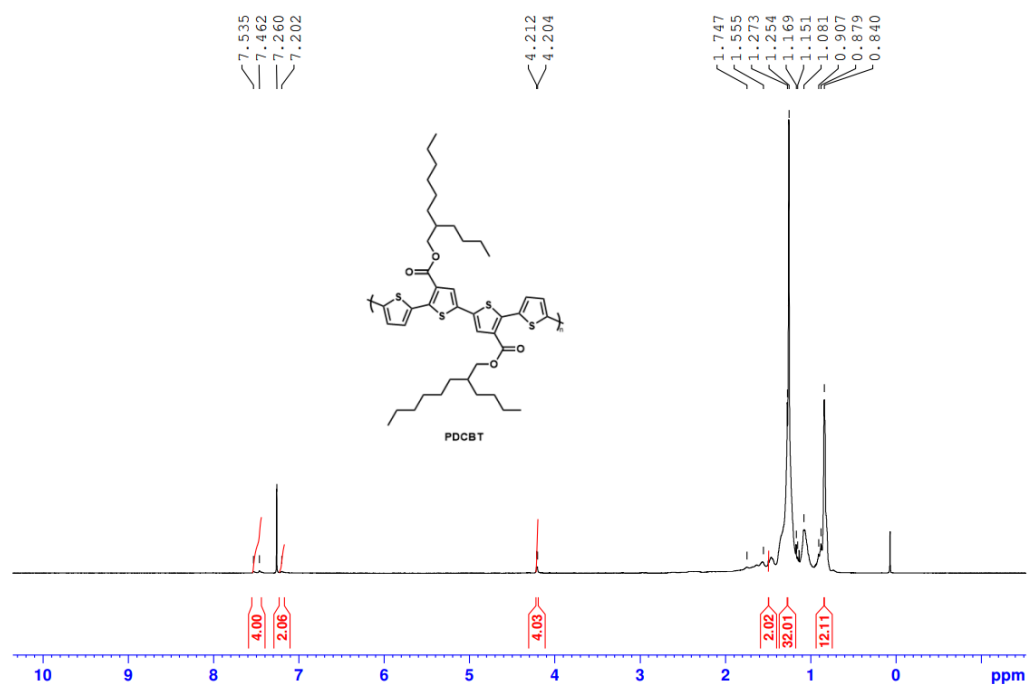


Figure 4.15 ¹H-NMR of PDCBT collected in CDCl₃, at 25 °C and 400 MHz

4.4 Overcoming high costs of purification

The most widely used purification technique for isolating pure compounds in organic chemistry is silica gel column chromatography. However, due to low solubility of the crude material in esters in the monomer 1 synthesis of PDCBT, even small-scale reactions require

large quantities of solvent, which increases cost dramatically. Also, silica gel column chromatography on a large scale is a laborious, time consuming and hazardous purification method.

In order to improve purification costs and safety in PDCBT polymer synthesis, we have modified the synthesis steps and work up methods. We have introduced recrystallisation, sublimation and distillation techniques. Successful application of distillation process for separating a mixture of chemical compounds according to their different boiling point was performed. In addition, the recrystallisation technique was considered for 5-bromothiophene-3-carboxylic acid purification, however sublimation was preferred as it proved a more efficient work up method.

4.5 Modified synthesis

Aiming towards the high yield, inexpensive and large-scale production, alternative methods have been incorporated into the synthesis of PDCBT polymer. A summary of the total modified synthesis of the PDCBT is shown in the Figure 4.16. Each step which has been changed from the published procedure [11] is demonstrated in the reaction scheme.

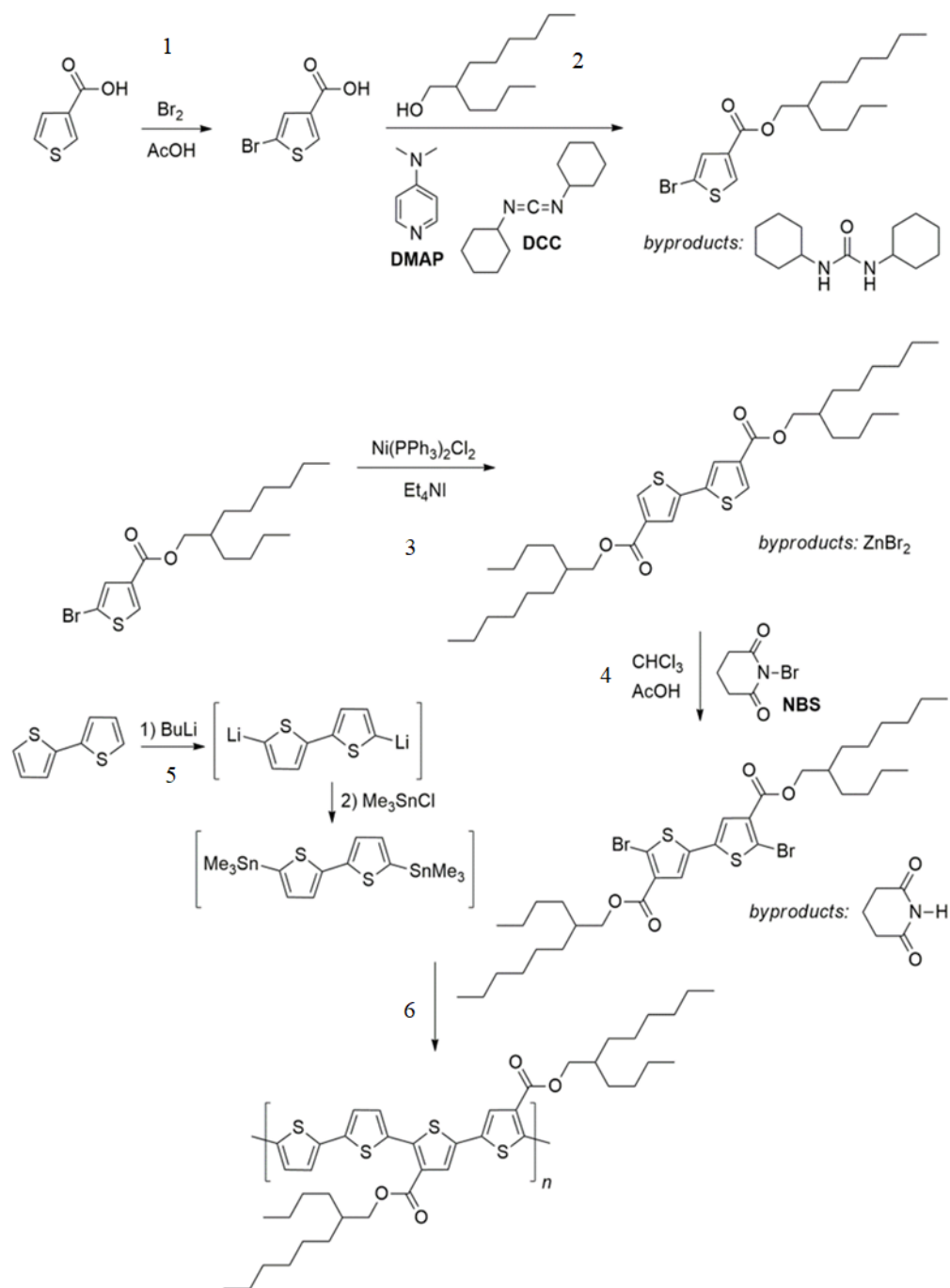


Figure 4.16 Modified synthesis of poly [5,5'- bis(2-butyloctyl) -(2,2'-bithiophene)-4,4'-dicarboxylate-alt- 5,5'-2,2'-bithiophene]; step 1 yield 97%, step 2 yield 54%, step 3 yield 25%, step 4 yield 51%, step 5 yield 84%, step 6 yield 64% (PDCBT)

4.5.1 Yield

In accordance with the published procedures of PDCBT polymer synthesis [11], we have modified the synthesis and achieved reasonably high yields with inexpensive procedures to perform the best synthesis [14]. Due to existing challenges of low solubility of the crude the purification yields were lower (40-55 %) than expected referring to the published outcomes of 76 % [11].

4.5.2 Characterisation

To characterise the morphology and chemical structure of the synthesised polymers UV-vis spectroscopy, fluorescence, TLC (chromatography), NMR and melting point determination, techniques were used. During the process of reactions, it is useful to use TLC, NMR and UV-vis spectroscopy for the characterisation of compounds synthesised and to monitor the progress of the reaction. These characterization methods for PDCBT polymer are discussed in detail in Section 4.8.2. The characteristics of PDCBT and ITIC active layer materials synthesised in this work and in-laboratory OPV device characteristics, results and discussions are introduced later in Chapter 6 of this thesis.

4.5.3 Costs and the scale up challenge

To simplify the synthesis, every step of the polymer production was analysed in terms of the cost. Firstly, the starting material; 5-bromothiophene-3-carboxylate, which costs AUD \$98.80/g from Sigma Aldrich, Australia and AUD \$4.6/g from Henan Tianfu Chemical, China was considered for synthesis in-house instead of purchased. To simplify synthesis and

reduce the cost of synthesis, we synthesised this starting material and require AUD \$1.76/g (detailed costing is shown in Table 4.1). The total for each step is detailed and summarised in the next Section 4.5 Table 4.1 for cost break down analysis. Considering basic rules regarding the large equipment, cleaning large glassware and chemicals safety measurements and disposal of unused extremely dangerous chemicals in the final stage of large synthesis must be obeyed. The challenge of mass production, in particular PDCBT's starting material, may cause potential hazards from the handling of large volumes of liquid bromine, which is a toxic, carcinogenic substance. Later in the synthesis the large-scale purification safety is a large concern, due to high flammability and toxicity of the solvents used in the silica gel chromatography technique, necessary for 3 out of 6 steps during the overall synthesis [15]. After estimating the costs of these purifications, and observing the synthesis cost increase, we have instead incorporated less expensive modified work up procedures as shown in the Table 4.1.

Overall, mass synthesis is a longer process which is more expensive. Also, it must be especially approached carefully and methodically due to potential hazards involved. In terms of safety, it is important to ensure safe procedures for personnel during the handling of multiple large-scale extractions, solvents and materials and the cleaning of large glassware where physical constraints can lead to broken glassware, that may cause lacerations or potential fire hazards [15]–[17]. Every reaction on a scale needs the right sized equipment, as it becomes hazardous due to large volumes of solvents used in extractions, quenches and rotavaping of solvent. For example, according to the disposal instructions of peroxide-forming solvents, it is critical to check peroxide levels, to avoid the fire risks [18]–[21].

Hence, these challenges increase the synthesis costs and also the cost of toxic waste disposal as well as the labour cost.

4.6 Actual cost verses theoretical cost of PDCBT polymer synthesis

After careful analysis of the costs for materials used in the synthesis of PDCBT, a summary for each step was tabulated in the Table 4.1. Each material has been upscaled to a 10 g of product scale and according to the cost for 100 g product scale (only materials used) was calculated for the 85 mg of laboratory obtained polymer. This cost is compared to the theoretical estimations of the published methods described in the Section 4.2 of this chapter. The theoretical total cost to synthesise and purify 85 mg of PDCBT came down to AUD \$5.42 and the actual cost to synthesise and purify 85 mg of PDCBT is AUD \$7.88. Consequently, the actual synthesis was approximately a third more expensive than what was predicted in theory. Costs on 100 g scale of material shows AUD \$9,269.74 in practice, compared to a theoretical value of AUD \$6,377.93 and a commercial cost of AUD 37,000.00 (i.e AUD 3,700.00/g from Ossila Ltd., UK) In particular, the silica gel chromatography purification method is not realistic for large-scale production due to safety hazards. These considerations of such high cost and dangerous procedures needs to be more investigated and improved to realise pilot scale of solar materials production.

Table 4.1 Comparing theoretical total cost to synthesise and purify PDCBT with actual cost to synthesise and purify PDCBT

STEP 1						
Paper yield and quantity of this step's product that is required for the next step	78.6 g (97 % yield)	We require 9.29 g of the product to use in Step 2	We require 92.91 g of the product to use in Step 2			
	78.60	14.43	144.33			
Scaling factor	X	0.18	1.84			
Material	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		Cost for 100 g product scale (only materials used)
thiophene-3-carboxylic acid	50.00	9.19	91.87	g		AUD 116.90
acetic acid	0.35	0.06	0.64	L		AUD 4.63
Br ₂	0.02	0.00	0.04	L		AUD 54.44
					Total for Step 1 reaction:	AUD 175.97
Work-up	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		
water	12.15	2.23	22.32	L		
					Total for Step 1 work-up:	
					Grand total for Step 1 (reaction and work-up):	AUD 175.97
STEP 2						
Paper yield and quantity of this step's product that is required for the next step	1.51 g (40 % yield)	We require 14.43 g of the product to use in Step 3	We require 144.33 g of the product to use in Step 3			
	1.51	14.43	144.33			
Scaling factor	X	9.58	95.84			
Material	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		Cost for 100 g product scale (only materials used)
5-bromothiophene-3-carboxylic acid	2.06	19.74	197.44	g		

DCC	1.2	11.50	115.01	g		AUD 90.86
DMAP	0.32	3.07	30.67	g		AUD 136.18
CH ₂ Cl ₂	0.05	0.48	4.79	L		AUD 23.96
2-butyloctan-1-ol	3.7	35.46	354.62	g		AUD 180.50
					Total for Step 2 reaction:	AUD 431.49
Work-up	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		
distillation method						Almost no cost
STEP 3						
Paper yield and quantity of this step's product that is required for the next step	1.07 g (25 % yield)	We require 17.11 g of the product to use in Step 4	We require 171.06 g of the product to use in Step 4			
	1.07	17.11	171.06			
Scaling factor	X	15.99	159.87			
Material	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		Cost for 100 g product scale (only materials used)
2-butyloctyl 5-bromothiophene-3-carboxylate	2.70	43.16	431.65	g		
Ni(PPh ₃) ₂ Cl ₂	0.71	11.35	113.51	g		AUD 565.27
PPh ₃	0.57	9.11	91.13	g		AUD 12.75
Zn powder	1.05	16.79	167.86	g		AUD 48.34
KI	0.04	0.64	6.39	g		AUD 4.60
DMF	0.11	1.69	16.95	L		AUD 209.92
					Total for Step 3 reaction:	AUD 840.89
Work-up	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		

ethyl acetate	0.64	10.23	102.32	L		AUD 798.07
water	0.64	10.23	102.32	L		
brine	0.64	10.23	102.32	L		
Na ₂ SO ₄	0.00	0.07	0.68	kg		AUD 25.24
silica gel	0.34	5.46	54.57	kg		AUD 555.48
n-hexane	1.02	16.37	163.71	L		AUD 1,350.57
dichloromethane	0.68	10.91	109.14	L		AUD 545.69
					Total for Step 3 work-up:	AUD 3,275.05
					Grand total for Step 3 (reaction and work-up):	AUD 4,115.94
STEP 4						
Paper yield and quantity of this step's product that is required for the next step	0.74 g (58 % yield)	We require 13.05 g of the product to use in the final Step	We require 130.47 g of the product to use in the final Step 6 to make 100 g of PDCBT			
	0.74	13.05	130.47			
Scaling factor	X	17.63	176.31			
Material	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		
bis(2-butyloctyl)-[2,2'-bithiophene]-4,4'-dicarboxylate (Step 3 product)	1.18	20.80	208.05	g		
chloroform	0.01	0.18	1.76	L		AUD 12.69
trifluoroacetic acid	0.00	0.04	0.35	L		AUD 244.01
N-bromosuccinimide	0.75	13.22	132.23	g		AUD 40.73
					Total for Step 4 reaction:	AUD 297.44
Work-up	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		
chloroform	0.225	3.97	39.67	L		AUD 109.09
silica gel	0.12	2.12	21.16	kg		AUD 215.37
n-hexane	0.48	8.46	84.63	L		AUD 698.19

dichloromethane	0.12	2.12	21.16	L		AUD 105.79
					Total for Step 4 work-up:	AUD 1,128.44
					Grand total for Step 4 (reaction and work-up):	AUD 1,425.88
STEP 5						
Paper yield and quantity of this step's product that is required for the next step	0.18 g (98% yield)	We require 8.58 g of the product to use in the final Step	We require 85.81 g of the product to use in the final Step 6 to make 100 g of PDCBT			
	0.18	8.58	85.81			
Scaling factor	X	47.67	476.72			
Material	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		Cost for 100 g product scale (only materials used)
5,5'-dibromo-2,2'-bithiophene	0.14	6.72	67.22	g		AUD 20.70
THF anhydrous	0.01	0.48	4.77	L		AUD 476.72
n-butyllithium 2.5M in hexane	0.00	0.02	0.20	L		AUD 169.56
trimethyltin chloride 1M in hexanes	0.00	0.05	0.54	L		AUD 1,578.38
					Total for Step 5 reaction:	AUD 2,245.36
STEP 6						
Paper yield and quantity of this step's product that is required for the next step	0.14 g (64 % yield)	10 g	100 g			
	0.14	10	100			
Scaling factor	X	71.43	714.29			

Material	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		Cost for 100 g product scale (only materials used)
bis(2-butyloctyl)-5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (Step 4 product)	0.22	16.03	160.29	g		
5,5'-bis(trimethylstannyl)-2,2'-bithiophene (Step 5 product)	0.15	10.54	105.43	g		
toluene anhydrous	0.01	0.71	7.14	L		AUD 367.86
Pd(PPh ₃) ₄	0.02	1.29	12.86	g		AUD 69.53
					Total for Step 6 reaction:	AUD 437.39
Work-up	Paper scale	10 g scale of PDCBT	100 g scale of PDCBT	Units		
Methanol	0.2	14.29	142.86	L		AUD 392.86
Methanol	0.5	1	3	L		AUD 8.25
Hexane	0.5	1	3	L		AUD 15.00
Chloroform	0.5	1	3	L		AUD 21.60
					Total for Step 6 work-up:	AUD 437.71
					Grand total for Step 6 (reaction and work-up):	AUD 875.09
Theoretical Total cost to synthesis and purify 85 mg of PDCBT =				AUD	5.42	
Actual Total cost to synthesis and purify 85 mg of PDCBT =				AUD	7.88	

4.7 ITIC synthesis and scale up

Despite high-performance contribution in organic solar cells and longer lifetime than fullerene materials, NFA synthesis is typically much more laborious and achieve only moderate reaction yields. Therefore, industrialisation of NFAs requires a more simplistic and profitable synthesis with higher yields of production. To target better organic photovoltaic implementation, reconsidering synthesis strategies and readjusting expensive purification methods is important [4]. The synthesis method for ITIC, which follows Yuze Lin et. al. [7], consists of two primary reactions as shown in Figure 4.17. Firstly, IT is lithiated and quenched with dimethylformamide (DMF) to obtain IT-CHO at 93 % yield, and then after reaction with INCN, the ITIC compound is synthesised [7].

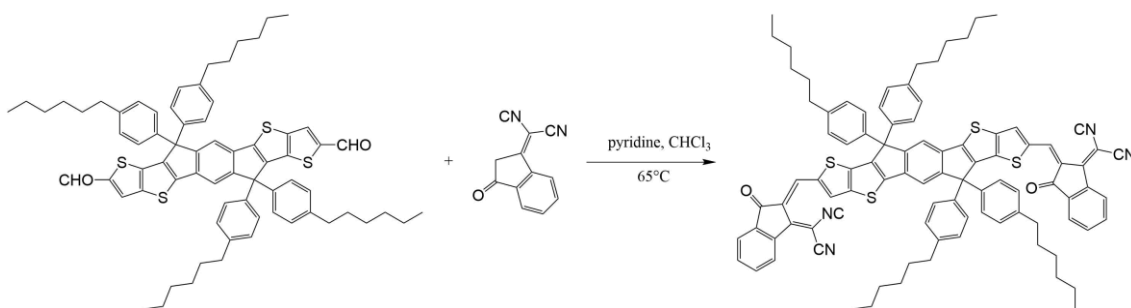


Figure 4.17 Synthesis route to synthesise ITIC

4.7.1 2,5-dithieno[3,2-b] thien-2-yl-1,4- benzenedicarboxylic acid-1,4-diethyl ester (1) synthesis

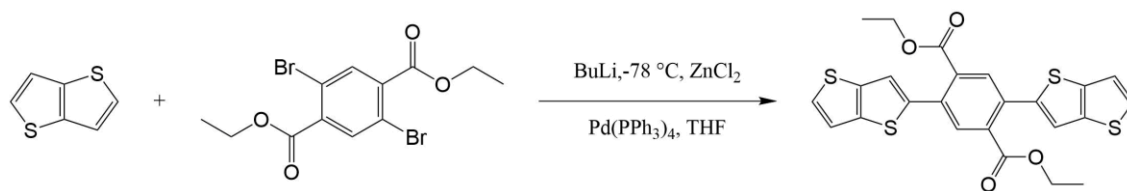


Figure 4.18 Synthesis of 2,5-dithieno[3,2-b] thien-2-yl-1,4- benzenedicarboxylic acid-1,4-diethyl ester

The method (Figure 4.18) follows Yun-Xiang Xu et. al. [22], with modification to the work up method. We performed recrystallisation instead of the silica gel column chromatography for improving costs and simplicity of crude purification. To a three-neck round bottom flask with a solution of thieno[3,2-b]thiophene (1.02 g, 7.3 mmol) in anhydrous THF (24 mL) was added slowly a 2.5 M solution of n-butyllithium in hexane (3 mL, 7.3 mmol) at -78 °C under nitrogen atmosphere. The reaction mixture was left to stir for 30 min at -78 °C and then warmed up to -34 °C to stir for an extra 15 min. Dry zinc chloride (0.99 g, 7.3 mmol) was dissolved in anhydrous THF (24 mL) and added to the solution, which was then stirred for 1 h at 0 °C. Then, diethyl 2,5-dibromoterephthalate (1.10 g, 2.90 mmol) and Pd(PPh₃)₄ (167 mg, 0.15 mmol) were subsequently added and the resulting mixture was refluxed for 20 h (Figure 4.19). Once, the reaction was finished, the mixture was filtered, extracted with ethyl acetate and solvent was removed after drying over sodium sulfate. The crude was recrystallised (Figure 4.20) from a mixture of hexane and ethyl acetate (1:1), to yield a pale-yellow solid product (1.03 g, 71%). ¹H-NMR (400 MHz, CDCl₃, δ) 7.89 (s, 2H), 7.38 (d, J = 5.4 Hz, 2H), 7.30 (s, 2H), 7.28 (d, J = 5.4 Hz, 2H), 4.27 (q, J=7.2 Hz, 4H), 1.11 (t, J= 7.2 Hz, 6H). ¹³C-NMR (125 MHz, CDCl₃, δ) 167.4, 142.0, 139.9, 139.3, 134.1, 133.8, 132.1, 127.4, 119.4, 119.3, 61.8, 13.8.

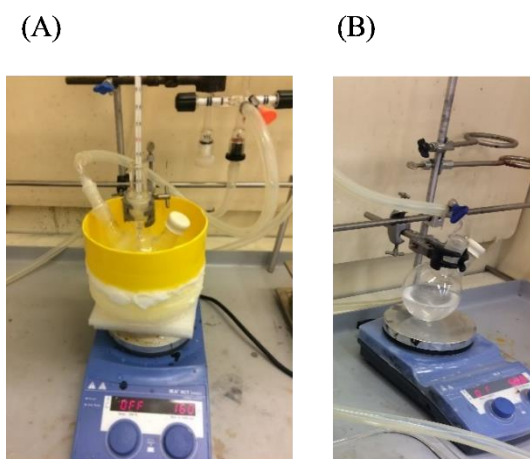


Figure 4.19 (A) solution prepared from thieno[3,2-b]thiophene in THF and added n-butyllithium in hexane; (B) a solution of zinc chloride dissolved in THF solvent

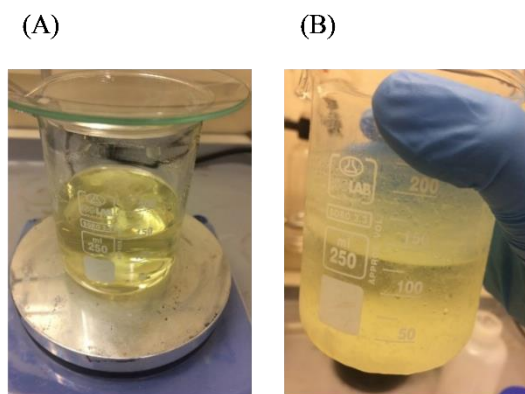


Figure 4.20 (A) and (B) recrystallisation technique

4.7.2 6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydro-dithieno[2,3-d:2', 3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (2) synthesis

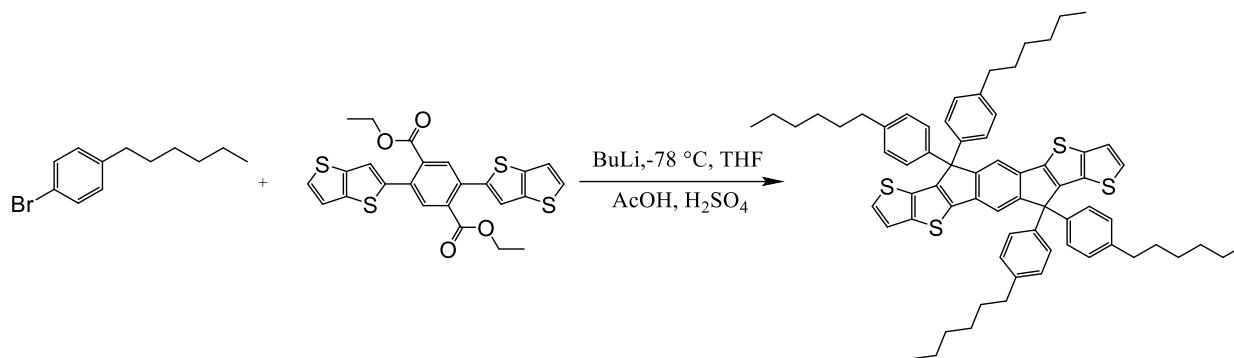


Figure 4.21 Synthesis of IT

The procedure is from a paper by Yun-Xiang Xu et. al. [6] (Figure 4.21). The method, was reproduced (Figure 4.22): n-BuLi (1.4 mL, 3.9 mmol, 2.5 M in hexane) was gradually added to a solution of 4-hexyl-1-bromobenzene (930 mg, 3.9 mmol) in 10 mL of dry THF at -78 °C. This mixture was stirred at -78 °C for 1 hour. Then, 2,5-dithieno[3,2-b]thien-2-yl-1,4-benzenedicarboxylic acid-1,4-diethyl ester (400 mg, 0.80 mmol) dissolved in 10 mL of THF and added slowly to the mixture, which was left stirring overnight at room temperature. The mixture was poured into water and extracted with ethyl acetate twice, dried with sodium sulfate and then solvent was removed. The resulting crude was refluxed with 20 mL of acetic and 0.4 mL of sulfuric acid for 3 hours at 130 °C. After extraction of the crude three times with ethyl acetate and drying over sodium sulfate (drying agent), a rotary evaporator was used to remove solvent. The resulting crude was purified by silica gel column chromatography using a mixture of hexane/dichloromethane (5:1) solvents to give a pale-yellow solid (114 mg, 14%). ¹H-NMR (400 MHz, CDCl₃, δ) 7.51 (s, 2H), 7.28 (d, J = 5.1 Hz, 2H), 7.25 (d, J = 5.1 Hz, 2H), 7.19 (d, J = 8.4 Hz, 8H), 7.07 (d, J = 8.4 Hz, 8H), 2.55 (t,

$J = 7.8$ Hz, 8H), 1.60-1.51 (m, 8H), 1.34 – 1.29 (m, 24H), 0.86 (t, $J = 6.3$ Hz, 12H). ^{13}C -NMR (125 MHz, CDCl_3 , δ) 153.2, 145.9, 143.2, 141.7, 141.6, 140.3, 136.1, 133.8, 128.4, 128.1, 126.3, 120.3, 116.9, 62.9, 35.6, 31.7, 31.2, 29.2, 22.6, 14.1.

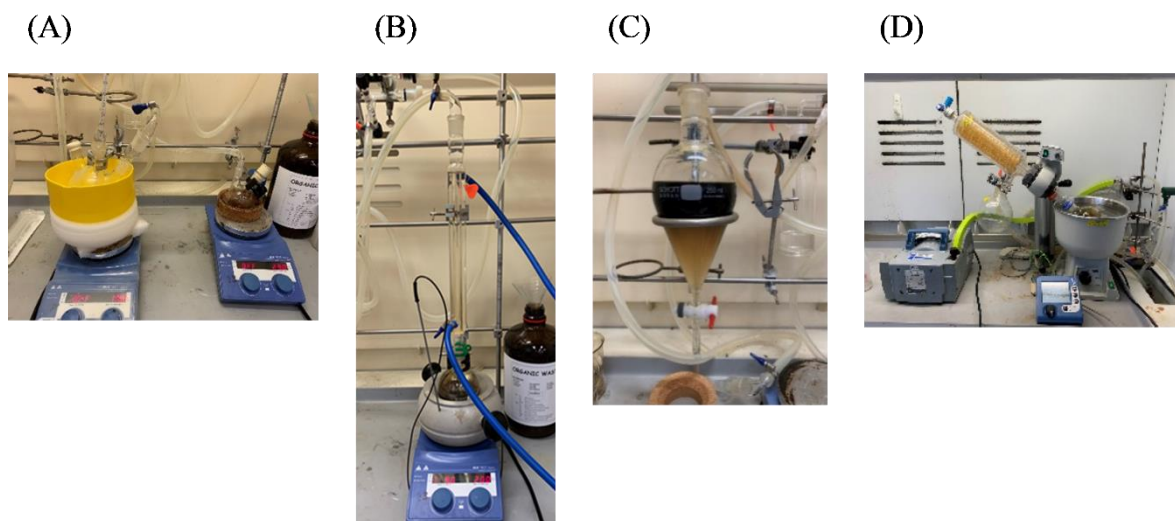


Figure 4.22 (A) a solution prepared from 4-hexyl-1-bromobenzene in THF and added *n*-butyllithium in hexane; (B) the solution refluxed with 20 mL of acetic and 0.4 mL of sulfuric acids for 3 hours at 130 °C; (C) extraction with ethyl acetate; (D) solvent evaporation after extraction in the mixture.

Modified procedure

Due to low solubility of the crude and poor column recovery (~25 %) the silica gel chromatography yield was only 114 mg, 14 %. Hence, the alternative method for purification of the crude was considered and silica gel purification method was substituted with recrystallisation. The crude was dissolved in 11.3 mL of ethyl acetate at 150 °C and adding 45.3 mL of hexane resulted in a precipitate which was then filtered. The yield was 163 mg,

20 %, which is higher than purification by column, however the process of recrystallisation had to be repeated twice in order to achieve the same high purity of the product as the silica gel column chromatography. This makes the process laborious, and preferred method for the purification remained as the column chromatography, however further exploration of recrystallisation for this step is warranted when larger scales are used.

4.7.3 6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene-2,8-dicarboxaldehyde (3) synthesis

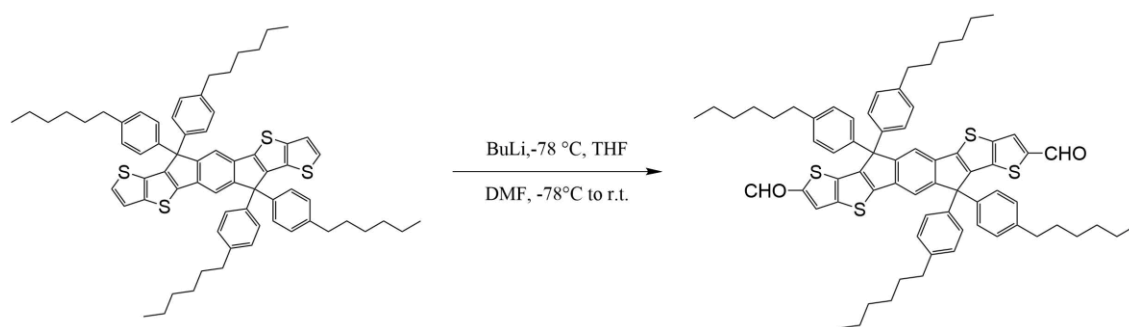


Figure 4.23 Synthesis of 3 6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene-2,8-dicarboxaldehyde

The Yun-Xiang Xu et. al. [6] procedure for the synthesis of IT-CHO (IT), was reproduced without any modifications (Figure 4.23): To IT (215 mg, 0.22 mmol) in a dry round bottom 3 neck flask, under the nitrogen atmosphere, was added 25 mL of anhydrous THF and the solution was deoxygenated with nitrogen for 30 minutes. Next, n-butyllithium (2.5 M in hexane, 0.20 mL, 0.51 mmol) was injected dropwise at -78°C and the mixture was kept at -78°C for 1 hour. Subsequently, anhydrous DMF (0.04 mL) was added. The resulting mixture was warmed to room temperature and then stirred overnight. The resultant mixture was

worked up with chloroform (54 mL) and brine (27 mL) extraction twice and the organic layer was dried over MgSO_4 (Figure 4.4 (A) and (B)). Once filtered, the solvent was removed, and the crude was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:1) as eluent to yield a yellow coloured solid. (201 mg, 87 %). ^1H -NMR (400 MHz, CDCl_3): δ 9.89 (s, 2H), 7.94 (s, 2H), 7.62 (s, 2H), 7.16 (d, J = 8.4 Hz, 8H), 7.11 (d, J = 8.4 Hz, 8H), 2.58 (t, J = 7.6 Hz, 8H), 1.66 (m, 8 H), 1.31 (m, 24H), 0.89 (m, 12 H). ^{13}C -NMR (100 MHz, CDCl_3): δ 182.89, 154.61, 149.50, 146.65, 144.40, 142.35, 141.77, 140.21, 139.21, 136.49, 129.86, 128.74, 118.03, 63.14, 35.58, 31.69, 31.27, 29.18, 22.56, 14.11.

4.7.4 2-(3-oxo-indan-1-ylidene)-malononitrile (4) synthesis

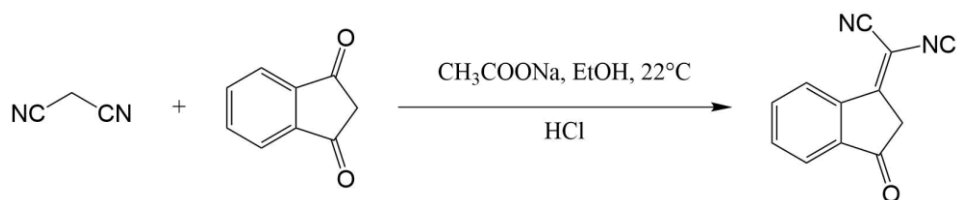


Figure 4.24 Synthesis of 2-(3-oxo-indan-1-ylidene)-malononitrile

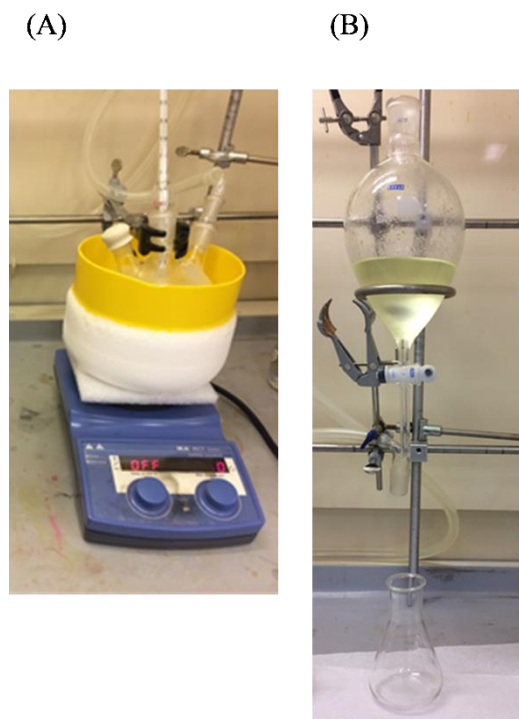


Figure 4.25 (A) Preparation of reaction mixture; (B) extraction with chloroform

Our synthesis method (Figure 4.25) reproduces Kasali A. Bello et. al. on a larger scale. Dry sodium acetate (3.2 g, 39.01 mmol) was added at 22 °C to a mixture of indane-1,3-dione (4.38 g, 29.97 mmol), malononitrile (3.96 g, 59.95 mmol) and ethanol (50 mL). Once the solid was slowly dissolved in the mixture a dark red coloration rapidly developed (Figure 4.26). The mixture was left to stir for 45 minutes. 100 mL of water was added, and the mixture acidified by 36 mL of 10 M hydrochloric acid to reach a pH between 1-2. Once acidified, the solution was stirred for an extra 10 minutes. The mixture was then filtered (Figure 4.27 (A)) and washed thoroughly with water several times, and the resultant crude was recrystallised twice from acetic acid. As shown in Figure 4.27 (B), the first recrystallisation was performed from 500 mL of water and 250 mL of acetic acid and the second from 500 mL of water and 100 mL of acetic acid) to obtain 2-(3-oxo-indan-1-ylidene)-malononitrile (3.49 g, 60 %), ^1H -

NMR (400 MHz, C_6D_6): δ 2.90 (s, 2H), 7.23 (m, 2H), 7.75 (m, 1H), 8.50 (m, 1H). ^{13}C -NMR (400 MHz, C_6D_6): δ 33.4, 83.6, 108.0, 108.7, 123.9, 130.0, 163.5, 195.6; m.p. 229 °C.

The main reason of the lower yields of this step may be due to the recrystallisation efficiency, which was cooled enough to reproduce the paper yield. Further optimisation of this recrystallisation method is required in order to achieve better yields.

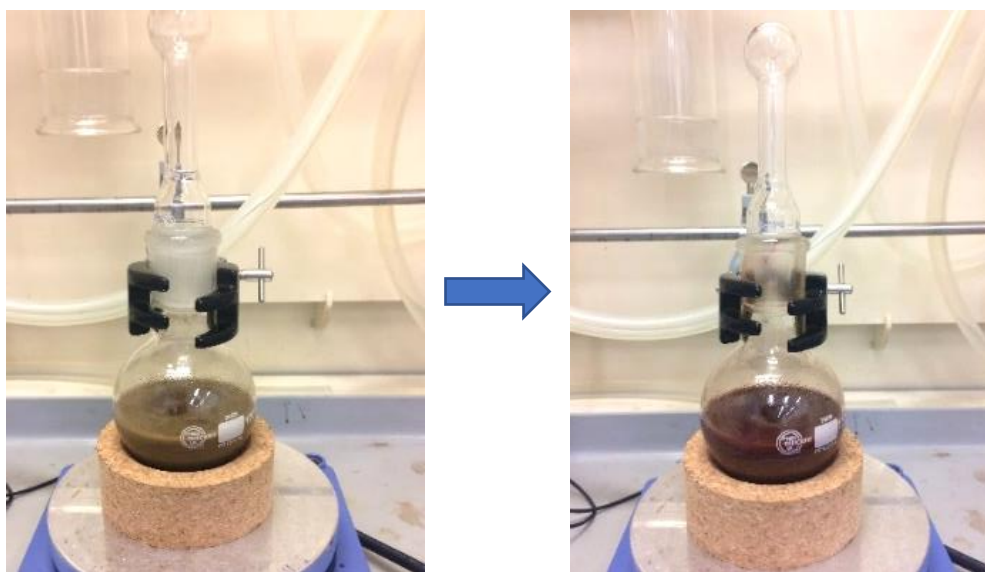
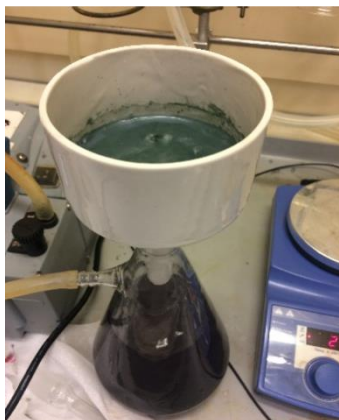


Figure 4.26 Immediate red coloration after addition of anhydrous sodium acetate from left to right

(A)



(B)



Figure 4.27 (A) vacuum filtration of the acidified suspension; (B) recrystallisation of the crude

4.7.5 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) synthesis

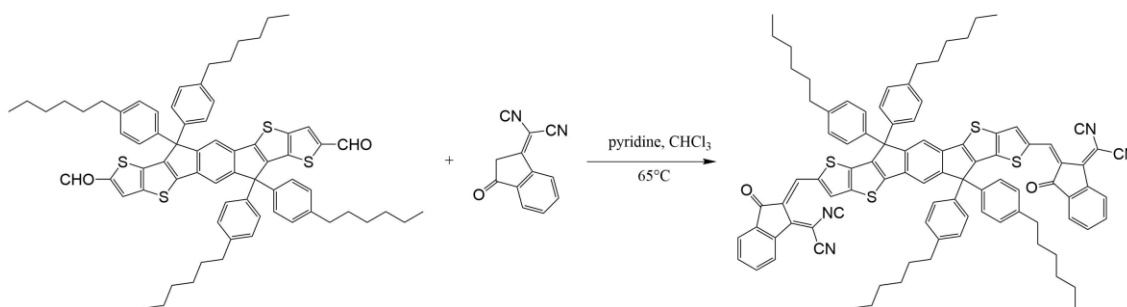


Figure 4.28 ITIC synthesis

The final ITIC synthesis method follows Yun-Xiang Xu et. al. [6] (Figure 4.28).

The Yun-Xiang Xu et. al. [6] procedure was reproduced successfully on a similar scale (Figure 4.28). IT-CHO (200 mg, 0.19 mmol) and 1,1-dicyanomethylene-3-indanone (281 mg, 1.4 mmol) were dissolved in a mixture of chloroform (50 mL) and pyridine (1 mL) and deoxygenated with nitrogen for 45 minutes. After 24 h of reflux under nitrogen, this mixture was poured into methanol (200 mL) and then filtered. The crude product was purified by silica gel column chromatography, using petroleum ether/dichloromethane (1:1), yielding a dark blue colored solid (55 mg, 20 %) ¹H-NMR (400 MHz, CDCl₃): δ) 8.87 (s, 2H), 8.70 (d, J = 7.6 Hz, 2H), 8.22 (s, 2H), 7.93 (d, J=6.4 Hz, 2H), 7.79 (m, 4H), 7.63 (s, 2H), 7.23 (d, J= 8.4 Hz, 8H), 7.15 (d, J=8.4 Hz, 8H), 2.58 (m, 8H), 1.61 (m, 8H), 1.33 (m, 24H), 0.87 (m, 12H). ¹³C-NMR (400 MHz, CDCl₃): δ) 187.19, 161.33, 155.35, 152.86, 147.61, 147.06, 143.64, 142.51, 140.02, 139.60, 138.94, 138.24, 136.95, 136.86, 135.19, 133.49, 128.87, 127.99, 125.32, 123.76, 122.73, 118.53, 114.63, 114.57, 70.38, 63.24, 35.61, 31.70, 31.27, 29.20, 21.59, 14.10.

For the final step of ITIC synthesis, the method of purification was first substituted with recrystallisation (Figure 4.29). 30 mg of crude was dissolved in 1:5 dichloromethane: petroleum ether for 30 min at 60 °C and 20 mg of purified product was collected upon cooling. The total recrystallisation recovery yield was 67 %, however the resulting product still contained impurities (mostly, residual 1,1-dicyanomethylene-3-indanone) so column chromatography was subsequently performed (with 83 % column recovery). Hence, this chosen method overall purified 154 mg of crude with a recovery of 55 mg, 20 % (Figure 4.30 (A)-(F)). An NMR of purified ITIC is shown in Figure 4.31.

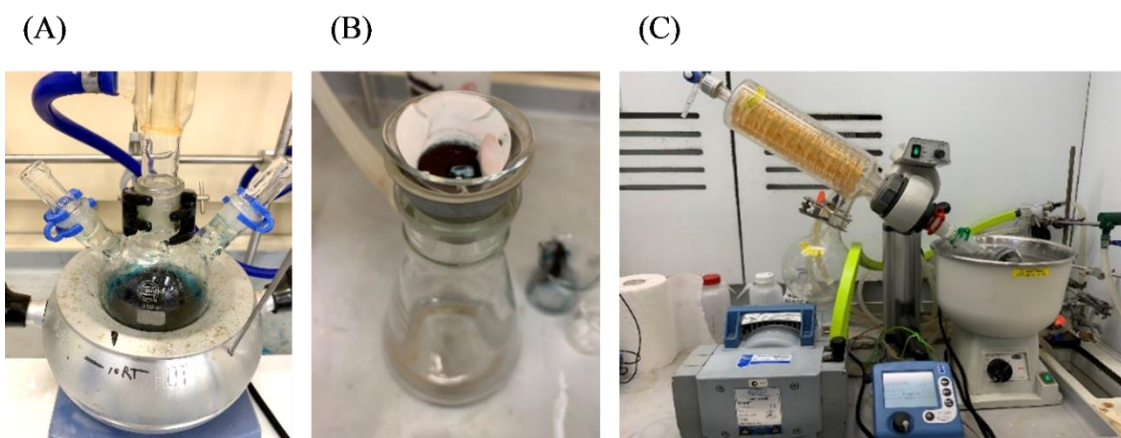


Figure 4.29 Synthesis of ITIC (A) reflux of the reaction mixture; (B) filtration of the crude; (C) rotary evaporation process for solvent removal

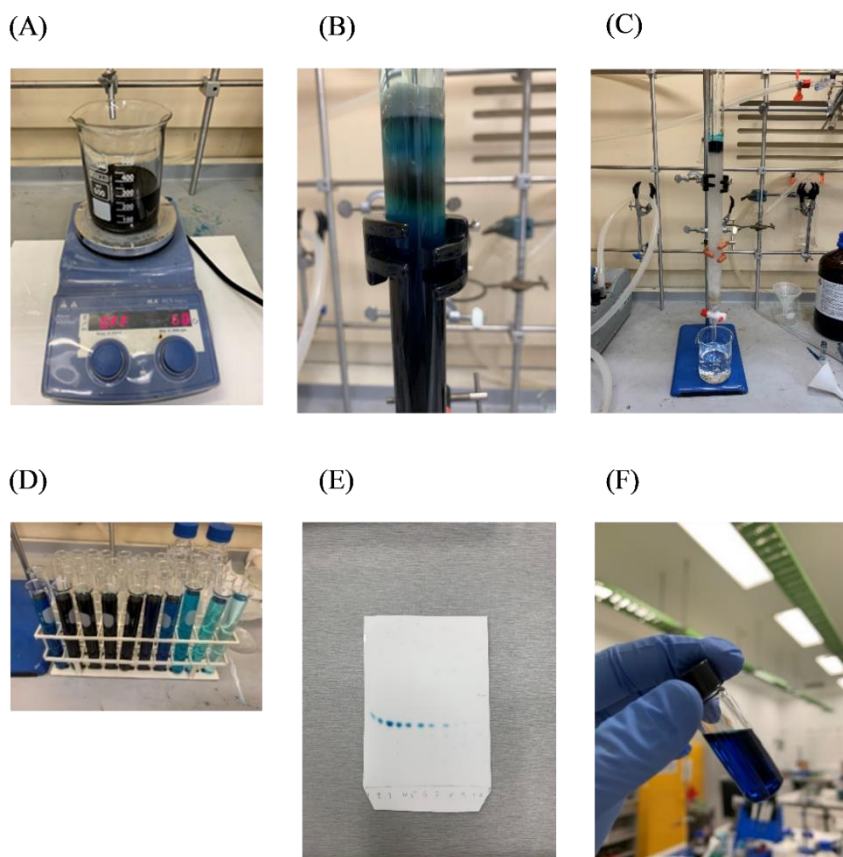


Figure 4.30 (A) recrystallisation of the crude; (B, C, D) column chromatography; (E, F) thin layer chromatography technique during the silica gel column purification

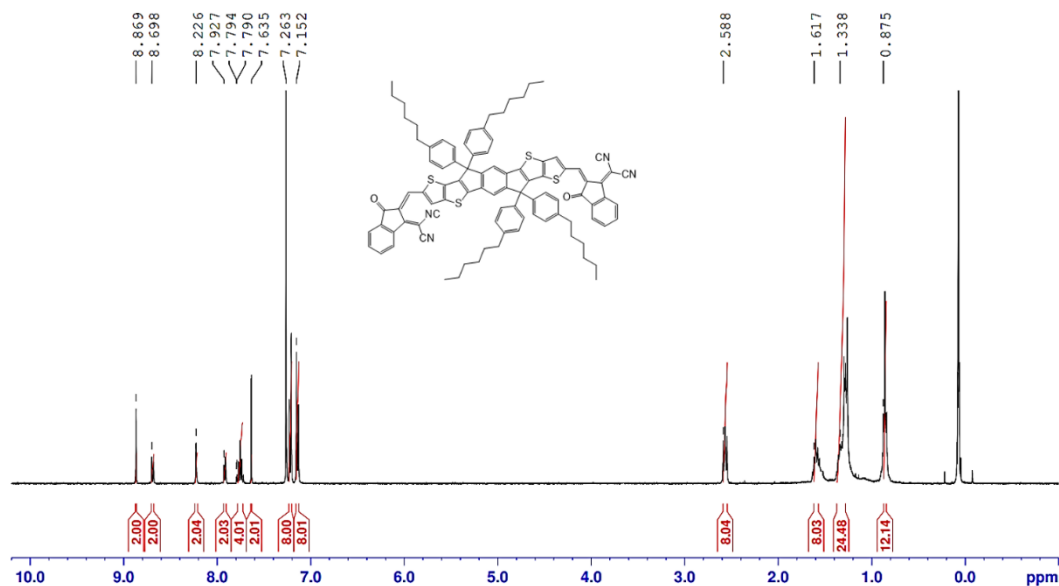


Figure 4.31 ¹H-NMR spectra of purified ITIC compound

4.8 Overcoming high costs of purification

Successful simplification of the ITIC small molecule acceptor molecule work up has been achieved in the overall synthesis route. The main issue encountered during column purifications, was the low solubility of the crude materials, that required large quantities of solvent (> 2 L) to clean up only small amounts (< 50 mg) of crude. This issue increases the silica gel chromatography purification cost drastically and hinders commercially viable scaleup. Therefore, recrystallisation as a preferred inexpensive work up procedure was

performed to purify the doubly coupled product (step 1, ITIC), synthesised by Pd-catalyzed coupling between diethyl 2,5-dibromoterephthalate with 2-thienothieryl zinc chloride (generated in situ through transmetalation of 2-thienothieryl lithium with ZnCl_2) to afford in 71 % yield.

Firstly, to simplify purification of the starting material for the synthesis of IT – one of the components in the ITIC production route, recrystallisation using various solvents (dichloromethane, hexanes, ethyl acetate etc.) was tested. This technique was improved by purifying 250 mg of crude. The crude was solubilised in 187.5 mL of hexane: ethyl acetate (1.5:1), and 122 mg, 49% of pure product was recovered.

Next, to improve the recrystallisation, the solvent system for recrystallisation was modified to increase obtained yield. For 360 mg of crude in 70 ml of hexane: ethyl acetate ratio (1:1), the recovered yield was 250 mg, 69%. This optimised ratio of hexane: ethyl acetate solvents, was repeated on a larger scale. 1.453 g of crude was dissolved in 270ml of hexane: ethyl acetate ratio (1:1), with a recovered yield of 1.03 g, 71%. Once, recrystallisation efficiency was improved up to 71 % from initial 49 %, it was chosen as a viable alternative method of work up instead of the expensive column chromatography technique particularly for this reaction step (step 1). This work also highlights the fact that recovery from recrystallisation methods tends to increase as the scale of recrystallisation increases, making this method even more promising for commercial scaleup of the ITIC synthesis.

To conclude, it is important to complete a detailed analysis of each reaction step to overcome the high cost of purification methods. The most widely used and investigated purification

techniques instead of silica gel column are recrystallisation, sublimation and distillation techniques. Successful application of recrystallisation processes was performed for the starting compound. Additionally, recrystallization was investigated for the IT synthesis (step 2), as shown in Figure 4.32. 10 mL of ethyl acetate:hexane (1:4) solvent ratio was used to dissolve 150 mg of crude to yield 9 mg, 6% of product. Therefore, silica gel purification was preferred (14 % column yield, instead of 6 % for recrystallisation method) due to being proved as a more efficient work up method. Overall, these adjustments to the procedures decreased the cost of the overall ITIC production (as discussed further in Section 5.5).



Figure 4.32 Recrystallisation of IT crude

In general, in order to overcome the high costs of purification procedures throughout the synthesis of ITIC small molecular compound, recrystallisation as an efficient substitutional method was identified effectively. It is suggested, to have further detailed research for each reaction step of ITIC, to approach simpler, less expensive, safe large-scale procedures, with alternative purifications, which may perfect it from industrial and economic point of view.

4.9 Modified synthesis

The major modifications in the synthesis are the starting material production (step 1) where instead of starting from the IT compound, we synthesise it from 2,5-dithieno[3,2-b]thien-2-yl-1,4-benzenedicarboxylic acid-1,4-diethyl ester and 1-bromo-4-hexylbenzene and 2-(3-oxo-indan-1-ylidene)-malononitrile (step 4) i.e. the synthesis of intermediate component for ITIC production. For a viable, high yield, large-scale synthesis, alternative work up methods have been incorporated into the synthesis of ITIC (section 4.6). The summary of the total modified synthesis of the ITIC is shown in the reaction scheme in Figure 4.33.

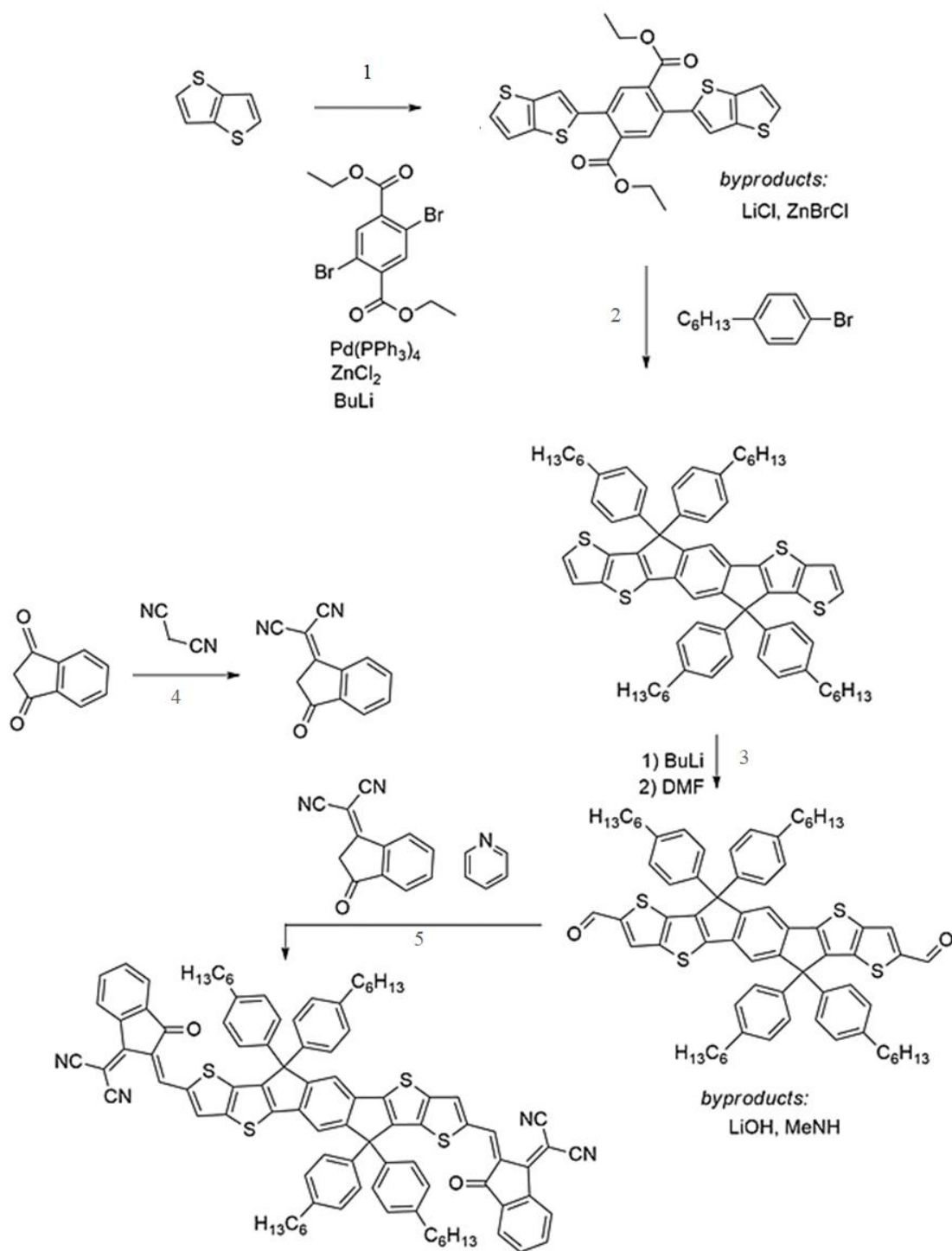


Figure 4.33 Modified ITIC synthesis (step 1 yield 71%, step 2 yield 14%, step 3 yield 87%, step 4 yield 60%, step 5 yield 20%)

4.9.1 Yield

The main issues encountered in the synthesis of ITIC was column purifications and the low solubility of crude, which needs large volumes of solvents (> 2.5 L) to clean up only small amounts (< 30 mg) of crude. To achieve the best results for each reaction step, various purification techniques were studied, and the yields were in accordance to the published results for various reactions. However due to low solubility of crude and poor column recoveries the yields were (25-30 %) lower than the published results [7], [22]–[24].

4.9.2 Characterisation

The ITIC and intermediate materials were characterized by UV-Vis and fluorescence spectroscopy, TLC (thin layer chromatography), NMR and melting point determination techniques. All the compounds for ITC synthesis, were characterised by ^1H -NMR and ^{13}C -NMR and compared to existing literature spectra.

For detecting impurities NMR spectroscopy is the best technique, also as alternative, TLC can be applied for monitoring reaction completion or impurity detection. During reactions, it is handy to use TLC (Figure 4.34, 4.35) and NMR (Figure 4.31) to monitor reaction completion. Once, compounds are synthesised, UV-vis and fluorescence spectra can be measured. Typical TLC characterisation was used for step 2 (IT synthesis) reaction monitoring as demonstrated in Figure 4.34. At the beginning of reaction, the spot of the starting material can be observed, then after 1 hour, 3 hours, 4 hours and overnight time the progress of formation product is shown. After overnight time, due to all starting material spot

disappearance, we can conclude that the reaction reached completion based on these results from the TLC plates.

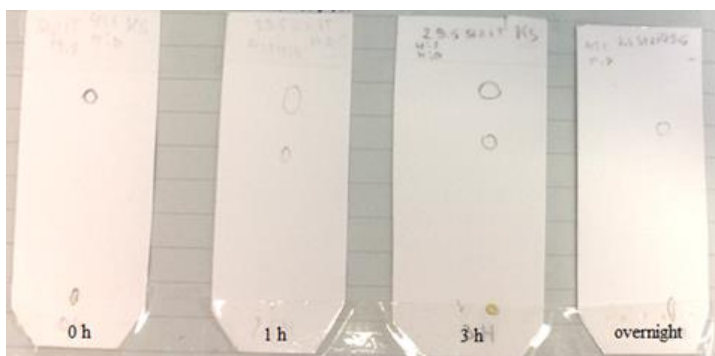


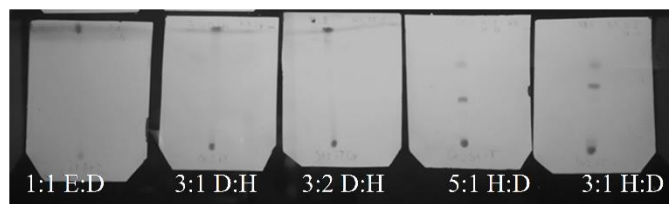
Figure 4.34 Step 2 – IT synthesis reaction has been monitored by TLC. At beginning of r-n, after 1 hour, 3 hours, and overnight time.

Another means to utilize TLC is for determination of the best solvent ratio solvent and during the column chromatography for selecting fractions containing the desired product for the next characterization step – NMR.

(A)



(B)



(C)

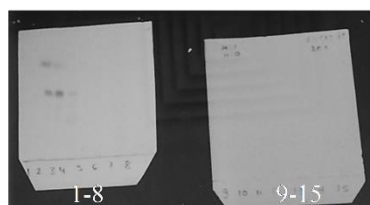


Figure 4.35 (A) and (B) solvent ratio determination for the IT crude material (the best solvent ratio is 5:1 hexane:dichloromethane); (C) column chromatography TLC spots of fractions collected 1-15.



Figure 4.36 Melting point apparatus for 2-(3-oxo-indan-1-ylidene)-malononitrile (step 4) characterisation

As shown in Figure 4.37, UV-visible studies of ITIC show an absorption maximum and edge at 608 nm and 650 nm, in contrast to PDCBT absorption spectra with similar wide absorption spectrum of P3HT from 450-650 nm. The solutions of P3HT, PDCBT and ITIC samples were typically diluted with chloroform or chlorobenzene solvent, with concentration 1×10^{-6} M. Corresponding to their complementary spectroscopic profiles, the maximum absorption peak agrees with the electronic transitions occurring in HOMO and LUMO levels [25].

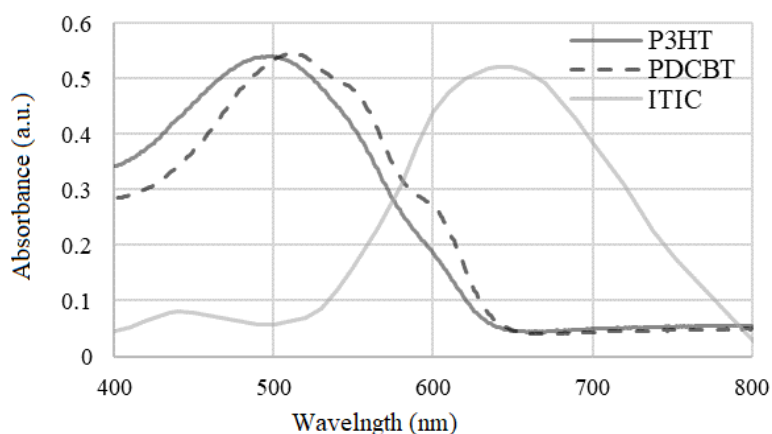


Figure 4.37 UV-vis absorption spectra of P3HT solution (dotted line); PDCBT solution (dashed line) and ITIC solution (solid line)

Photoluminescence (PL) spectra of each component was measured individually. With excitation at 450 nm and 600 nm (Figure 5.19 (A)), broad PDCBT emission is at 650 nm and 700 nm and ITIC emission at 720-840 nm. The non-radiative energy of ITIC [4], [26]–[29] aids generation of additional ITIC excitons. As shown in Figure 4.38 (B), this allows efficient

donor acceptor electron transfer for PDCBT and ITIC system which exhibits the emission peak at 780 nm and 800 nm. PL behavior characteristic of a binary blend (PDCBT:ITIC) suggests efficient donor acceptor energy transfer in the blend [30].

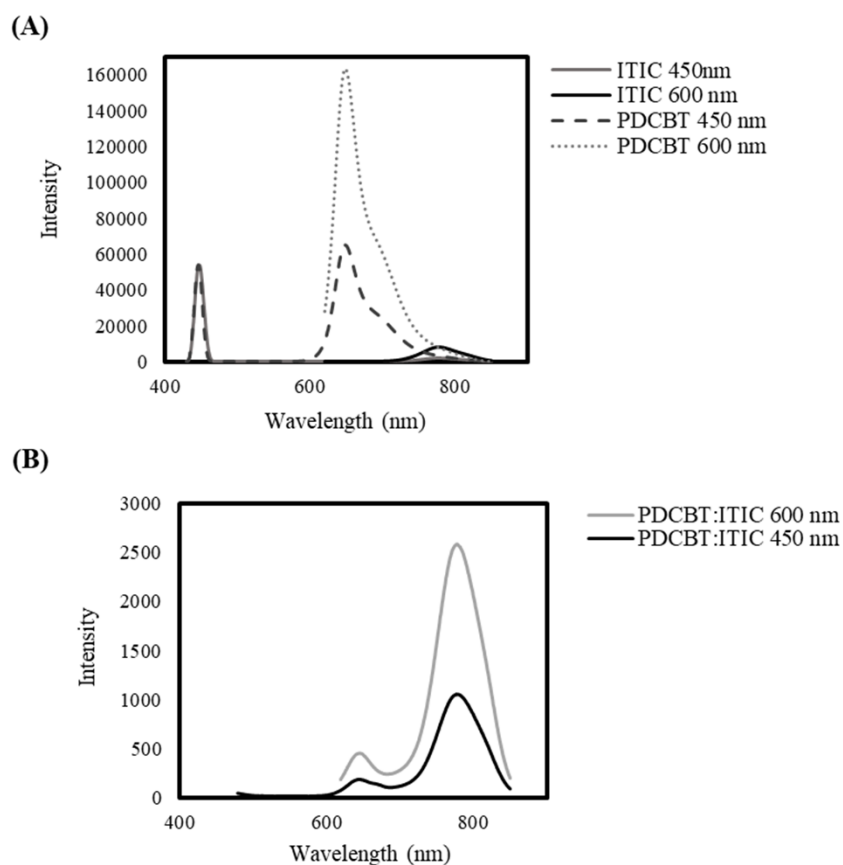


Figure 4.38 Fluorescence of single component PDCBT and ITIC at excitation wavelength 450 nm and 600 nm (A) and (B)

In laboratory PDCBT and ITIC active layer materials OPV device fabrication and their detailed characteristics, results and discussions are introduced later in Chapter 6 of this thesis.

4.9.3 Costs and scaling up challenge

As discussed in the previous chapter there are challenges existing with the scaling up due to large equipment, cleaning large glassware and chemicals safety measurements and disposal of unused extremely hazardous compounds during the synthesis. These challenges apply to the mass production of ITIC as well. Large-scale synthesis may cause potential hazards due to handling large volumes of n-butyllithium organometallic reagent (which is used to transfer the organic group/ the lithium atom to the substrates in synthetic steps, through nucleophilic addition or simple deprotonation) and is pyrophoric and may catch fire spontaneously on contact to air if not handled correctly. Instead, a flow chemistry method for handling large scale of n-butyllithium reagent can be potentially used for the cost improvement and safety of the reaction [31]–[33]. In this method the large volume of the reagent is introduced into the system by small portions, pumping through the syringe into reservoir where reaction occurs. Further research is required to confirm reaction safety and costs for successful application of the flow chemistry as a new method in a procedure.

Another major safety concern of a large-scale reactions is the purification by silica gel chromatography, due to high flammability and toxicity of the solvents which requires industrial scale equipment in order to carry out the work up and handle the purification efficiently [15]. ITIC synthesis requires three column chromatography purifications in the overall synthesis, considering the first step was successfully substituted by the recrystallisation method (which is a safer and cheaper alternative).

4.10 Actual cost verses theoretical cost of ITIC synthesis

Once, the overall cost analysis of each individual step of ITIC was completed, it was summarised, including all of the used reagents and purification techniques as shown in Table 4.2 in this section.

All materials used, were upscaled to a 10 g of product scale and the cost for 100 g product scale was calculated from the 55 mg of laboratory obtained ITIC small molecule. In the end of the costing summary a theoretical cost of 55 mg AUD \$12.40 (based on all literature procedures including original purification methods and yields, as introduced in section 4.6 of this chapter earlier [34]) is compared the actual cost to synthesise and purify 55 mg of ITIC which is AUD \$11.82. The actual unoptimised synthesis of ITIC is 5 % less expensive, however, it is still challenging to perform mass production due to reasons explained above. Costs on 100 g scale of material shows AUD \$21,492.25 in practice, compared to theoretical value of AUD \$22,542.09.

Table 4.2 ITIC step-by-step costing

STEP 1						
Paper yield and quantity of this step's product that is required for the next step	0.496 g (83 % yield)	We require 26.48 g of the product to use in Step 2	We require 264.82 g of the product to use in Step 2			
	78.60	26.48	264.82			
Scaling factor	x	53.39	533.91			
Material	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		Cost for 100 g product scale (only materials used)
thieno[3,2-b]thiophene	0.421	22.478	224.78	g		AUD 1,215.57
THF anhydrous	0.020	1.068	10.68	L		AUD 1,067.82
n-butyllithium 2.5M in hexane	0.00124	0.066	0.66	L		AUD 566.05
ZnCl ₂ anhydrous	0.409	21.837	218.37	g		AUD 77.52
diethyl 2,5-dibromoterephthalate	0.456	24.346	243.46	g		AUD 470.89
Pd(PPh ₃) ₄	0.0690	3.684	36.84	g		AUD 199.23
					Total for Step 1 reaction:	AUD 3,597.07
Work-up	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		
<i>Recrystallisation</i>						
Celite	0.005	0.27	2.7	kg		AUD 123.87
Na ₂ SO ₄	0.0006	0.03	0.3	kg		AUD 11.81
Ethyl acetate	0.0529	2.83	28.28	L		AUD 220.30
dichloromethane	0.0529	2.83	28.28	L		AUD 141.49
					Total for Step 1 work-up:	AUD 497.46
					Grand total for Step 1 (reaction and work-up):	AUD 4,094.54
STEP 2						

Paper yield and quantity of this step's product that is required for the next step	0.530 g (65 % yield)	We require 35.09 g of the product to use in Step 3	We require 350.88 g of the product to use in Step 3			
	0.53	35.09	350.88			
Scaling factor	x	66.20	662.04			
Material	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		Cost for 100 g product scale (only materials used)
2,5-dithieno[3,2-b] thien-2-yl-1,4-benzenedicarboxylic acid-1,4-diethyl ester (step 1 product)	0.400	26.482	264.82	g		
1-bromo-4-hexylbenzene	0.930	61.570	615.70	g		AUD 561.72
THF anhydrous	0.020	1.324	13.24	L		AUD 1,324.08
n-butyllithium 2.5M in hexane	0.00154	0.102	1.02	L		AUD 871.71
acetic acid	0.020	1.324	13.24	L		AUD 95.33
H ₂ SO ₄	0.0004	0.026	0.26	L		AUD 1.99
					Total for Step 2 reaction:	
Work-up	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		
Water	0.040	2.65	26.5	L		Water – almost no cost
Ethyl acetate	0.245	16.19	161.9	L		AUD 1,263.17
Na ₂ SO ₄	0.0008	0.054	0.540	kg		AUD 19.97
Silica gel	0.065	4.32	43.2	Kg		AUD 439.61
Petroleum ether	0.163	10.80	108.0	L		AUD 777.33
dichloromethane	0.163	10.80	108.0	L		AUD 539.82
					Total for Step 2 work-up:	AUD 3,039.90
					Grand total for Step 2 (reaction and work-up):	AUD 5,894.73
STEP 3						

Paper yield and quantity of this step's product that is required for the next step	0.200 g (93 % yield)	We require 35.09 g of the product to use in Step 4	We require 350.88 g of the product to use in Step 4			
	0.2	35.09	350.88			
Scaling factor	x	175.44	1754.40			
Material	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		Cost for 100 g product scale (only materials used)
IT (step 2 product)	0.200	35.088	350.88	g		
THF anhydrous	0.025	4.386	43.86	L		AUD 4,386.00
n-butyllithium 2.5M in hexane	0.00019	0.033	0.33	L		AUD 285.00
DMF anhydrous	0.00004	0.007	0.07	L		AUD 10.88
					Total for Step 3 reaction:	AUD 4,681.88
Work-up	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		
brine	0.025	4.39	43.9	L		AUD 10.88
chloroform	0.100	17.54	175.4	L		AUD 1,263.17
MgSO ₄ anhydrous	0.0002	0.04	0.4	kg		AUD 10.06
silica gel	0.017	3.02	30.2	kg		AUD 307.25
petroleum ether	0.043	7.55	75.5	L		AUD 543.30
dichloromethane	0.043	7.55	75.5	L		AUD 377.29
					Total for Step 3 work-up:	AUD 2,501.07
					Grand total for Step 3 (reaction and work-up):	AUD 7,182.95
STEP 4						
Paper yield and quantity of this step's product that is required for the next step	2.64 g (90 % yield)	We require 48.94 g of the product to use in the final Step 5 to make 10 g of ITIC	We require 489.47 g of the product to use in the final Step 5 to make 100 g of ITIC			
	2.64	48.95	489.47			

Scaling factor	x	18.54	185.41			
Material	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		Cost for 100 g product scale (only materials used)
malononitrile	1.98	36.71	367.10	g		AUD 124.81
1,3-indandione	2.19	40.60	406.03	g		AUD 816.32
anhydrous sodium acetate	1.6	29.66	296.65	g		AUD 30.85
ethanol	0.025	0.46	4.64	L		AUD 13.91
					Total for Step 4 reaction:	AUD 985.89
Work-up	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		
water	0.050	0.93	9.3	L		Water – almost no cost
acetic acid	0.125	0.46	4.64	L		AUD 166.86
					Total for Step 4 work-up:	AUD 166.86
					Grand total for Step 4 (reaction and work-up):	AUD 1,152.76
STEP 5						
Paper yield and quantity of this step's product that is required for the next step	0.057 g (21 % yield)	10 g	100 g			
	0.057	10	100			
Scaling factor	x	175.44	1754.39			
Material	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		Cost for 100 g product scale (only materials used)
IT-CHO (step 3 product)	0.200	35.088	350.88	g		
1,1-dicyanomethylene-3-indanone	0.279	48.947	489.47	g		
chloroform	0.050	8.772	87.72	L		AUD 631.58
pyridine	0.001	0.175	1.75	L		AUD 51.93

					Total for Step 5 reaction:	AUD 683.51
Work-up	Paper scale	10 g scale of ITIC	100 g scale of ITIC	Units		
methanol	0.200	35.09	350.9	L		AUD 964.91
silica gel	0.022	3.81	38.1	kg		AUD 387.79
petroleum ether	0.054	9.52	95.2	L		AUD 685.71
dichloromethane	0.054	9.52	95.2	L		AUD 476.19
					Total for Step 5 work-up:	AUD 2,514.61
					Grand total for Step 5 (reaction and work-up):	AUD 3,198.12
Theoretical Total cost to synthesis and purify 55 mg of ITIC =				AUD	12.40	
Actual Total cost to synthesis and purify 55 mg of ITIC =				AUD	11.82	

4.11 Results and discussion

PDCBT (85 mg, 64%) was successfully synthesised on a small laboratorial scale at total actual cost of synthesis AUD \$92.70/g vs AUD \$63.78/g predicted in accordance with the modified methods introduced in this chapter. Each step aims to keep the costs inexpensive while affording higher yields and utilising a safe synthesis process. Material purity and characterization was conducted and OPV device performance studies of the PDCBT:ITIC material pairing are presented later in the thesis as part of conclusive selection studies of the best candidates for beneficial mass production.

ITIC (55 mg, 20 %) scale was also successfully synthesised in laboratory scale at total actual cost of synthesis AUD \$214.91/g vs AUD \$225.42/g predicted using the modified methods introduced in this chapter. Each step was again designed to keep the costs low-cost while affording higher yields during the synthesis.

These results show that gains can be made in material costs by improving purification of materials. It is anticipated that increased cost and yield improvements will be achieved when production is scaled up and the synthesis and methods further optimised.

4.12 Conclusion

One of the key features and challenges of successful material incorporation into a solar cell is the scalability. Ability to upscale the synthesis fundamental to OPV becoming part of the solution to meet mankind's sustainable energy demands and afford a fossil fuel-free future. Less expensive and highly efficient materials need to be developed achieve these goals. In this chapter on PDCBT and ITIC synthesis, we have assessed various low

budget purification methodologies, alternative synthesis procedures, as well as the required significant improvements to be done to the safety of a large scale production [29][35].

More focus in this research area to reach sustainable, commercially viable OPV production. Therefore, once the industrial scale equipment, safety gear and handling challenges are met, shown all the research conducted, ITIC and PDCBT have been shown to be viable compounds for large scale production.

References

- [1] Al-Ahmad, A.Y., Almayhi, F., Al-Mudhaffer, M.F., Griffith, M.J., Liu, W., Li, S., Sivunova, K., Elkington, D., Cooling, N.A., Feron, K. and Shi, M., 2020. A nuanced approach for assessing OPV materials for large scale applications. *Sustainable Energy & Fuels*, 4(2), pp.940-949.
- [2] Po, R. and Roncali, J., 2016. Beyond efficiency: scalability of molecular donor materials for organic photovoltaics. *Journal of Materials Chemistry C*, 4(17), pp.3677-3685.
- [3] Meng, L., Zhang, Y., Wan, X., Li, C., Zhang, X., Wang, Y., Ke, X., Xiao, Z., Ding, L., Xia, R. and Yip, H.L., 2018. Organic and solution-processed tandem solar cells with 17.3% efficiency. *Science*, 361(6407), pp.1094-1098.
- [4] Colsmann, A., Röhm, H. and Sprau, C., 2020. Shining light on organic solar cells. *Solar RRL*, 4(6), p.2000015.
- [5] Du, X., Heumueller, T., Gruber, W., Classen, A., Unruh, T., Li, N. and Brabec, C.J., 2019. Efficient polymer solar cells based on non-fullerene acceptors with potential device lifetime approaching 10 years. *Joule*, 3(1), pp.215-226.
- [6] Anthony, J.E., Facchetti, A., Heeney, M., Marder, S.R. and Zhan, X., 2010. n-Type organic semiconductors in organic electronics. *Advanced Materials*, 22(34), pp.3876-3892.

- [7] Lin, Y., Wang, J., Zhang, Z.G., Bai, H., Li, Y., Zhu, D. and Zhan, X., 2015. An electron acceptor challenging fullerenes for efficient polymer solar cells. *Advanced materials*, 27(7), pp.1170-1174.
- [8] D. R. Klein, *Organic Chemistry*. Wiley, 2016, pp.234-241
- [9] Pankow, R.M., Ye, L. and Thompson, B.C., 2019. Influence of an ester directing-group on defect formation in the synthesis of conjugated polymers via direct arylation polymerization (DArP) using sustainable solvents. *Polymer Chemistry*, 10(33), pp.4561-4572.
- [10] Pankow, R.M. and Thompson, B.C., 2020. Approaches for improving the sustainability of conjugated polymer synthesis using direct arylation polymerization (DArP). *Polymer Chemistry*, 11(3), pp.630-640.
- [11] Zhang, M., Guo, X., Ma, W., Ade, H. and Hou, J., 2014. A polythiophene derivative with superior properties for practical application in polymer solar cells. *Advanced Materials*, 26(33), pp.5880-5885.
- [12] Heuvel, R., Colberts, F.J., Wienk, M.M. and Janssen, R.A., 2018. Thermal behaviour of dicarboxylic ester bithiophene polymers exhibiting a high open-circuit voltage. *Journal of Materials Chemistry C*, 6(14), pp.3731-3742.
- [13] Pierre M. Beaujuge, John R. Reynolds, Stefan M. Ellinger, Chad Martin Amb "Black Soluble Conjugated Polymers with High Charge Carrier Mobilities," US8383762B2, University of Florida Research Foundation Inc, 2013 pp. 45-60.
- [14] Choi, J., Kim, K.H., Yu, H., Lee, C., Kang, H., Song, I., Kim, Y., Oh, J.H. and Kim, B.J., 2015. Importance of electron transport ability in naphthalene diimide-based polymer acceptors for high-performance, additive-free, all-polymer solar cells. *Chemistry of Materials*, 27(15), pp.5230-5237.
- [15] Li, N., McCulloch, I. and Brabec, C.J., 2018. Analyzing the efficiency, stability and cost potential for fullerene-free organic photovoltaics in one figure of merit. *Energy & Environmental Science*, 11(6), pp.1355-1361.
- [16] Zhao, Z.W., Pan, Q.Q., Geng, Y., Wu, Y., Zhao, L., Zhang, M. and Su, Z.M., 2019. Theoretical insight into multiple charge-transfer mechanisms at the P3HT/nonfullerenes interface in organic solar cells. *ACS Sustainable Chemistry & Engineering*, 7(24), pp.19699-19707.
- [17] Li, Y., 2012. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. *Accounts of chemical research*, 45(5), pp.723-733.

- [18] Sheldon, R.A., 2008. E factors, green chemistry and catalysis: an odyssey. *Chemical Communications*, (29), pp.3352-3365.
- [19] Sheldon, R.A., 2007. The E factor: fifteen years on. *Green Chemistry*, 9(12), pp.1273-1283.
- [20] Kilty, P.A. and Sachtler, W.M.H., 1974. The mechanism of the selective oxidation of ethylene to ethylene oxide. *Catalysis Reviews Science and Engineering*, 10(1), pp.1-16.
- [21] Anastas, P. and Eghbali, N., 2010. Green chemistry: principles and practice. *Chemical Society Reviews*, 39(1), pp.301-312.
- [22] Xu, Y.X., Chueh, C.C., Yip, H.L., Ding, F.Z., Li, Y.X., Li, C.Z., Li, X., Chen, W.C. and Jen, A.K.Y., 2012. Improved charge transport and absorption coefficient in indacenodithieno [3, 2-b]thiophene-based ladder-type polymer leading to highly efficient polymer solar cells. *Advanced materials*, 24(47), pp.6356-6361.
- [23] Bello, K.A., Cheng, L. and Griffiths, J., 1987. Near-infrared absorbing methine dyes based on dicyanovinyl derivatives of indane-1, 3-dione. *Journal of the Chemical Society, Perkin Transactions 2*, (6), pp.815-818.
- [24] Tirelli, N., Amabile, S., Cellai, C., Pucci, A., Regoli, L., Ruggeri, G. and Ciardelli, F., 2001. New terthiophene derivatives for ultrahigh molecular weight polyethylene-based absorption polarizers. *Macromolecules*, 34(7), pp.2129-2137.
- [25] Xiao, L., He, B., Hu, Q., Maserati, L., Zhao, Y., Yang, B., Kolaczowski, M.A., Anderson, C.L., Borys, N.J., Klivansky, L.M. and Chen, T.L., 2018. Multiple roles of a non-fullerene acceptor contribute synergistically for high-efficiency ternary organic photovoltaics. *Joule*, 2(10), pp.2154-2166.
- [26] Sapsford, K.E., Berti, L. and Medintz, I.L., 2006. Materials for fluorescence resonance energy transfer analysis: beyond traditional donor–acceptor combinations. *Angewandte Chemie International Edition*, 45(28), pp.4562-4589.
- [27] Clapp, A.R., Medintz, I.L., Mauro, J.M., Fisher, B.R., Bawendi, M.G. and Mattoussi, H., 2004. Fluorescence resonance energy transfer between quantum dot donors and dye-labeled protein acceptors. *Journal of the American Chemical Society*, 126(1), pp.301-310.
- [28] Q.-Q. Pan, Z.-W. Zhao, Y. Wu, Y. Geng, M. Zhang, and Z.-M. Su, “A theoretical 252 / 325 exploration on why the replacement of hexyl group by alkoxycarbonyl in P3HT could greatly improve the performance of non-fullerene organic solar cell,” *J. Taiwan Inst. Chem. Eng.*, vol. 100, pp. 160–167, 2019.

- [29] Hou, J., Inganäs, O., Friend, R.H. and Gao, F., 2018. Organic solar cells based on non-fullerene acceptors. *Nature materials*, 17(2), pp.119-128.
- [30] Pan, Q.Q., Li, S.B., Wu, Y., Geng, Y., Zhang, M. and Su, Z.M., 2018. Exploring more effective polymer donors for the famous non-fullerene acceptor ITIC in organic solar cells by increasing electron-withdrawing ability. *Organic Electronics*, 53, pp.308-314.
- [31] Stueckler, C., Hermsen, P., Ritzen, B., Vasiloiu, M., Poechlauer, P., Steinhof, S., Pelz, A., Zinganel, C., Felfel, U., Boyer, S. and Goldbach, M., 2019. Development of a continuous flow process for a Matteson reaction: From lab scale to full-scale production of a pharmaceutical intermediate. *Organic Process Research & Development*, 23(5), pp.1069-1077.
- [32] Power, M., Alcock, E. and McGlacken, G.P., 2020. Organolithium bases in flow chemistry: a review. *Organic Process Research & Development*, 24(10), pp.1814-1838.
- [33] Lovato, K., Fier, P.S. and Maloney, K.M., 2021. The application of modern reactions in large-scale synthesis. *Nature Reviews Chemistry*, 5(8), pp.546-563.
- [34] Osedach, T.P., Andrew, T.L. and Bulović, V., 2013. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy & Environmental Science*, 6(3), pp.711-718.
- [35] Bundgaard, E., Livi, F., Hagemann, O., Carlé, J.E., Helgesen, M., Heckler, I.M., Zawacka, N.K., Angmo, D., Larsen-Olsen, T.T., dos Reis Benatto, G.A. and Roth, B., 2015. Matrix organization and merit factor evaluation as a method to address the challenge of finding a polymer material for roll coated polymer solar cells. *Advanced Energy Materials*, 5(10), p.1402186.

Chapter 5: Introducing novel “green” PDCBT: ITIC nanoparticle ink synthesis and its performance in NPOPV devices

5.1 Introduction

Bulk heterojunction solar cells based on organic photovoltaic materials are a competitive solar technology with inexpensive production, lightweight and flexibility. However, OPVs are usually processed from toxic organic solvents such as chloroform and chlorobenzene. Using these toxic organic solvents is disappointingly not viable for the printing of polymer solar cells on a commercial scale from perspective of increased production cost, health safety risk, and environmental toxicity [1]–[3].

Consequently, a unique eco-friendly alternative; nanoparticulate organic photovoltaics is utilised in this chapter. There is increasing interest in OPV device fabrication from water-dispersed nanoparticle ink (solar paint). In particular, the ability to process devices in the absence of an organic solvent and the morphological control afforded by the method are highly desirable. However, nanoparticle performance in OPV devices have been traditionally lower than BHJ [1] due, in part, to the infancy of the research into NP device function. Importantly, by tailoring the device morphology of synthesised nanoparticles we begin to address these issues in this work.

In this study, binary-component nanoparticles of P3HT: ICx_A and PDCBT: ITIC were prepared and characterised using photoluminescence, UV-vis spectroscopy, transmission electron microscopy measurements, as well as, scanning transmission X-ray microscopy (STXM) and scanning electron microscopy (SEM) to describe the film morphology. NP OPV devices were then prepared from these materials and characterised to benchmark the materials prepared in Chapter 4 and to allow further calculation of the cost-effectiveness of the PDCBT:ITIC material combination as a potential commercial material system.

5.2 Preparation processes of aqueous PDCBT and ITIC nanoparticle inks

Nanoparticle inks were prepared by using the miniemulsion method [2], by blending PDCBT and ITIC at 1:1 ratio with chloroform solvent to form the organic active layer (15 mg/mL) as shown in the Figure 5.1. The aqueous phase was prepared with 33 mg of SDS dissolved in DI water (12 mg/mL). This combination of organic and aqueous phases was sonicated using a small-ultrasound booster horn and then purified by the centrifugal ultrafiltration technique as illustrated in Figure 5.1 (A) and (B). As shown in Figure 5.1 (B) the small-scale ultrasound equipment (Hielscher ultrasound booster horns UIP400S, 400 W, 24 kHz, sonotrode 3 mm diameter) was clamped with the top of the horn about 5 mm from the top of the vial. Once it was ensured that the horn is not touching the side of the glass vial a beaker of ice-cold water (0 °C) was placed under the vial to cool the dispersion. The horn was active for 2 minutes. Afterwards the vial was transferred to a hotplate (at 60 °C) and stirred overnight to evaporate the chloroform. The water dispersion was dialysed by using a ultrafiltration process to remove excess SDS surfactant from the nanoparticles suspension by using ultracentrifuge dialysis tubes [Millipore (10

kDa MWCO)], with samples spun at 4000 rpm for 7 min (the time required to reduce the NP ink from 2.5 mL to 0.5 mL. Reference nanoparticle devices were prepared from P3HT and ICxA organic phase at 1:0.8 ratio blend (54 mg/mL) and the aqueous layer was prepared with 33 mg of SDS dissolved in DI water (12 mg/mL). These samples were following the same miniemulsion process described above.

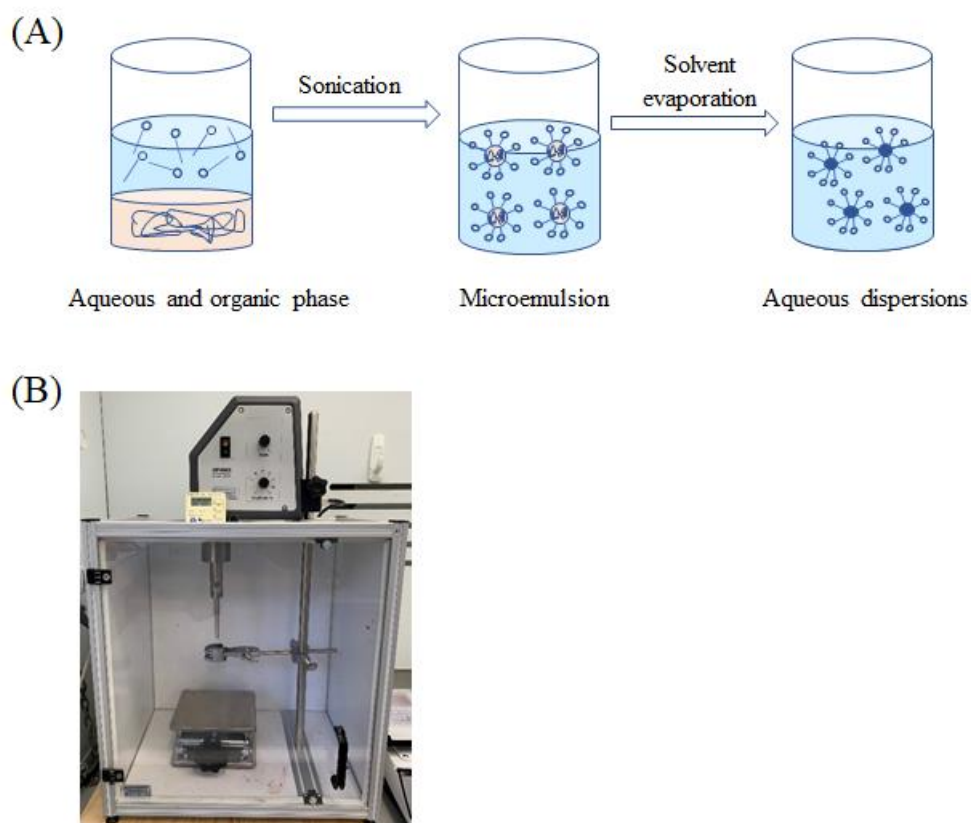


Figure 5.1 (A) Micro-emulsion preparation (B) Small-scale ultrasound equipment (Hielscher ultrasound booster horns UIP400S, 400 W, 24 kHz, sonotrode 3 mm diameter)

5.3 NP organic photovoltaic device fabrication versus BHJ

Nanoparticle OPV devices were successfully prepared using the structure glass/ITO/PEDOT:PSS/NP active layer/ZnO/Al. The thickness of the NP active layer was

optimized to 110 nm for both PDCBT:ITIC and P3HT:ICxA active layers. The PDCBT:ITIC (25 μ L) was spin-coated at 3000 rpm/min under nitrogen atmosphere (in a glovebox) onto a PEDOT:PSS Al4083 layer (spun at 5000 rpm/min under ambient conditions) to form the photosensitive layer. Then the device stack was thermally annealed at 160 °C for 10 mins to remove residual solvent. Next, a ZnO in acetone (10 mg/mL) solution was deposited onto the active layer to give an interfacial layer (~35 nm thick) at 5000 rpm/min. The devices were transferred to a thermal evaporator and the aluminum top electrode (~86 nm) was evaporated to complete the device structure. The same method was used for the P3HT:ICxA nanoparticle devices.

For comparison PDCBT:ITIC, PDCBT: PC₇₀BM and P3HT:ICxA bulk heterojunction devices were also fabricated with a glass/ITO/PEDOT:PSS/BHJ active layer/ZnO/Al architecture. The thickness of active layer was around 104-110 nm for PDCBT:ITIC, PDCBT:PC₇₀BM and P3HT:ICxA active layers. As an example, firstly PEDOT:PSS Al4083 layer was spun at 5000 rpm/min (in air/wet lab) to form a photosensitive layer ~100 nm thick. Next, 25 μ L of PDCBT:ITIC solution (15 mg/mL) in 1027 μ L of chloroform was spin-coated at 3000 rpm/min in a glovebox onto the substrate. After thermal annealing at 160 °C for 10 mins, ZnO in acetone (10 mg/mL) solution was deposited at 5000 rpm/min onto the active layer to give an interfacial layer (~40 nm thick). Devices were transferred to the evaporator and an aluminium top electrode (~86 nm) was subsequently evaporated to the complete device structure.

The UV-visible spectra of as spun nanoparticles films consisting of P3HT:PCBM and PDCBT:ITIC are presented in Figure 5.2. The P3HT:PCBM NPs show a maximum peak at 500 nm. These peaks as has been studied previously [4], and demonstrate the crystalline ordering of the P3HT inside the nanoparticle. The PDCBT:ITIC film exhibits an increase

in the light absorbance with maxima peaks shown at 600 and 710 nm. PL spectra are shown in Figure 5.2 and show two transitions at 650 nm and 800 nm for both materials. They indicate that P3HT:PCBM nanoparticles include J-aggregates and H-aggregates from interchain and intrachain ordering [4]. When testing PDCBT:ITIC films we observe an increase in PL emission, relative to P3HT:PCBM films suggesting a higher number of exciton dissociations and showing that most of the excitons are generated in PDCBT domains.

As demonstrated in the Figure 5.3 (A) SEM images PDCBT:ITIC nanoparticles are similar to SEM images of the P3HT:PCBM nanoparticles images, Figure 5.3 (B). However, when we compare the P3HT:PCBM structure to the PDCBT:ITIC nanoparticles we observe higher PL emission of the PDCBT-based particles, suggesting that exciton separation in the P3HT system may be superior. The fact that significant PL spectra are observed for these films is interesting. The inference is that emission from the particles is much higher than from standard blended films. In particular, we speculate that the observation of the band at 800 nm for P3HT:PCBM (which is not seen in a standard blend) is likely to be due to emission from a “trapped” P3HT:PCBM exciplex which would separate in a standard film. Further work will be required to confirm this hypothesis.

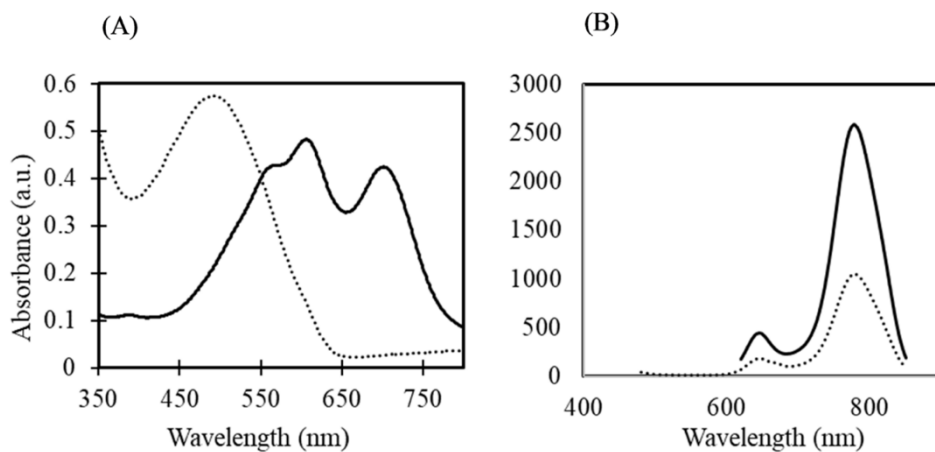


Figure 5.2 UV-visible spectra (A) and photoluminescence (PL) measurements (B) of nanoparticle film from a 1:1 P3HT:PCBM NP ink (dotted line) and 1:1 PDCBT:ITIC ink, as cast film (black line)

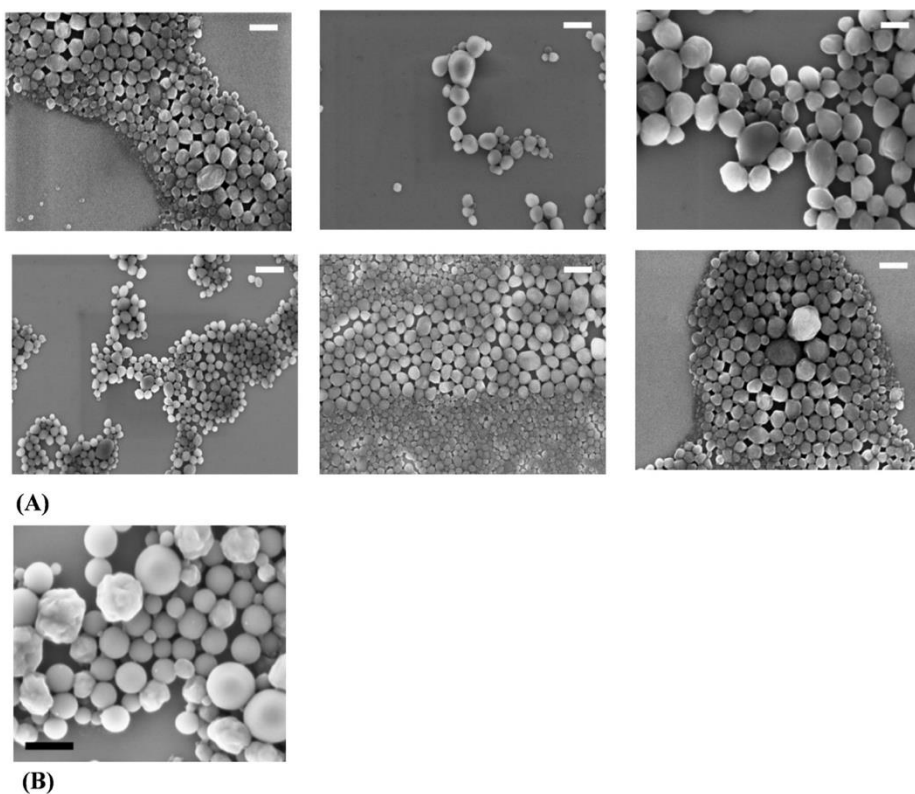


Figure 5.3 SEM images of PDCBT:ITIC nanoparticles (A); P3HT:PCBM nanoparticles (scales bars are 200 nm) (B) [4]

5.3.1 NP device characterisation and performance

In this section we characterise NP-OPV devices fabricated (by using procedure described earlier in this chapter) from water dispersed PDCBT:ITIC and P3HT:ICx A nanoparticles which exhibit power conversion efficiencies (PCEs) of 2.11 % and 0.87 %, respectively. Figure 5.4 shows I - V characteristics for these devices and the summary of device OPV parameters is shown in the Table 5.1 for annealed devices at 160 °C for 4 min. Overall, hereo device fabricated from PDCBT:ITIC nanoparticles exhibited a performance of $PCE_{max} = 2.11$ %, comparing to corresponding devices made from P3HT:ICx A, with a $PCE_{max} = 0.87$ %. The EQE spectral response of devices was measured and is shown in Figure 5.6 and shows that the current output for PDCBT:ITIC generating is superior above 580 nm to 750 nm. By comparison the P3HT:ICx A, shows the expected EQE peak in the region below 500 nm.

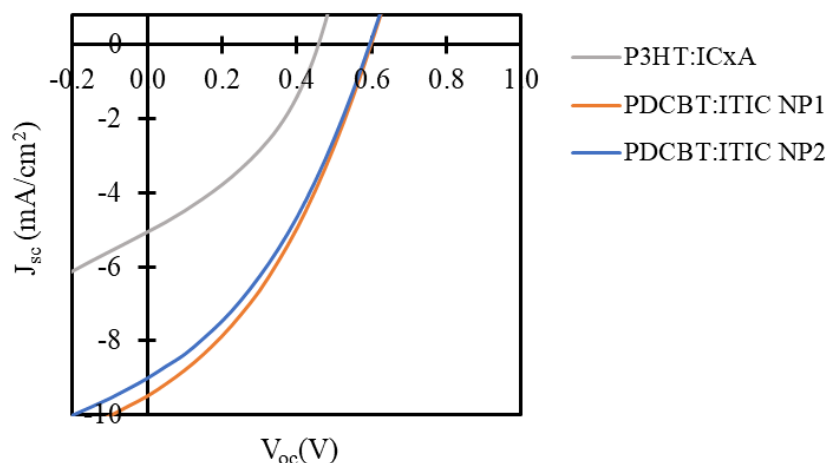


Figure 5.4 I - V characteristic curves of masked PDCBT:ITIC and P3HT:ICx A nanoparticles devices

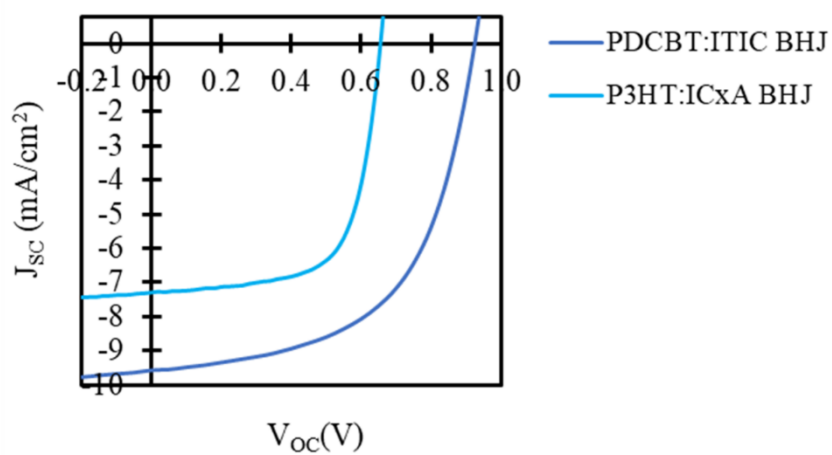
Table 5.1 OPV parameters of fabricated PDCBT:ITIC and P3HT:ICx A nanoparticle devices

Device	PCE (%)	V _{OC} (V)	Fill Factor	J _{SC} (mA/cm ²)
PDCBT:ITIC ^a	2(2.05)±0.06	0.59±0.01	0.36±0.01	9.31±0.26
PDCBT:ITIC ^b	1.3(1.48)±0.14	0.5±0.07	0.35±0.01	7.68±0.69
P3HT:ICx A	0.72(0.86)±0.1	0.43±0.02	0.34±0.02	4.89±0.14

^a Annealing conditions: 160°C for 4 min, dried at 110 °C for 10 min; ^b Annealing conditions: 160°C for 4 min, dried at 110 °C for 5 min.

Bulk-heterojunction (BHJ) devices were also fabricated with a PDCBT:ITIC active layer for comparison, as well as PDCBT:PC₇₀BM, P3HT:ICx A and P3HT:PCBM. Figure 5.5 A and B shows the *I-V* curves for BHJ devices from PDCBT:ITIC, PDCBT:PC₇₀BM, P3HT:ICx A and P3HT:PCBM. The I-V characteristics for these devices are included in Table 5.2 below. As demonstrated, the best device efficiency attained for PDCBT:ITIC was 5.27 %. Whilst this value is lower than the 10.16% reported by Qin et al. [8], it is typical of the efficiencies achieved for this system within our laboratories. Differences in the molecular weight of the PDCBT used may contribute to this discrepancy. By comparison, PDCBT:PC₇₀BM PCE_{max} = 4.13 %, P3HT:ICx A PCE_{max} = 3.39 % and P3HT:PC₆₀BM PCE_{max} = 2.07 % devices gave lower efficiencies. In terms of external quantum efficiency data, the devices demonstrated high current output in the region above 580 nm to 700 nm, in the region where the ITIC absorbs, similar to the PDCBT:ITIC NP EQE results.

(A)



(B)

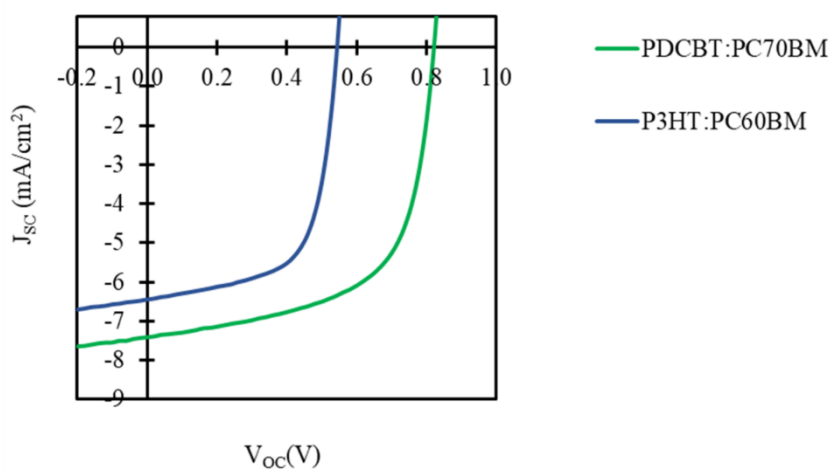


Figure 5.5 *I-V* characteristics curves of masked PDCBT:ITIC and P3HT:ICx A BHJ devices (A); *I-V* characteristics curves of masked PDCBT:PC₇₀BM and PDCBT:PCBM (B)

Table 5.2 OPV parameters of fabricated PDCBT:ITIC and P3HT:ICx A bulk heterojunction devices; Annealing conditions: 160°C for 4 min, dried at 110 °C for 10 min.

Device	PCE (%)	V _{OC} (V)	Fill Factor	J _{SC} (mA/cm ²)
PDCBT:ITIC	5.02(4.77)±0.25	0.92±0.00	0.57±0.01	9.12±0.59
P3HT:ICx _A	3.22(3.02)±0.17	0.65±0.00	0.66±0.02	7.04±0.24
PDCBT:PC ₇₀ BM	3.92(3.21)±0.21	0.82±0.01	0.61±0.02	7.36±0.23
P3HT:PC ₆₀ BM	2.07(1.88)±0.16	0.53±0.01	0.60±0.04	6.43±0.07

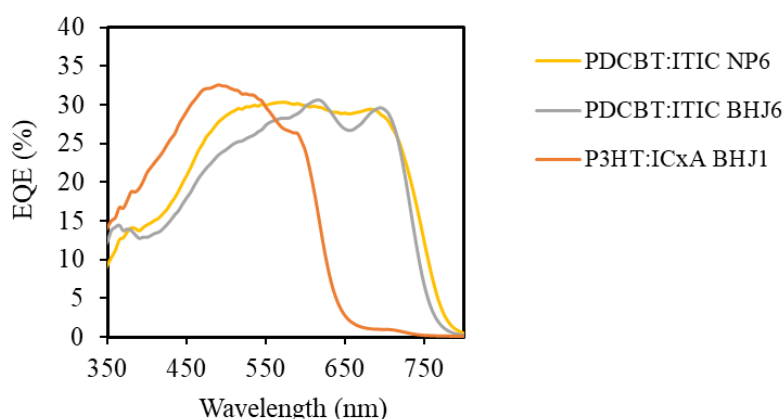


Figure 5.6 External quantum efficiency (EQE)

5.3.2 Surface morphology study of PDCBT:ITIC NPs

To study the surface morphology of the nanoparticle films SEM technique was performed on disperse NP films. The particles size, shape and nanoscale morphology were analysed by the SEM. These investigations were performed by Dr. Natalie Holmes using a Zeiss Sigma ZP field emission FESEM at hastening voltages of 1 to 3 kV, and amplifications of up to x 400k. SEM samples were prepared by mixing Milli-Q water at 1:10 ratio with the nanoparticle inks and spun onto conductive silicon substrates. The SEM images bear topological data for the sample.

Unlike circular shaped P3HT:PCBM nanoparticles the PDCBT:ITIC nanoparticles present as non-circular ellipse-shaped particles. Their geometry is considered in terms of

the two-dimensional particle shape modelling as shown in Figure 5.7 ((A) and (B)), it suggests that there will be a greater contact between the elliptical particles rather than circular and hence improvements in the nanoparticle device morphology inside the PDCBT:ITIC active layer.

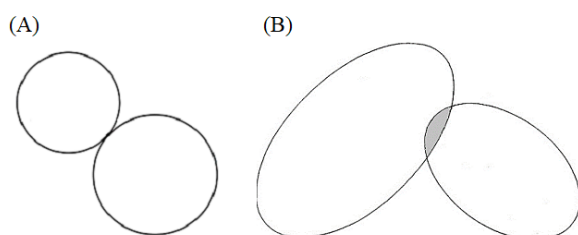


Figure 5.7 Two circular shaped particles in a contact position (A); two elliptical particles in contact position

5.3.3 Internal morphology structure characterisation of PDCBT:ITIC NPs

Internal morphology is a major factor in nanoparticle device optimisation in order to achieve high performance. Internal morphology is a result of the material crystallinity, particle size and degree of phase separation in the device structure.

To investigate the internal structure of PDCBT:ITIC NPs films, the scanning transmission X-ray microscopy (STXM technique (See Chapter 2 Section 2.9)) was performed and results are shown in the images in Figure 5.9. The STXM samples studied for this thesis were fabricated by depositing 2.5 μL of NP inks of P3HT:ICx A and PDCBT:ITIC onto low stress silicon nitride (Si_3N_4) window membrane substrates with silicon dioxide coating (purchased from Norcada, Canada). The silicon nitride window dimensions were 250 x 250 μm^2 , membrane thickness of 15 nm, silicon frame dimensions of 5 x 5 mm^2 . Spin coating conditions were as follows: 3000 rpm, low acceleration of 112 rpm/s, 1 min.

The measurements were conducted by Dr Natalie Holmes, Dr Matthew Barr and Dr Adam Fahy at the Advanced Light Source synchrotron, beamline 5.3.2.2 Polymer STXM. To start with, it was necessary to determine the near edge X-ray absorption fine structure (NEXAFS) spectrum for each of the component in the nanoparticles film, in order to determine absorption energies which were unique to each material. Then the STXM beam energies were necessary to proceed with the measurements. Energies of 285.13 eV and 288.17 eV were chosen for ITIC and PDCBT, respectively (Figure 5.8). The absorption is strong relative to another materials, which helps to determine the composition.

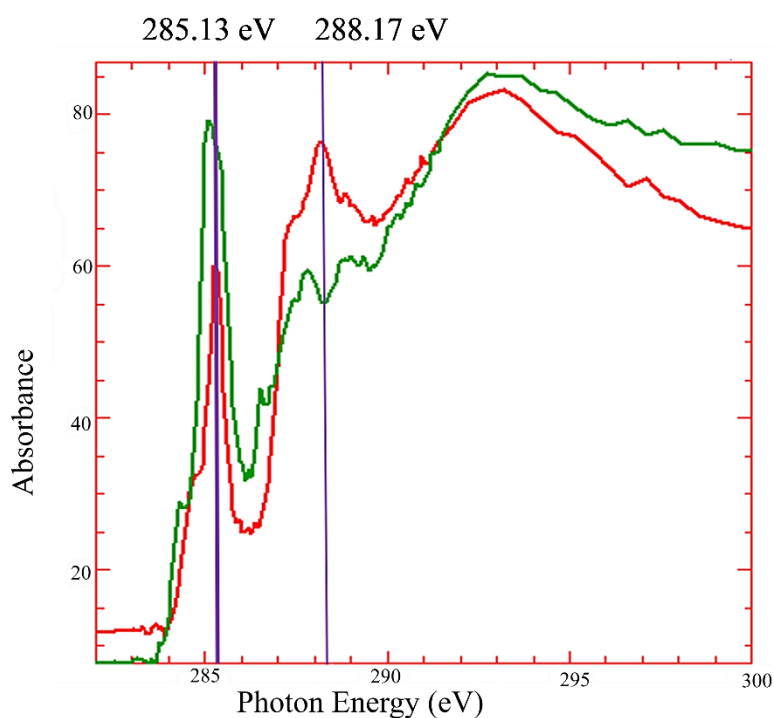


Figure 5.8 Near edge X-ray absorption fine structure (NEXAFS) spectra of PDCBT (red) and ITIC (green) with orthogonal energies for PDCBT 288.17 eV and ITIC 285.13 eV

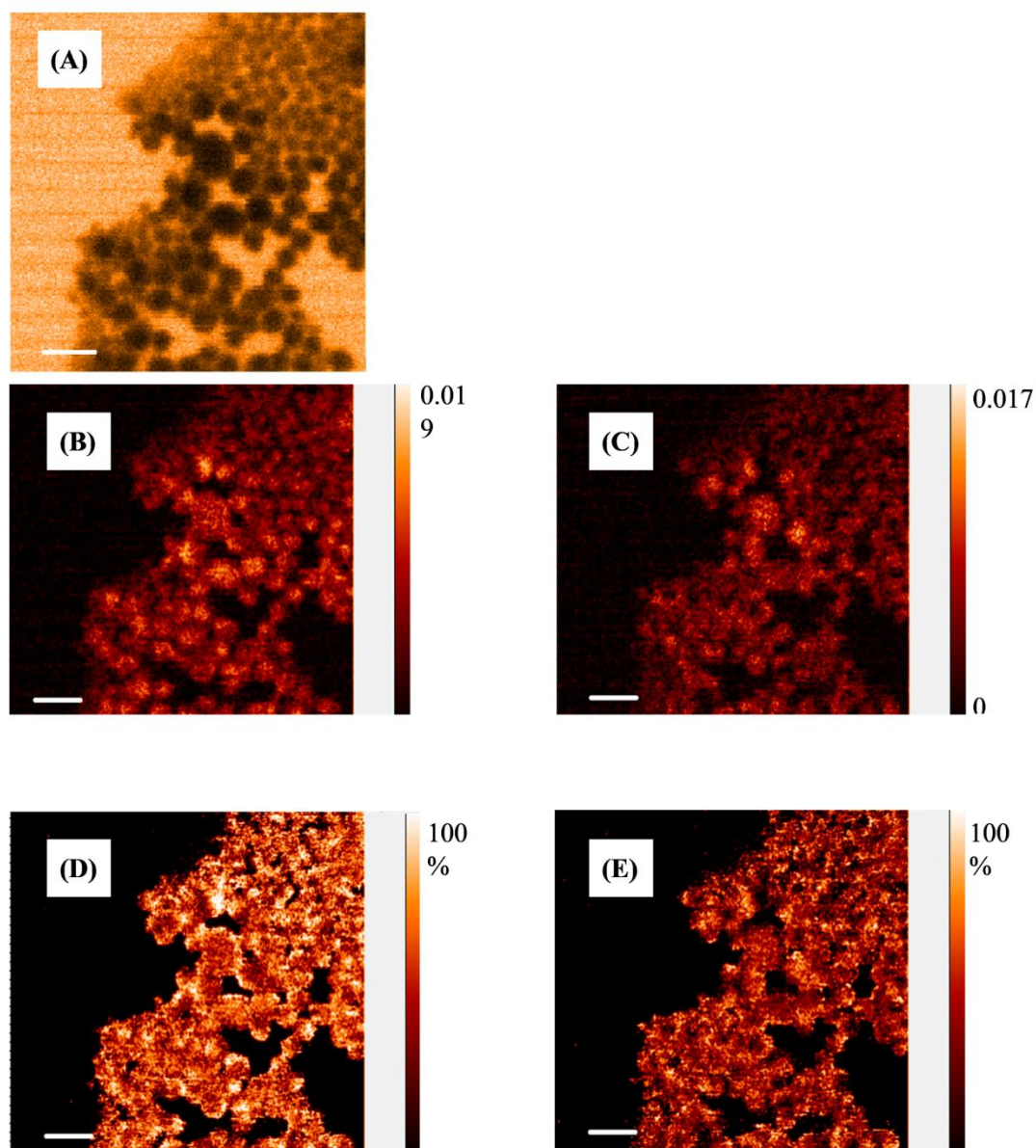


Figure 5.9 (A) TEM image of 1:1 PDCBT:ITIC nanoparticles as cast (no thermal treatment) related to area of STXM analysis. STXM mass plots for PDCBT (B) and ITIC (C) are shown with corresponding STXM fractional composition maps showing the concentration of PDCBT (D) and ITIC (E). All scale bars are 1 μm . The colour contrast is scaled such that light colours correspond to higher component concentrations. For (B) and (C) the colour scale bars indicate concentration of component in mg/cm^2 . Minima and maxima for the colour scale bar in (D) and (E) are black = 0 and white = 100 %

Transmission electron microscopy (TEM) was used to reimage the nanoparticles at positions matching the STXM images. TEM was performed by using a Jeol 1200 EXII at an accelerating voltage of 80kV. The NP inks were diluted 1/10 in reverse osmosis water and 5 ml of the diluted dispersion were deposited at 3000 rpm, for 1 min onto a low stress silicon nitride Si_3N_4 substrates. These measurements confirmed that deposited films contain regions that are localised in a pseudo-hexagonal packed structure. The lighter contrast regions represent small nanoparticles in the TEM images that were collected by Dr Natalie Holmes.

The data collected from STXM confirms that both donor (PDCBT) and acceptor (ITIC) materials have been incorporated into each nanoparticle. That is, the nanoparticles are blends rather than single component nanoparticles. A wide range of particle sizes, from ~ 500 nm down to the resolution limit of the technique (~ 30 nm) are observed. Compared to the P3HT:PCBM nanoparticle morphology which exhibits core shell nanoparticles structure [4] (as demonstrated in Figure 5.10), PDCBT:ITIC nanoparticles were observed to have more molecularly intermixed morphology of the particles. The STXM data shows morphology which is not clearly core-shell, with no substructure resolved for the PDCBT:ITIC nanoparticles. This observation is either due to the small size of the nanoparticles (not likely since the P3HT:PCBM particles are of similar size) or due to more intermixing of materials. We suggest that the surface energy differences of PDCBT and ITIC are sufficiently small that the materials do not tend to form a core-shell since we would expect the higher surface energy material to be driven to the core and the lower surface energy material to the shell. [7]. Also, the EQE for these NP materials demonstrated broad current generation which suggests a well-mixed blend and no full phase segregation.

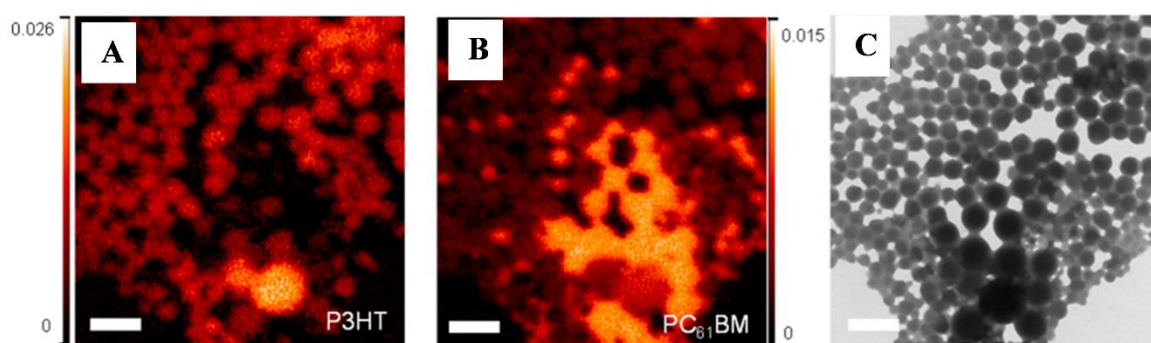


Figure 5.10 STXM images showing concentration of P3HT (A) and PCBM (B) in a P3HT:PCBM nanoparticle film (thermally treated at 110 °C 4 minutes and annealed at 140 °C for 10 minutes) . The color scale bars show each component concentration in mg/cm²; TEM image is a position matched image for the P3HT:PCBM NPs film corresponding to the STXM plots. All scale bars are 600 nm [4]

5.4 Conclusion

In this chapter we showed how novel nanoparticles devices, which is the first time nanoparticles blend of PDCBT and ITIC, were fabricated, tested, and characterised morphologically from PDCBT and ITIC components. The preparation of nanoparticles ink is presented in detail, as well as the device architecture and performance. The device exhibited excellent J_{SC} performance of 9.3 mA/cm², with 2.11 % PCE when device was thermally treated for 10 minutes at 110 °C and then thermally annealed at 160 °C for 4 minutes. The performance dropped slightly when drying conditions were changed, so the PCE was 1.62 % when the thermal treatment was 110 °C for 5 minutes and annealing 160 °C for 4 minutes. The performance of these devices was limited by poor FF and V_{OC} factors. In summary, these devices with highly blended nanostructure exhibit performance which is promising for commercial viability on a large-scale production. SEM, TEM and STXM data revealed the morphology of the particles, their size,

crystallinity, phase separation in the film, which allows us to design the highly efficient OPV solar cells for large OPV module fabrication.

References

- [1] Holmes, N.P., Nicolaidis, N., Feron, K., Barr, M., Burke, K.B., Al-Mudhaffer, M., Sista, P., Kilcoyne, A.D., Stefan, M.C., Zhou, X. and Dastoor, P.C., 2015. Probing the origin of photocurrent in nanoparticulate organic photovoltaics. *Solar Energy Materials and Solar Cells*, 140, pp.412-421.
- [2] Landfester, K., Montenegro, R., Scherf, U., Güntner, R., Asawapirom, U., Patil, S., Neher, D. and Kietzke, T., 2002. Semiconducting polymer nanospheres in aqueous dispersion prepared by a miniemulsion process. *Advanced Materials*, 14(9), pp.651-655.
- [3] Ameri, M., Al-Mudhaffer, M.F., Almyahi, F., Fardell, G.C., Marks, M., Al-Ahmad, A., Fahy, A., Andersen, T., Elkington, D.C., Feron, K. and Dickinson, M., 2019. Role of stabilizing surfactants on capacitance, charge, and ion transport in organic nanoparticle-based electronic devices. *ACS applied materials & interfaces*, 11(10), pp.10074-10088.
- [4] Holmes, N.P., Marks, M., Cave, J.M., Feron, K., Barr, M.G., Fahy, A., Sharma, A., Pan, X., Kilcoyne, D.A., Zhou, X. and Lewis, D.A., 2018. Engineering two-phase and three-phase microstructures from water-based dispersions of nanoparticles for eco-friendly polymer solar cell applications. *Chemistry of Materials*, 30(18), pp.6521-6531.
- [5] Kafashan, J., Wiącek, J., Abd Rahman, N. and Gan, J., 2019. Two-dimensional particle shapes modelling for DEM simulations in engineering: A review. *Granular Matter*, 21(3), pp.1-19.
- [6] Rothenburg, L. and Bathurst, R.J., 1991. Numerical simulation of idealized granular assemblies with plane elliptical particles. *Computers and geotechnics*, 11(4), pp.315-329.
- [7] Wang, J., Zheng, Z., Zhang, D., Zhang, J., Zhou, J., Liu, J., Xie, S., Zhao, Y., Zhang, Y., Wei, Z. and Hou, J., 2019. Regulating bulk-heterojunction molecular orientations through surface free energy control of hole-transporting layers for high-performance organic solar cells. *Advanced Materials*, 31(17), p.1806921.
- [8] Qin, Y., Uddin, M.A., Chen, Y., Jang, B., Zhao, K., Zheng, Z., Yu, R., Shin, T.J., Woo, H.Y. and Hou, J., 2016. Highly Efficient Fullerene-Free Polymer Solar Cells Fabricated with Polythiophene Derivative. *Advanced Materials*, 28(42), p.9416.

Chapter 6: Flow synthesis of P3HT and upscaled production

6.1 Introduction

Materials produced by batch and flow chemistry methods are benchmarked in this chapter. Over the past decade, a new alternative method of chemical production has been developed to allow continuous materials synthesis of modern organic chemicals: flow chemistry [1]. P3HT polymer synthesis as an ideal scalable and reproducible material for large scale production and has been synthesised by flow chemistry method in previous literature, [6]–[21]. However, modification/upgrading of existing ‘flow’ synthesis apparatus, addressing of the issues of blockages in the system [6] was required. In the current study, a monomer solution and a catalyst solution were used to improve the flow synthesis of P3HT on an upscaled production. In this chapter, P3HT synthesis is introduced by both large-scale batch and flow chemistry methods. The resulting P3HT was tested for purity by NMR and quality was benchmarked by checking performance in small scale organic solar cells. A new medium-scale flow chemistry apparatus was built, and optimisation of the flow system was undertaken to achieve a sustainable flow chemistry facility suitable for effective P3HT material upscale, with improved reaction time, cost, and yields.

6.2 Experimental

The reaction method to produce P3HT polymer in this thesis follows Grignard metathesis polymerisation (GRIM). By this method we were able to produce large batch scale P3HT

(100 g) and flow chemistry production of 21 g per day. In terms of reaction mechanism (Figure 6.1), in the GRIM method 2,5-dibromo-3-dodecylthiophene is reacted with methyl magnesium bromide in THF to synthesise 2-bromo-5-chloromagnesio-3-dodecylthiophene and 5-bromo-2-chloromagnesio-3-dodecylthiophene in a 80/20 ratio, followed by a Kumada coupling using Ni(dppp)Cl_2 [17]. There is a regioisomerism observed by McCulloch et al. in this reaction with typical percentages of 80 % yield of isomer 2 and 20 % yield of isomer 3, as shown in Figure 6.1 below. The ratio of these isomers depends on the temperature of the reaction, with higher temperature favouring isomer 3. When the polymer is produced in the next polymerisation step, isomer 3 does not react due to steric effects between the β hexyl chain and the nickel ligand, which leads to a decrease in the polymer yield.

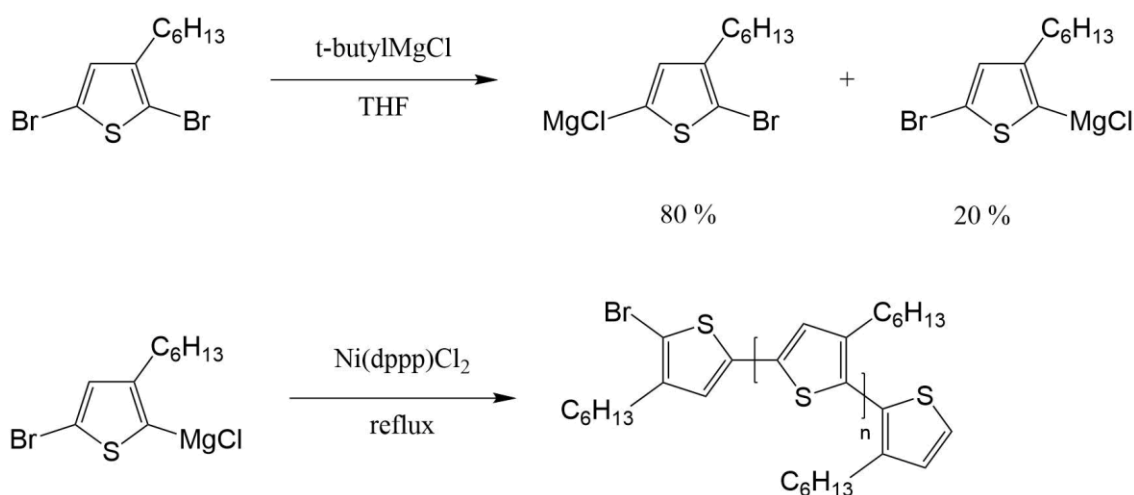


Figure 6.1 P3HT synthesis by following Grignard Metathesis polymerization

The only disadvantage of the Grignard metathesis reaction method for the flow chemistry is the poor solubility and dissociation of the nickel initiator (Ni(dppp)Cl_2) and high molecular weight P3HT in THF [6]. The solubility is a serious issue in flow chemistry

where it can cause precipitation in the flow chemistry reactor and thus create blockages of the tubing in the system. In order to overcome this challenge 3,4-ethylenedioxythiophene (EDOT) solvent was explored as an alternative solvent/additive and details of this change are introduced in this chapter.

6.2.1 Scale up of materials via batch and flow chemistry

As discussed previously in Chapter 1, flow chemistry is an advantageous synthetic method as it is continuous, easy scalable with better reaction control and lower risk for hazardous reaction processes. In this chapter is demonstrated that by using flow chemistry method we can generate 32.04 g/day of uninterrupted P3HT polymer which is at total of 224.28 g/week at a cost lower than that obtained for batch chemistry (See Section 6.3.2). By simply utilising a higher flow chemistry system, this allows us large scale reaction without actual handling and monitoring of batches.

6.2.1.1 Large scale batch synthesis of benchmark materials

Large scale batch synthesis of standard materials such as P3HT, PCBM, ICxA and PEDOT:PSS was carried out in the Priority Centre for Organic Electronics (PRCOE) group. P3HT polymer was successfully synthesised by following Grignard methathesis (GRIM) method [18] with the experimental procedure detailed below.

In a 5 L three-neck round bottom flask 2,5-dibromo-3-hexylthiophene monomer (258 g, 170 mL, 0.80 mol) and 1 L of anhydrous THF was added under nitrogen atmosphere. Then Grignard reagent (400 mL of 2M *t*-butylMgCl in diethylether) was added at temperatures below 40 °C to avoid the exothermic reaction heating the solution above the boiling temp of THF (66 °C). After 30 min of stirring, another 3 L of anhydrous THF was

carefully added. Then 4.335 g (0.008 mol) of Ni(dppp)Cl_2 was added to the reaction mixture. As the solution starts to polymerise (after ~5 minutes) there is a colour change from the red colour of the Ni complex to orange and then after 10 minutes deep orange as the polymer occurs. At this point the polymerisation is completed and the solution was left overnight to thicken. The polymerised solution of P3HT was quenched with 4 L of methanol, 1.878 g of dimethylglyoxime and 12.6 mL of 32 % concentrated HCl. The quenched solution was then filtered immediately and purified by Soxhlet extraction using methanol and hexanes as a solvent. The P3HT polymer yield collected was 89 g, 67 % following Soxhlet extraction, Figure 6.2.

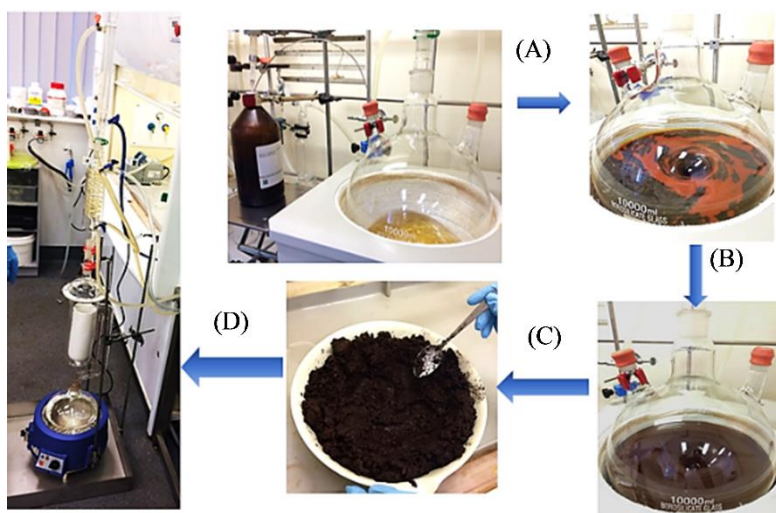


Figure 6.2. (A)-(C) Poly(3-alkylthiophene) P3HT synthesis by Grignard methathesis (GRIM) method; (D) soxhlet extraction purification method with methanol, hexanes and chloroform solvents. Yield 89 g (67 %)

The resulting P3HT batch was tested in BHJ devices, Figure 6.3, and Table 6.1. Figure 6.3 introduces, this P3HT's batch device performance comparison with the latest batch

P3HT(20K) as well as with the P3HT(40K) as for a reference, to explain the similarity in efficiencies obtained.

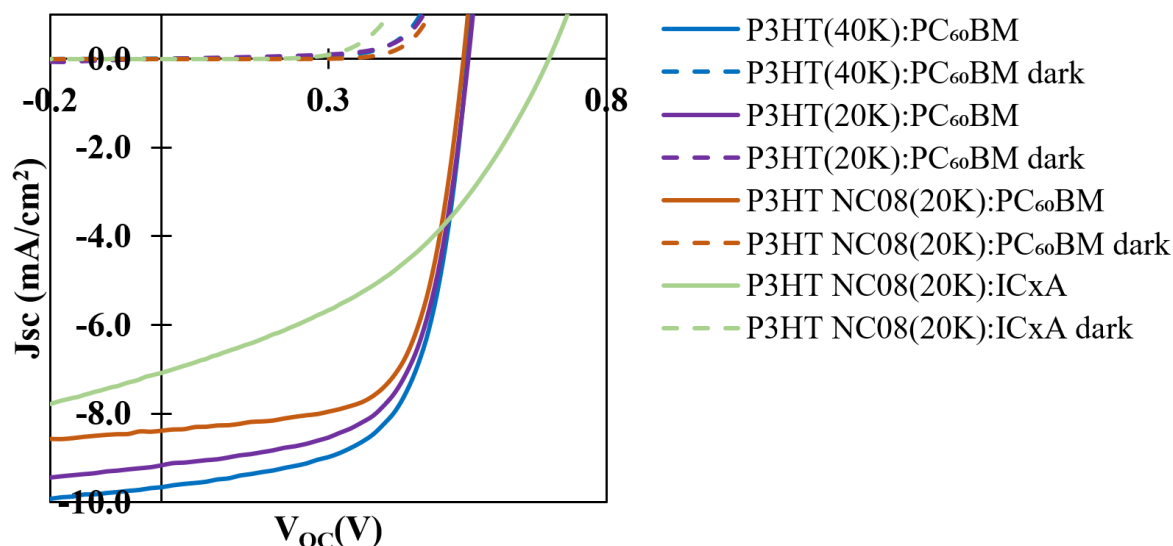


Figure 6.3 *I-V* characteristics of BHJ polymer:fullerene OPVs. Masked not annealed device average of all 6 cells (one substrate only per blend)

Table 6.1 Polymer:fullerene BHJ solar cells

Active Layer	PCE (%)	V_{OC} (V)	J_{SC}	FF (%)
P3HT	2.97 ± 0.02	0.54 ± 0.00	8.37 ± 0.02	0.66 ± 0.00
P3HT NC08(20K):ICxIA	1.64 ± 0.04	0.68 ± 0	5.37 ± 0.09	0.45 ± 0
P3HT(20K):PC ₆₀ BM*	3.02 ± 0.17	0.55 ± 0.01	8.84 ± 0.38	0.62 ± 0.02
P3HT(40K):PC ₆₀ BM*	3.10 ± 0.15	0.55 ± 0.01	9.45 ± 0.60	0.60 ± 0.02

*P3HT:PC₆₀BM control devices from the batch P3HT NC05

We synthesised PCBM (0.546 g, 30%) following the original synthesis method by Hummelen et. al. [18]. Firstly, a starting material for PCBM (methyl-4-benzobutyrate p-tosylhydrazone) was prepared by adding methyl 4-benzobutyrate (25.343 g, 0.123 mol), p-toluenesulfonyl hydrazide (27.445 g, 0.147 mol) and methanol (90 mL) into a 250 mL round bottom flask. This solution was stirred for 10 min at 85 °C and then refluxed for 6

hours. Once, reaction was completed, it was cooled down to room temperature and stored in the freezer overnight to crystallise. The mixture was filtered, washed with methanol and dried to afford the product as white crystals. Yield 43.749 g. (95 %).

Next, solution 1, methyl-4-benzobutyrate *p*-tosylhydrazone (0.14 g, 0.37 mmol), sodium methoxide (0.02 g, 0.38 mmol) and 2.7 mL of anhydrous pyridine were added into a 250 mL 3-neck round bottom flask under inert atmosphere at 70 °C for 30 minutes until dissolved. Solution 2 was prepared in another 3-neck round bottom flask, where C₆₀ (0.13 g, 0.18 mmol) was stirred in anhydrous 1,2-dichlorobenzene (9 mL) for 30 minutes. Then solution 1 was added to solution 2 over 35 minutes and stirred for 1 day at 70 °C. The resulting mixture was then filtered, washed with 1.08 L of methanol, extracted with 4 x 35 mL of chloroform and then filtered with a further 1.35 L of methanol to collect the crude. The crude product was column chromatographed with an open-fulleroid PCBM yield 0.546 g, 30 %. The rest of the column chromatography fractions (bis-PC₆₀BM, tris-PC₆₀BM) were not recovered. Synthesis of the PCBM, the purification and thin layer chromatography (TLC) characterisation technique used to determine purity of the material are displayed in the picture Figure 6.4.

ICxA is another cheap and effective that we synthesised as for the fullerene mixture for OPV fabrication. It was prepared following the published synthesis by N.A.Cooling et. al. [20]. In a 100 ml round bottom flask, C₆₀ fullerene (4.26 g, 0.006 mol), 1,2-dichlorobenzene (0.074 L) and indene (1.38 g, 0.012 mol) were refluxed for 48 hours. The reaction mixture was then cooled down to room temperature and precipitated with 0.35 L of methanol. The precipitate was subsequently filtered, and the brown coloured solid was collected. This filtered solid was mixed in 60 mL of chloroform and stirred for 1 hour. The fraction which was soluble in chloroform was collected and the extraction

process was repeated four times. Once completed, the ICxA was precipitated in 178 mL of methanol, filtered, dried and collected as a brown powder crude. The obtained yield of the fullerene mixture was 4.685 g, 73 % based on an average ICMA : ICBA : ICTA ratio of 36:52:12 [20] (Figure 6.4).

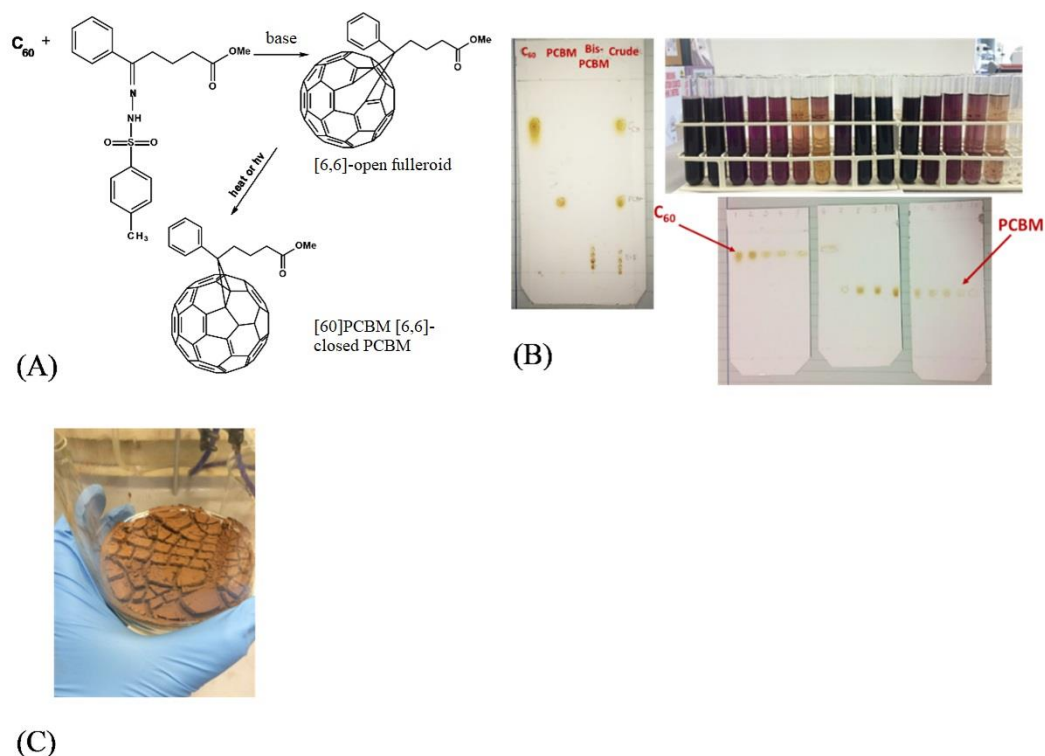


Figure 6.4. (A) Synthesis of PC₆₀BM. Recovered C₆₀ = 0.290g, PC₆₀BM yield: 0.546 g (30%) bis-PC₆₀BM, tris-PC₆₀BM were not recovered; (B) thin layer chromatography characterization of PC₆₀BM; (C) ICxA batch synthesis yield: 4.685 g (73.4%)

Another benchmark material: PEDOT:PSS performs as a hole-transport layer an OPV device, or as an electrode layer if modified for high conductivity through the addition of DMSO. The PEDOT part is a polythiophene which is insoluble in water but is synthesised in the presence of PSS to form an aqueous dispersion. PEDOT:PSS was prepared by us, following a published synthesis method [6] Figure 6.5. To a 6 wt % NaPSS solution (48

g NaPSS made up to 800 mL with RO water was added 19.20 g of EDOT (14.4 mL, 0.135 mol) to give a mass ratio of 1:2.5 PEDOT:PSS and an initial solids content of 6.72 %. 38.4 g of $\text{Na}_2\text{S}_2\text{O}_8$ initiator (0.161 mol) was added and the reaction mixture made up to 3000 mL with RO water to give an approximate solids content (EDOT and NaPSS) of 1.79%. After stirring for 10 mins, 300 mg of $\text{Fe}_2(\text{SO}_4)_3$ (7.5×10^{-4} mol) 370 mg of $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (approx. 7.5×10^{-4} mol) was added and the solution stirred vigorously for 20 hours. To measure the conductivity of resulting PEDOT:PSS, sheet resistance was measured on a section of single R2R stripe as 2610 Ω/sq . This was a 2 point measurement on $\sim 1 \text{ cm}^2$ square of PEDOT:PSS film (approximately 200 nm thick) with highly conducting busbars positioned on opposing sides of the square. R2R-coated single stripe printed layers were coated from an ink formulated by volume as 75% of a $\sim 1\%$ PEDOT:PSS suspension in water, 19.9 % IPA, 5 % DMSO and 0.1 % FSO. The synthesised PEDOT:PSS batch had relatively higher sheet resistance than previous batches with $\sim 600 \Omega/\text{sq}$, compared to a typical commercial hole-transport PEDOT:PSS with 40 Ω/sq . While there are some challenges that exist in PEDOT preparation, particularly around the selection and use of ion exchange membranes during purification, this process, as well as doping methods, are very poorly described so far due to the commercial nature of the material. PEDOT (in PSS solution) polymerisation (1:2.5 PEDOT:PSS), ion exchange, dialysis through a 3000 molecular weight cut off (MWCO) PES filter are shown in the Figure 6.5.

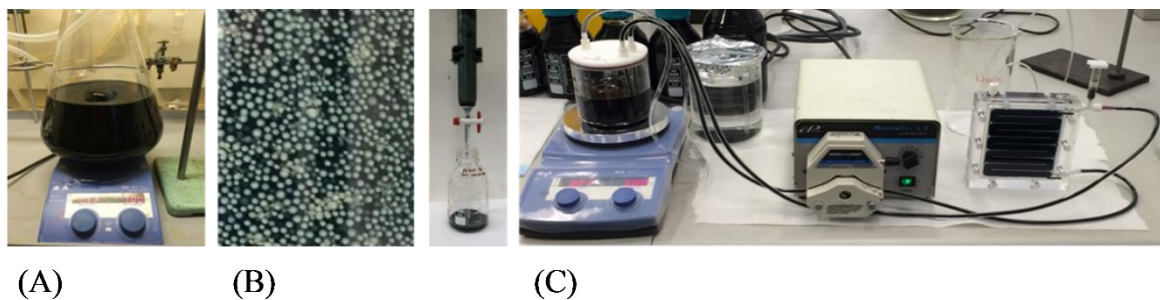


Figure 6.5 PEDOT:PSS synthesis (Sheet resistance measured on a single R2R stripe = 2610 Ω/sq) (A) PEDOT (in PSS solution) polymerisation (1:2.5 PEDOT:PSS); (B) Ion exchange; (C) Dialysis through a 3000 molecular weight cut off (MWCO) PES filter should remove both ions and unreacted EDOT from the solution.

The synthesised materials were tested in the small scale OPV devices, following the procedure as published by M. Griffiths [24] and compared to the control P3HT:PCBM device from previous COE batch NC05. BHJ devices were prepared from P3HT:PCBM and P3HT:ICxA solutions with concentration of 36 mg mL^{-1} and a donor:acceptor ratio of 1:0.8. The P3HT and PCBM were dissolved in chlorobenzene by sonication, without heat, for 30 min and stirred on a hotplate at 60 $^{\circ}\text{C}$ for 2 hrs. The same procedure was applied to the P3HT:ICxA prepared solution. A PEDOT (Al4083) layer with a thickness of 40 nm was deposited into ITO patterned substrates. Then the active donor:acceptor layer 100-104 nm was deposited by spin coating and dried at 60 $^{\circ}\text{C}$ for 5 min under nitrogen atmosphere. Calcium and aluminium electrode layers were deposited by vacuum deposition onto these BHJ layers. The substrates were then pre-annealed at 140 $^{\circ}\text{C}$ for 4 minutes.

As it is shown in the Table 6.1 above, devices with the synthesised materials incorporated in the active layer P3HT NC08(20K):PCBM and P3HT NC08(20K):ICxA possess similar

performance (PCE = 2.97 % and 1.64 %, respectively) with the compared benchmark device P3HT(20K):PCBM (PCE = 3.02 %). The slight decrease in the power conversion efficiency can be explained by natural variations in the fabrication procedure which can affect the overall device structure and subsequently the device efficiency. Overall, synthesised P3HT polymer, fullerenes such as PCBM and ICxA and the conductive polymer PEDOT:PSS had very similar device performance as previous batches made in the Priority Research Centre for Organic Electronics (COE) group at the University of Newcastle.

6.2.1.2 Flow chemistry synthesis method for benchmark and selected materials

Detailed synthesis of the benchmark standard OPV polymer; P3HT, by flow chemistry is introduced in this section. This work details the chemistry of the flow method, successful reaction upscale, P3HT physical characteristic and concludes with results of the synthesised P3HT incorporated in photovoltaic devices.

After careful examination of the synthesis of selected new OPV materials (PDCBT and ITIC) for the upscaled production in this thesis, it was found that they were not directly suitable for flow chemistry. Despite excellent temperature and reaction concentration control in the flow reactor, the main obstacle for synthesising polymers in flow reactors is blockages due to precipitation of high molecular weight and low solubility products and hence reaction failures. Reactions at the bromination step (see Chapter 4 section 4.2) for PDCBT and using n-butyllithium solution with maintaining temperature below -78 °C in some of the steps for producing ITIC (see Chapter 4 section 4.6), make the synthesis of these materials incompatible with the flow synthesis technique. However, it is possible

that individual steps in these syntheses could be adapted to flow chemistry with advantages to cost and yield.

6.2.2 General design for P3HT flow synthesis

6.2.2.1 First apparatus design for P3HT flow synthesis via dual pump system

Recent publications on the synthesis of P3HT using Grignard Metathesis (GriM) were reviewed with the view to upscale and improve production of P3HT using flow synthesis. This literature review focused on “flow” synthesis of highly regular, and low PDI P3HT to achieve an understanding of the current “state of the art”. It also helped to find a suitable way of upscaling the flow synthesis as well as necessary improvements required for the current P3HT “flow” synthesis apparatus.

As discussed previously in Chapter 1 (section 1.7), initially a dual pump assembly was designed as shown in Figure 6.6 to synthesis P3HT polymer using flow chemistry. This system was designed and fabricated following the process described by previous PhD student M. Wilson’s study [21]. The system maintained a constant flow rate with low back pressure. In this dual pump system, two solutions were used; one solution was kept in pump 1 and the other solution was taken in an air-tight glass syringe and then placed into pump 2 (see Figure 6.6). In the current study, a monomer solution and a catalyst solution were used. Post reaction, the mixed solutions were pumped into a receiving reservoir, where the polymer was quenched. However, some blockages occurred during P3HT polymer production using this dual pump system, which was a major issue that encouraged design improvements for this system (See section 6.6.2.2.2).

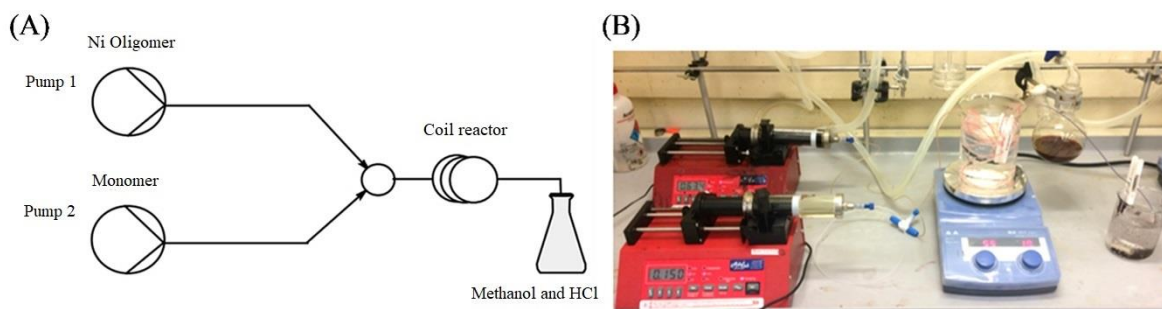


Figure 6.6 (A) Dual pump continuous P3HT flow synthesis diagram [6] and (B) dual-pump flow chemistry assembly.

Based on this literature review, the following issues were identified in the dual pump system:

- The apparent poor stability (e.g., high sensitivity to trace contaminants such as water) of the commonly utilised $\text{Ni}(\text{dppp})\text{Cl}_2$ catalyst.
- Low solubility of $\text{Ni}(\text{dppp})\text{Cl}_2$ in the THF solvent typically employed in GRIM.
- Limitation of reaction rate imposed by operating temperature constraints ($< \sim 55^\circ\text{C}$) imposed by the low THF solvent boiling point.

6.2.2.2 Optimisation of the flow chemistry setup to the upscale

In light of insight collected from the literature review [2]-[16], as well as that presented in Mitchell's thesis [21] the following modification/upgrading of our existing 'flow' synthesis apparatus was required:

- larger, 1.6 mm² diameter bore polytetrafluoroethylene (PTFE) tubing to facilitate a higher volumetric throughput (and possibly increase reliability by lowering the risk of blockage or fouling).
- larger, gas-tight reagent syringes to allow greater syringe batch size and reducing possibility of reagent contamination.
- improved mixing tee for 1.6 mm² bore tubing.
- non-return valves of inert construction (Viton is incompatible with THF) suitable for use with the 1.6 mm² PTFE tubing to allow continuous feeding (from N₂ blanketed, reagent reservoirs) and fill – discharge cycling of the syringe pumps, converting the apparatus to a continuous flow method.
- components for N₂ gas blanketed reservoir or enclosure (e.g. Schott bottles or large pipe tee with transparent flanges and possibly pressurised – see Figure 6.7 below).
- components for development of an in-line mixing system based on an axially oscillating “flea” driven by an external solenoid (e.g., from a fuel injector).

A schematic diagram of the modified continuous flow reactor system is illustrated in Figure 6.7 and comprises the single length of PTFE tubing of ≥ 1.5 mm² inner diameter into which one syringe injects the monomer solution, whilst the catalyst solution is injected by the second syringe. P3HT polymerisation starts in the mixing tee piece, where the coil is immersed into a water bath at chosen modified temperature. Resulting growing beads of the polymer are then quenched in acidified methanol. Monomer, catalyst and reaction quenched solutions are stored in N₂ gas blanketed reservoirs.

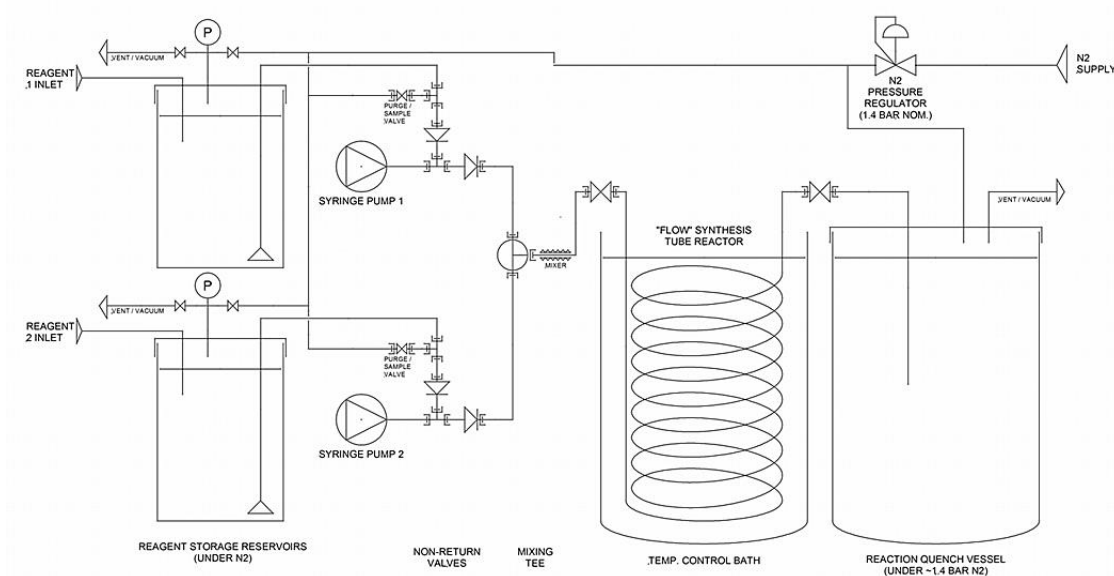


Figure 6.7. Schematic diagram of proposed flow synthesis apparatus

Several major changes from the initial dual syringe system were proposed and implemented:

- an alternative solvent / catalyst different to the THF / Ni(dppp)Cl₂ combination typically used, such as those used by Kumar et al (2014) or Bannock et al (2016) that would allow us to avoid the often experienced problems of catalyst solubility and stability and possibly allow operation at an elevated temperature due to an elevated solvent boiling point.
- a moderately pressurised (~ 1.5 bar / 20 psi) N₂ enclosure or (more simply) a blanketed quench vessel (Figure 6.8 (A)) headspace that allows flow synthesis to occur at a moderately increased pressure that again allows a raised solvent boiling point. This is almost certainly a better alternative to the original idea of using a standard 20 psi chromatography back pressure

regulator (BPR) at the end of the reactor tube, due to the likelihood of fouling of the BPR.

- the proposed in-line mixing system possibly as part of a customised mixing tee (since mixing in the initiation stage of the polymerisation has been identified as critical for low PDI product [11].

Subsequently, in the further development of the system it was necessary to introduce software control for running the apparatus syringe pump continuously and to regulate the transport of monomer and catalyst solutions under the applied pressure in the system.

Figure 6.8 (B))

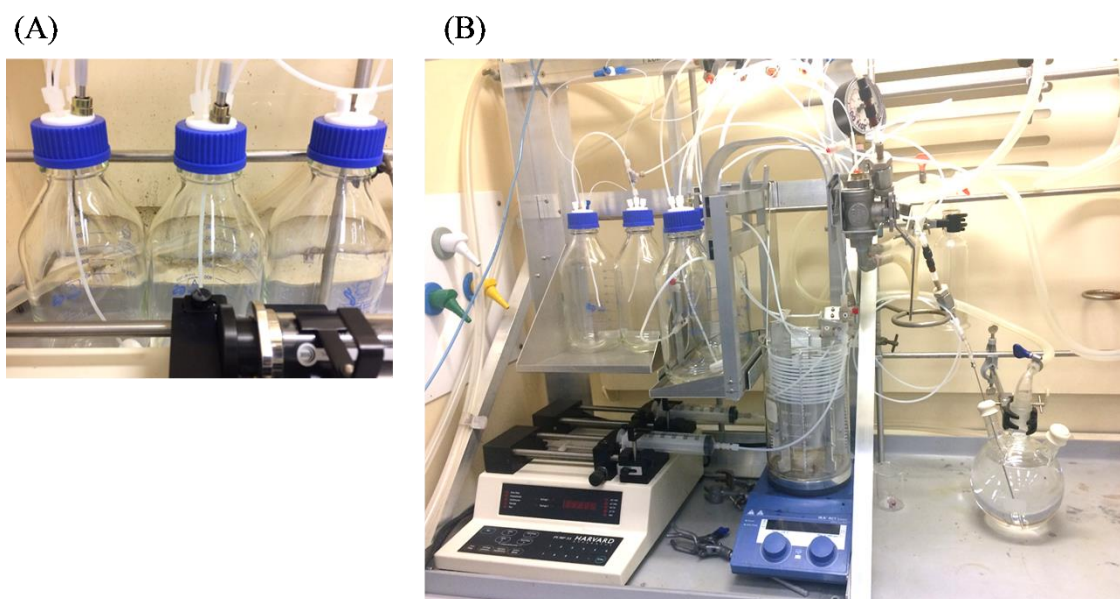


Figure 6.8 (A) Schott bottles with transparent pressurised flanges; (B) updated apparatus for the flow chemistry run

6.2.2.3 Effect of micro-mixing during P3HT production and its importance in the flow synthesis

In order to achieve good synthetic outcomes every aspect of the physics of flow in the reactor must be investigated. To resolve the polymer blockages which occurred during the synthesis and ceased the flow reaction, Dr Tim Lewis introduced a mixing component; a magnetically operated active mixing tee piece, as shown in Figure 6.9 (A) and (B). In the photo a copper wire insulated inside glass was placed inside the mixing piece, when connected to a power source it vibrates under the influence of the magnet which allows us to achieve proper mixing of the solutions and improve the ratio for polymerisation. Ultimately, the constant motion achieves best results for the flow reactor in a continuous manner during the synthesis which potentially makes the flow synthesis less expensive, easier, and less dangerous for the scaling up, and critically, allows better control of polymer molecular weight.

(A)



(B)

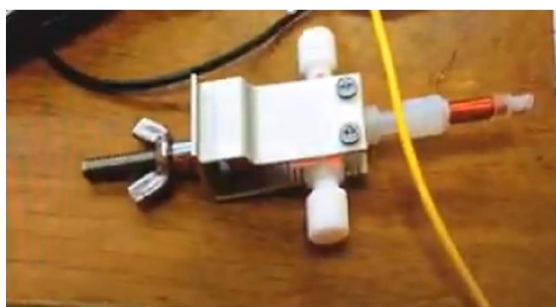


Figure 6.9 (A) copper rod encapsulated inside glass; (B) magnetically driven active mixing tee for the flow chemistry apparatus

6.2.2.4 P3HT flow synthesis development from a small scale up to large scale

The initial experiment was performed using the dual pump flow chemistry apparatus shown in the Figure 6.6. Based on the literature survey [2],[3], [4]–[6], [8]–[16], there are two most effective continuous flow chemistry methods which have been applied to improve and upscale the flow synthesis of P3HT by Grignard metathesis polymerization method.

The first method we have adapted is an optimisation of a method developed by former COE PhD student Dr Mitchell Wilson, who was able to remove the poorly soluble neat Ni(dppp)Cl_2 initiator and instead use oligomer chains complexed to Ni to improve the suitability for flow chemistry by improving catalyst solubility in organic solvents, Figure 6.10. However, based on the previous investigations on optimisation for the flow system (with rrP3HT yields of 32-55 % [21]) which is represented earlier in Figure 6.6 (A), a few improvements were considered to aid the situation:

1. Find a better solvent for the Ni(dppp)Cl_2 and P3HT, to avoid blockages in the flow chemistry tubing.
2. Determination of P3HT solubility in THF during the flow reaction.
3. Determination of the Ni(dppp)Cl_2 solubility in THF and EDOT in particular
4. Scale up by increasing tubing diameter and achieve consistent flow rate control.

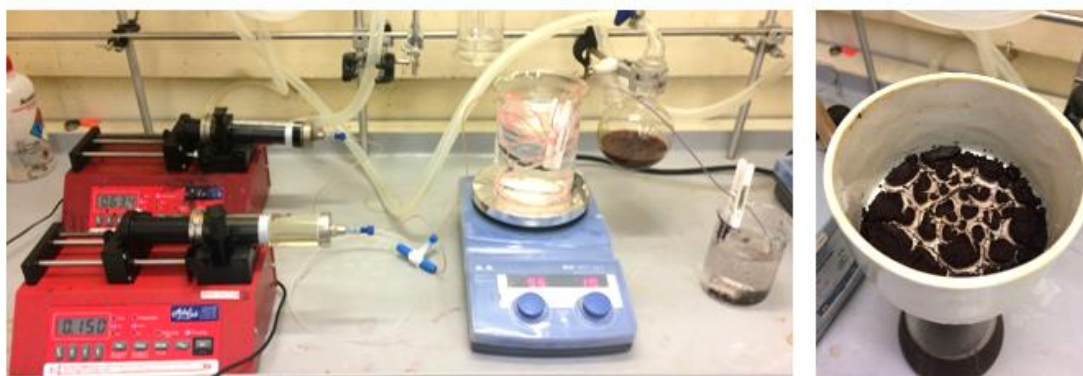


Figure 6.10. P3HT flow synthesis 0.5 g scale. Mass recovered 0.305 g (yield = 53 %)

In the second method, I have modified the procedure described by Kumar et al., where they achieved rapid P3HT flow synthesis [22] by using 3,4-ethylenedioxythiophene (EDOT) to improve the solubility of Ni(dppp)Cl_2 , as this catalyst has poor solubility in pure THF. We are trying to achieve a similar result and dissolve Ni(dppp)Cl_2 sufficiently to perform flow chemistry without requiring the preforming of an oligomer solution [22]. An added advantage of this method is that the introduction of EDOT into the catalyst solution increases its stability and it remains reactive for up to two weeks, as Kumar et al. report, whereby typically the instability of the oligomer solution is observed over few hours. This advantage increases the potential in scalability of the flow system.

To investigate the effect of EDOT in my standard P3HT polymer synthesis, successful batch synthesis experiments were performed, by simply adding EDOT to a batch reaction (standard batch reaction) which demonstrated that the polymerisation remained successful in the presence of EDOT, Table 6.2. The aim of this experiment was to check that EDOT does not hinder the reaction or cause other problems with a standard batch synthesis method, so that we can proceed with the flow chemistry optimisation. We proceeded with the soxhlet purification of P3HT with methanol and hexane solvents.

However, the polymer ^1H -NMR showed that polymer may not be as pure as the standard batch. Therefore, the polymer was further purified by reprecipitation in methanol from a chloroform solution and ^1H -NMR results improved.

Table 6.2. P3HT with EDOT and without EDOT batch synthesis results

	Theoretical yield	Actual yield	Expected yield
P3HT with EDOT	~ 0.5 g (100 %)	0.346 g (69.2 %)	64 %
P3HT w/o EDOT	~ 1 g (100 %)	0.705 g (70.5 %)	64 %

With optimal batch conditions determined, an attempt to modify the flow system by the two methods described above was made by introducing identical monomer and catalyst concentrations, where catalyst solution concentration is exchanged with equimolar oligomer solution. This variation to the suggested concentrations reported in Kumar et.al [11] paper, performed well with high yield, which should be further optimised by variation of other parameters in the flow system and use of larger vessels will enable future mass production. However, so far, our attempts made in order to achieve improved flow synthesis of P3HT for a larger scale showed relatively low throughput of the product, so we chose to focus on small scale modifications firstly.

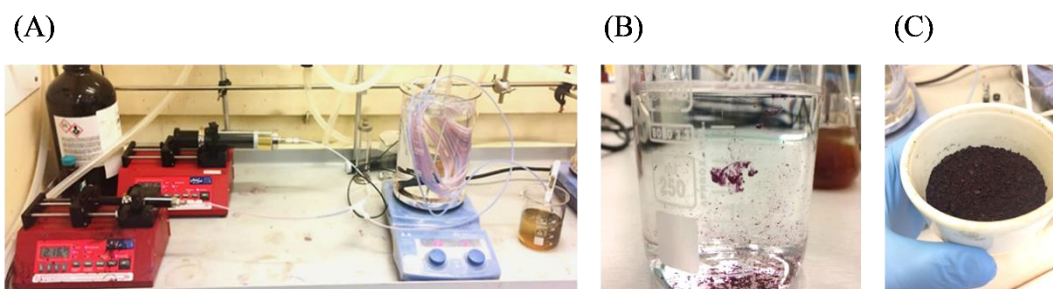


Figure 6.11. P3HT5KS flow synthesis with Ni catalyst solution without preinitiation. Flow synthesis (A); quenching of P3HT in acidified methanol (B); P3HT vacuum filtration (C). Yield: 1.0 g (56 %)

In Figure 6.11 (A) shown above, an upscaled tubing inner diameter of 1.5 mm² rather than 0.8 mm was introduced, which allows better free flowing of particulates (P3HT can precipitate in the tube as molecular weight increases) which reduces blockages. To achieve higher throughput for the flow chemistry polymerisation reactions, the flow reaction monomer and catalyst solution parameters such as concentration, pumping flow rates, temperature, mixing control and the residence time and their variation have been studied. A more detailed description of the flow chemistry parameters in my experiment are represented in Table 6.3 below.

Table 6.3 Upscaled flow chemistry experiment with 10, 20, 30 and 45 minutes residence time yields

Residence time (min)	Flow rates monomer	Flow rates catalyst	Volume collected (mL/min)	Monomer volume used (mL)	Catalyst volume used (mL)	Theoretical yield (g) at 100 %	Yield (%)
10	1.5	0.083	1.59 (135 ml)	127.5 (5.8 g)	7.1	3.01	1.78 (59%)
20	0.75	0.041	1.75 (350 ml)	331.7 (15.3 g)	18.3	7.90	1.35 (17%)
30	0.50	0.028	1.12 (280 ml)	265.3 (12.2 g)	14.7	6.29	1.58 (25%)
45	0.33	0.018	0.24 (110 ml)	104.2 (4.63 g)	5.8	2.39	0.90 (38%)

To increase the throughput of the polymerisation reaction, we firstly introduced larger diameter tubing, which improved the flow of particulates at temperatures above 50 °C, however blockages were formed in the tubes at the temperatures below that range (35-40°C) as a result of more efficient polymerisation reaction (i.e., better mixing in the narrower tubing). Therefore, in this reaction the temperature of 38 °C degrees have been applied, giving a purified yield of 1.0 g (56 %). Fabricated bulk heterojunction device from the same experiment but different P3HT batch (P3HT3KS) performance is compared in Table 6.4.

Table 6.4. Bulk heterojunction OPV devices performance (P3HT3KS: PC₆₀BM and reference P3HT 20K:PC₆₀BM blends). The *I-V* characteristics is represented for masked device average of 6 solar cells. Devices were annealed at 140 °C temperature for 4 min

Material	PCE (%)	V _{OC} (v)	J _{SC}	Fill Factor [%]
P3HT(P3HT3KS):PC ₆₀ BM	2.79±0.37	0.56±0.01	7.9±0.38	0.62±0.08
P3HT 20K:PC ₆₀ BM	2.47±0.25	0.55±0	6.65±0.67	0.67±0.01

The next step was to optimise the existing flow chemistry setup with the goal of improving reaction yield, considering further improvements as discussed above. The new upscaled setup, as shown in the pictures above in Figure 6.8 (A) and (B) was used for the large scale (theoretical amount of 21.36 g P3HT as 100 % yield) polymer synthesis. Firstly, 41.45 g of 2,5-dibromo-3-hexylthiophene (~30 mL) was loaded in a 1 L three neck round bottom flask with 200 mL of tetrahydrofuran (THF). Then 63 mL of t-butyl magnesium chloride was added. Monomer solution volume used was less than 72 mL and it was transferred slowly into a Schott bottle reaction vessel. For the catalyst solution,

initially 6.01 g of Ni(dppp)Cl₂ was dissolved in the mixture of 240 mL of EDOT and 24 mL of THF solvents. The solution was then heated for 10 minutes at 215 °C and ultrasonicated for 5 minutes without applying any heat. The catalyst solution of around 45 mL in volume was then transferred into another reaction vessel. At the same time, quenching solution was prepared for the polymer collection in the flow chemistry system, by dissolving 280 mg of DMGO in 700 mL of methanol with 14 mL of HCl (39%) and stirring solution for 15 minutes without heat applied. Polymer quenching solution was stored in the Schott bottle and connected in the flow chemistry setup. Preparation of these solutions and THF solvent transfer by cannula method under nitrogen atmosphere is shown in the pictures in Figure 6.12 (A), (B) and (C) below. Upon completion of solution preparations, these were transferred into the flow chemistry system as shown in Figure 6.13 (A), each of reagents were transferred into the appropriate reservoirs in the flow chemistry apparatus.

The system software was set to inject the catalyst solution at the flow rate of 0.5 mL/hr and monomer solution at 0.15 mL/min into the tubing. The tube diameter used was 1.5 mm² and the reaction pathway length was 3 m. Reaction temperature was controlled by a stirred water bath, placed on hotplate which was set up to 40 °C and 350 rpm speed. The flow chemistry apparatus during its operation is shown in Figure 6.13 (B), (C) and the final crude collected in the quenched solution is shown in Figure 6.13 (D).

In this experiment flow synthesis efficiency was tested by varying only one parameter which is a residence time. The residence time for each of 4 trials performed arise from setting a different flow rate for the reaction. For 10 minutes residence time the monomer flow rate was 1.5 mL/min and catalyst 0.083 mL/min; for 20 minutes 0.75 mL/min and 0.041 mL/min; for 30 minutes 0.50 mL/min and 0.028 mL/min; for 45 minutes 0.33

mL/min and 0.018 mL/min. There is a trend where flow rates decrease by a factor of 2 resulting in the residence time increasing by 10 minutes. More details are shown in the Table 6.3. Volumes of monomer and catalyst solutions used each set of experiments was recorded, as well as the volume of the collected mixture inside the quenching vessel. Yields for each test was recorded and are presented in Table 6.3 above. As we can see that the lowest residence time resulted in a higher yield outcome. This observation suggests that the active mixing component results in rapid mixing and reaction of the reagents. However, once the residence time is increased longer chain polymers are produced resulted in blockage due to the insolubility of the higher molecular weight polymer precipitating inside the tubing. Therefore, in this set of experiments management of the flow synthesis residence time for P3HT was performed successfully and 10 minutes residence time yielded 1.78 g, 59 % of P3HT. To meet higher yields goals for this synthesis improvement of the active mixing tee will help to avoid blockages and allow collection of larger quantities of the crude product, however the performance of active mixing tee was satisfactory with the shorter periods of residence times.

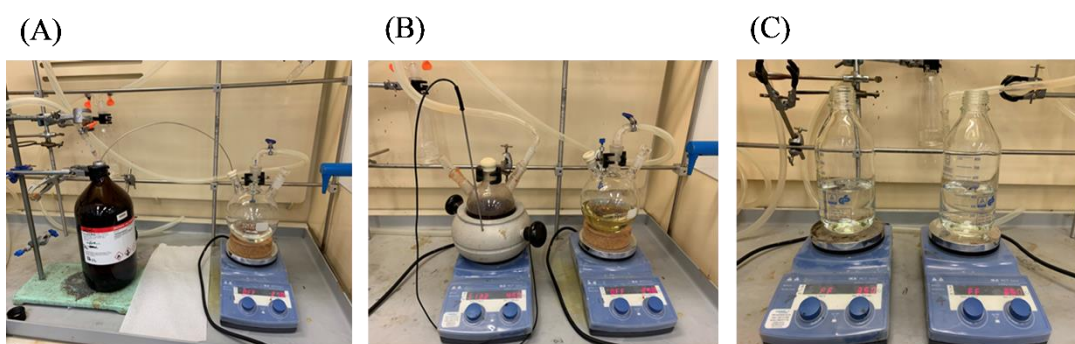
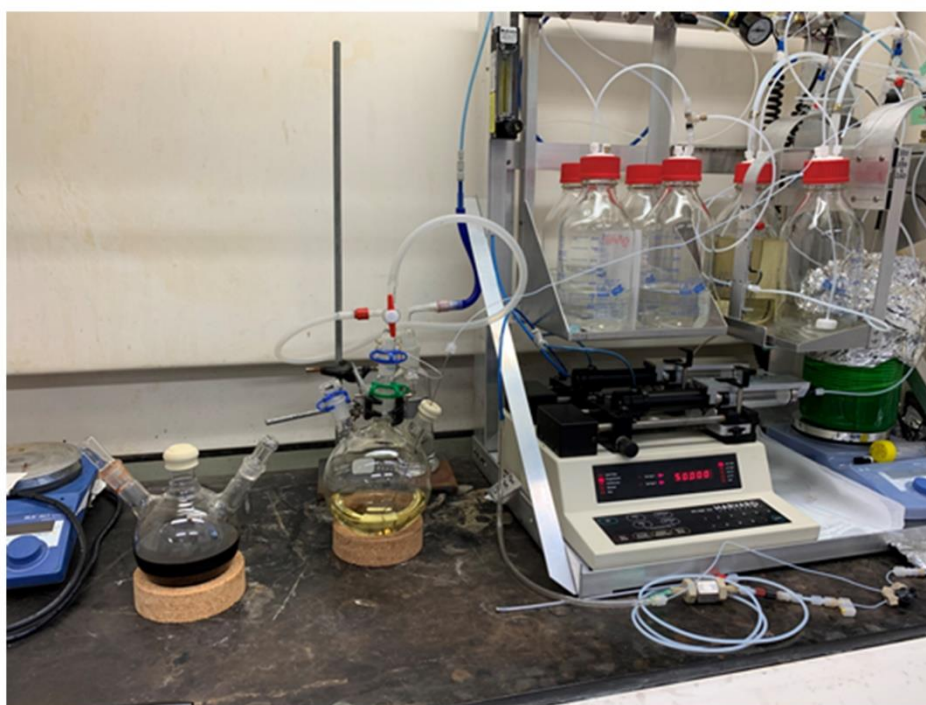


Figure 6.12 (A) THF solvent transfer under nitrogen to the reaction vessel by using cannula method; (B) monomer and catalyst solutions preparation; (C) quenching solution preparation

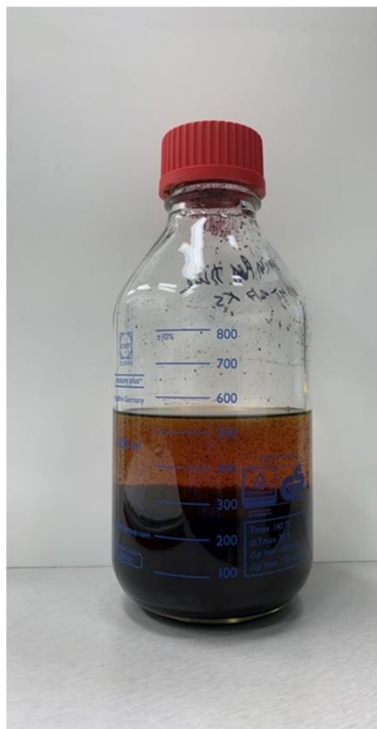
(A)



(B)



(C)



(D)



Figure 6.13 (A) transfer of reagent solutions into the flow chemistry system; (B) flow synthesis; (C) and (D) collection/quenching of P3HT polymer into acidified methanol

(A)



(B)



(C)



Figure 6.14 (A) dilution of acidified methanol; (B) and (C) vacuum filtration of crude P3HT

Once the P3HT crude from the 10, 20, 30 and 45 minutes residence times experiments was collected inside the quenching solution it was poured into methanol, in order to dilute

the acidified methanol, and then vacuum filtered to obtain crude P3HT (as shown in Figure 6.14 (A), (B) and (C))

Next, the Soxhlet extraction method with methanol and n-hexane solvents was performed on the crude materials to obtain the best purity quality since the crude material is likely to contain residual Ni catalyst and low molecular weight oligomers. Figures 6.15 (A), (B) and (C) demonstrate the process of P3HT purification by Soxhlet extraction method with the solvents used. It is common to purify P3HT with methanol first to remove remaining metal salts and monomers. Once the solvent becomes clear n-hexane was used to remove lower molecular weight chains from the obtained polymer to narrow the molecular weight distribution (MWD) [23].

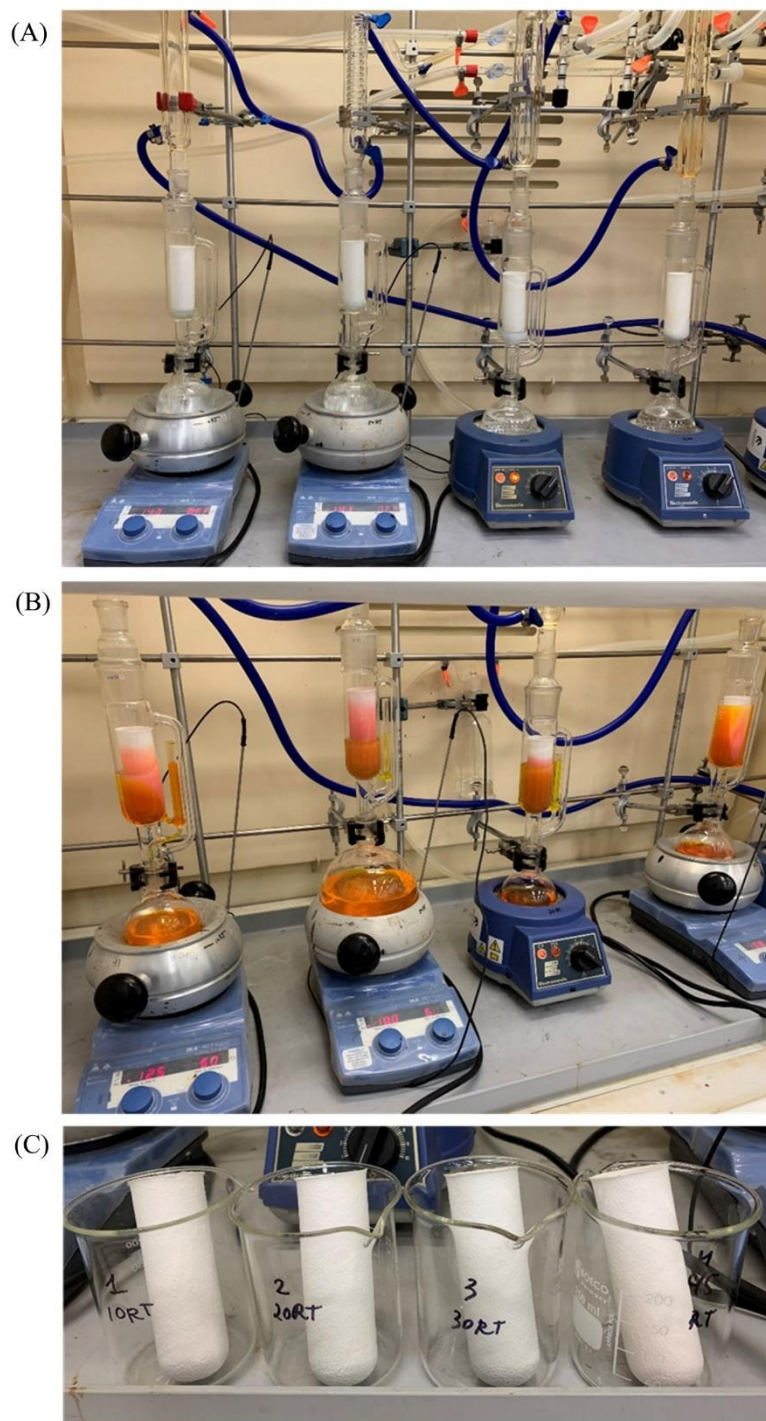


Figure 6.15 (A) Soxhlet extraction of polymer with methanol solvent; (B) Soxhlet extraction of polymer with n-hexane solvent; (C) thimbles with crude materials

6.3.2 OPV performance of flow synthesised P3HT in BHJ OSCs

After purification and vacuum drying, the P3HT device performance of the flow chemistry synthesised materials was tested on a small scale OPV devices. In particular 10 minute and 45 minutes residence time P3HT batches were chosen due their highest yields performances. These bulk-heterojunction photovoltaic devices were fabricated by following standard device making procedure as published by M. Griffiths et.al [24]. The active layers of the BHJ devices were prepared from P3HT:PCBM solutions (concentration of 36 mg mL^{-1}) and ratio of 1:0.8. The P3HT and PCBM were dissolved in chlorobenzene by sonication without heat for 30 min and stirred on a hotplate at 60°C for 2 hrs. A PEDOT (Al4083) layer with a thickness of 40-42 nm was deposited into substrate. Then a P3HT:PCBM layer of 100 nm deposited and dried at 60°C for 5 min under nitrogen atmosphere. Finally, calcium and aluminium electrode materials were deposited onto the BHJ layers. The substrates were then annealed at 140°C for 4 minutes.

Once devices were fabricated, they were transferred to a Newport Class A solar simulator with AM 1.5 spectrum filter for testing the OPV performance. The simulator and associated recording equipment records current density–voltage (J – V) curves and determines the OPV parameters: V_{OC} , J_{SC} , FF and PCE (%). In addition, EQE response was measured for the best devices from I - V characterisation. Overall, the hero device fabricated from P3HT (by flow chemistry) exhibited a slightly better performance of PCE $\text{max} = 2.04\%$, comparing to benchmark devices made from P3HT synthesised by batch with a PCE $\text{max} = 1.87\%$. The I - V characteristics for the devices are shown in Figure 6.16 below and the OPV parameters are further shown in the Table 6.5 (the value of OPV parameters is defined by (average $\pm$ standard deviation)). The EQE spectral response of devices is shown in Figure 6.17 and shows that the current output for

KS10RTP3HT:PCBM generates more current across the measured spectrum, consistent with the observed increased J_{SC} for these devices.

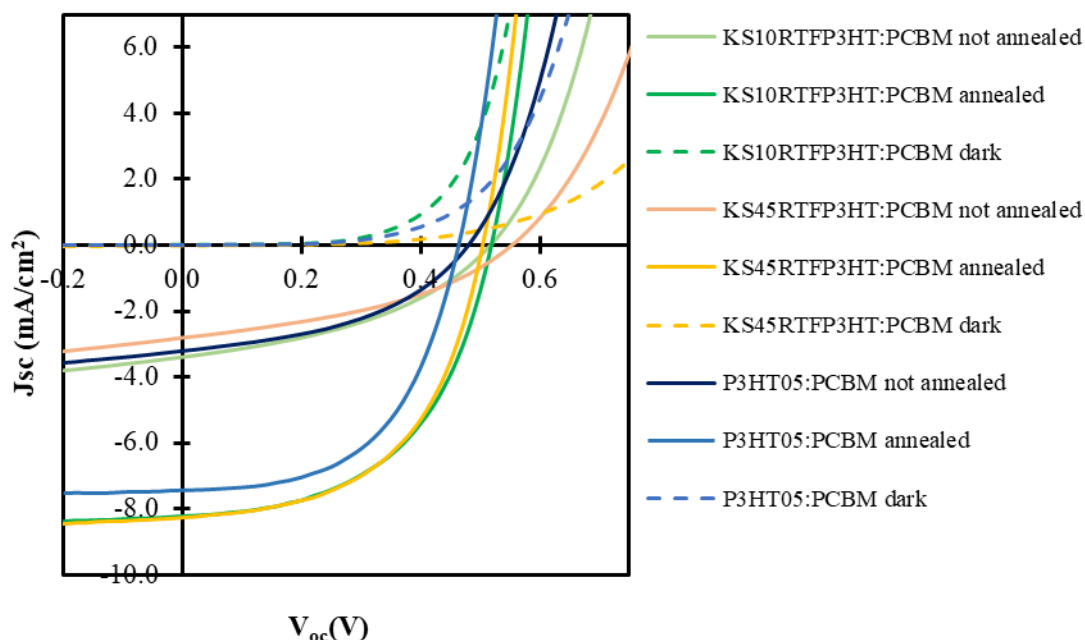


Figure 6.16 I - V characteristics of flow chemistry P3HT (KS10RTP3HT, KS45RTP3HT) comparing to batch synthesised P3HT (P3HT05) incorporated into OPV bulk heterojunction devices. Annealing conditions: 140°C for 4 min

Table 6.5 Flow chemistry P3HT (KS10RTP3HT, KS45RTP3HT) performance versus batch chemistry P3HT (P3HT05) OPV solar cells

Device	PCE (%)	V_{oc} (V)	FF (%)	J_{sc} (mA/cm ²)
KS10RTP3HT:PCBM	1.98±0.06	0.54±0.01	0.50±0	7.40±0.32
KS45RTP3HT:PCBM	1.95±0.02	0.56±0.01	0.50±0.01	7.05±0.33
P3HT05:PCBM	1.79±0.08	0.54±0.02	0.51±0.01	6.55±0.15
Annealed 140°C/4min				
KS10RTP3HT:PCBM	2.14±0.06	0.50±0	0.53±0.01	8.35±0
KS45RTP3HT:PCBM	2.16±0.03	0.50±0	0.52±0.01	8.25±0.11
P3HT05:PCBM	2.03±0.05	0.53±0.01	0.49±0.01	7.51±0.12

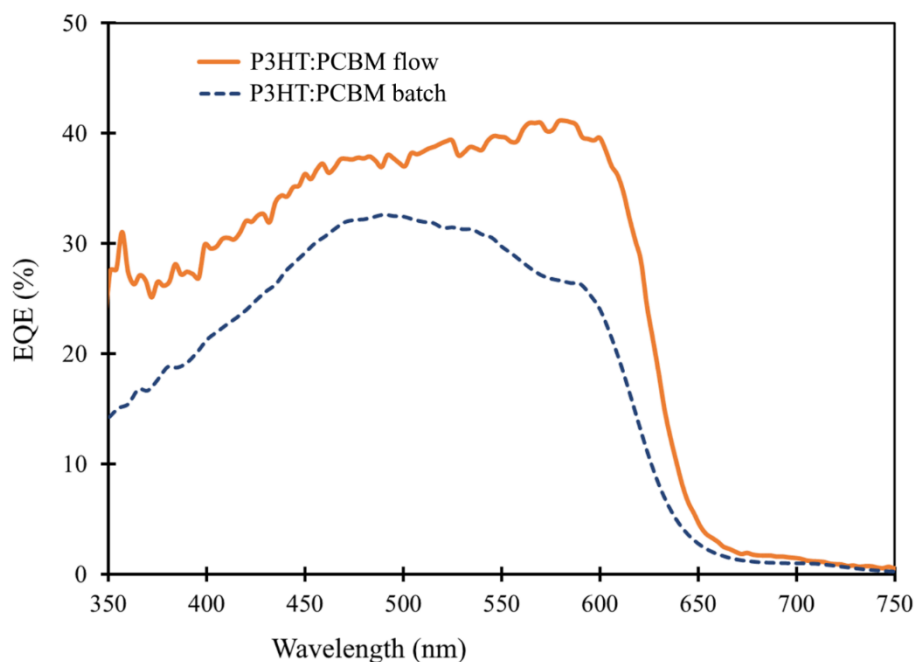


Figure 6.17 Batch P3HT05:PCBM dotted line and flow chemistry KS10RTFP3HT:PCBM solid line

6.3 Results and discussion

6.3.1 Yield calculation of P3HT synthesised by flow chemistry and its physical characteristics

A sample of 5 mg/mL concentration P3HT (KS10RTFP3HT) polymer in CDCl_3 solvent was analysed by ^1H -NMR recorded on a Bruker Avance-300DPX NMR spectrometer, and is shown in Figure 7.18. P3HT ^1H -NMR (300 MHz, CDCl_3): d H 0.94 (t, 3H), 1.37–1.43 (m, 6H), 1.70 (t, 2H), 2.84 (t, 2H), 7.0 (s, 1H).

The peaks of P3HT polymer have been labelled and were used for a molecular weight calculation technique. This method has been developed by Dushanthi S.Dissanayake et.al.

[24], it allows us to estimate molecular weight of the P3HT polymer by focusing on two peaks in the spectra at 2.6 and 2.8 ppm. The peak at 2.6 ppm arises from the α -methylene protons on the terminal tail of 3-hexylthiophene units and that at 2.8 ppm corresponds to the α -methylene protons of the hexyl polymer chain. The ratio of these two peaks gives us degree of polymerisation (DP_n). Once DP_n is known, by simply multiplying it with the P3HT repeating unit mass 166.282 g/mol we can determine the molecular weight of P3HT.

Flow chemistry P3HT batches molecular weights were compared for 10 minute and 45 minute residence time experiments (with the highest obtained yields). For 10 minutes, the DP of the polymer was calculated to be 35 and molecular weight of $\sim 6,233$ g/mol.

$$DP = 17/0.5 = 35$$

Where, M_w of $-CH_2 = 17$; and the integration is 0.5

Therefore,

$$M_n = 35 \times 166.282 = 5,819.87 + 167.282 + 166.282 + 79.90 = 6,233 \text{ g/mol}$$

Where, M_w of repeating P3HT unit = 166.282 g/mol; M_w bromine atom = 79.90 g/mol

Similarly, the M_n of the 45 minute residence time flow chemistry polymer was calculated. It appeared to be lower than that of the 10 minute residence time at $M_n \sim 3,240$ g/mol. To compare this data, we have estimated the batch P3HT molecular weight which is around 20K is shown in the Figure 6.18, 6.19 and 6.20. It is hypothesised that this drop in molecular weight of the isolated material is a result of the higher molecular weight

polymer precipitating in the flow system tubing and thus, artificially lowering the molecular weight of the remaining isolated material.

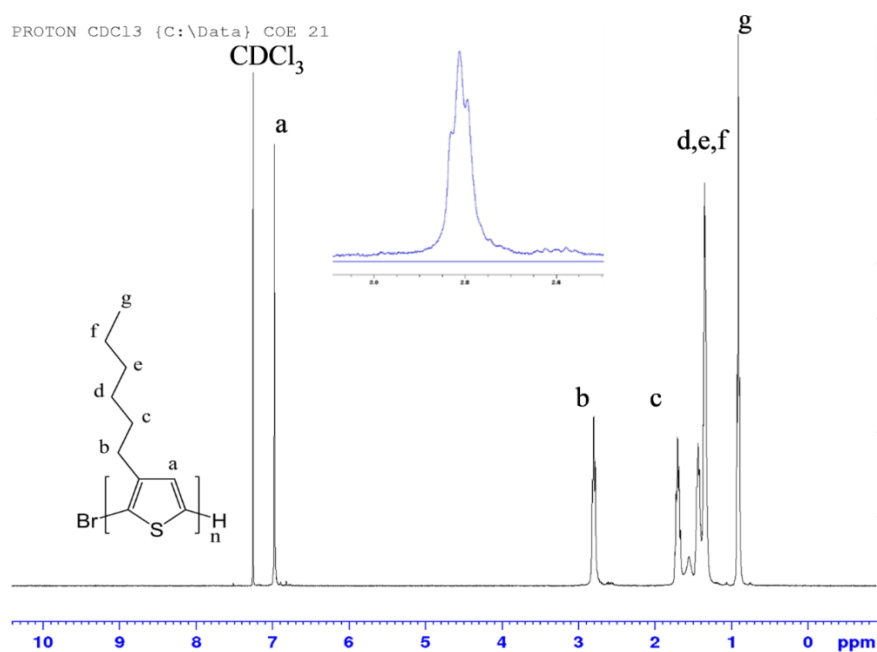


Figure 6.18 Flow chemistry P3HT ¹H-NMR peak assignment (KS10RTFP3HT)

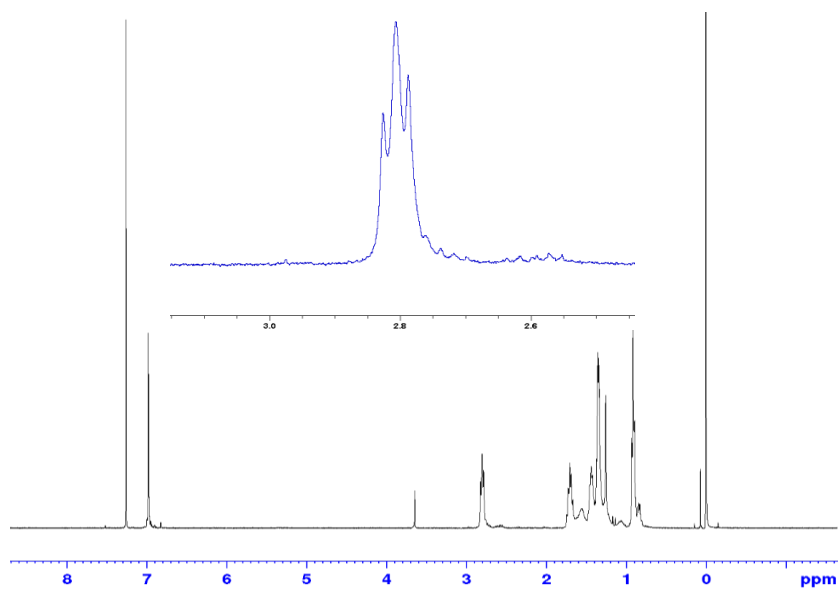


Figure 6.19 Flow chemistry P3HT ¹H-NMR peak assignment (KS45RTFP3HT)

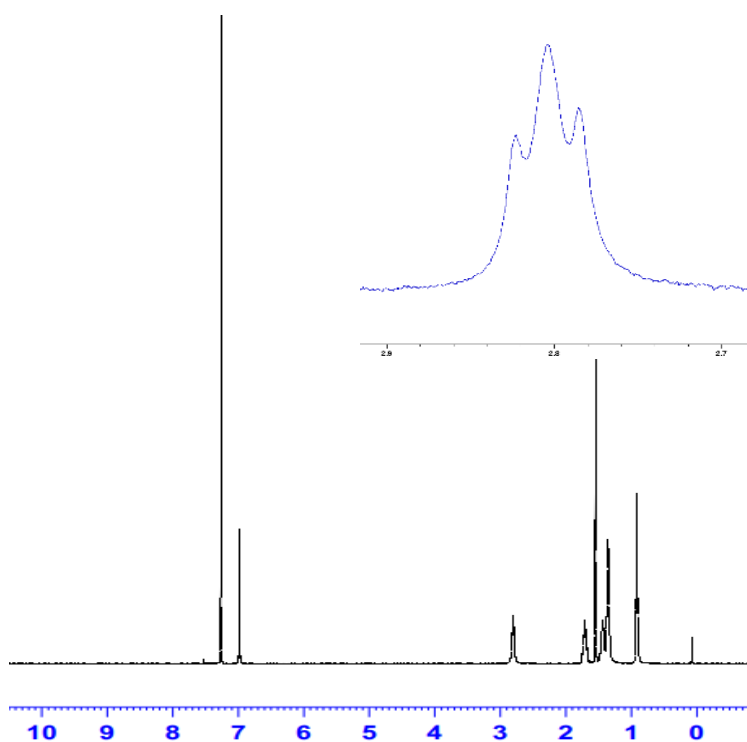


Figure 6.20 ^1H -NMR of batch P3HT

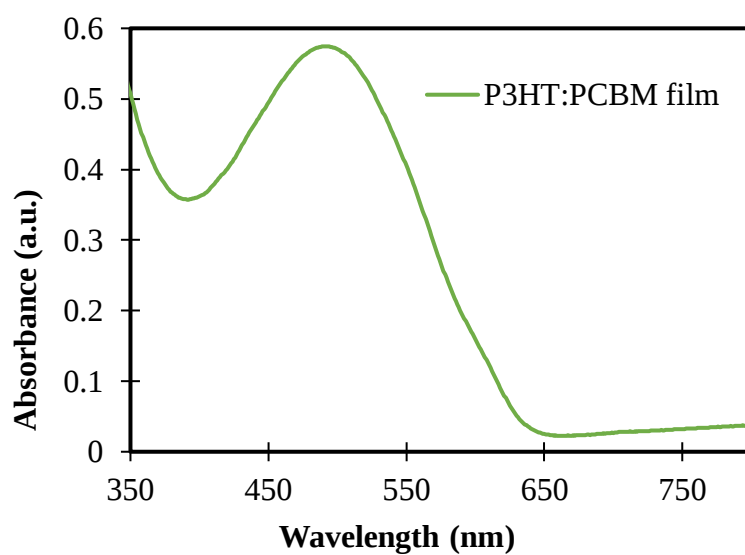


Figure 6.21 UV-vis Spectroscopy of P3HT:PCBM solution

The UV-vis spectra of active layer solution made of flow synthesised P3HT:PCBM is shown in Figure 6.21. A vibronic band at 550 nm is observed – indicating low crystallinity of the P3HT in this film, an indication of the low molecular weight of the material. The absorbance intensity is within the wavelength range of 400 –700 nm with the absorbance maximum at 500 nm, which is typical for P3HT films with low crystallinity.

6.3.2 Costing of optimised flow chemistry apparatus

The cost (AUD) breakdown of the flow chemistry apparatus components is shown below in the Table 6.6. Where items were not purchased for this project an estimation of purchase cost is given.

Table 6.6 Flow chemistry estimated cost

Valves, tubing and reagent reservoirs (inert materials)	\$5000
Glass syringes refitted with FFKM seals	\$2000
Dual channel syringe pump	\$10000
Vacuum pump	\$5000
Hot plate / magnetic stirrer	\$2000
Frame, gas regulators, manifold and valves for N ₂ /vacuum	\$2000
TOTAL	\$26000

Finally, the total cost per g was calculated for the flow chemistry synthesis of P3HT at \$7.97/g (Table 6.7), which compares favourably with the batch chemistry P3HT cost of \$8.56/g (Table 6.8).

Table 6.7 Cost to synthesise P3HT by flow chemistry

Material	Cost per unit (kg or L)	Amount required for 21.4 g scale of P3HT	Cost (AUD)
2,5-dibromo-3-hexylthiophene	\$632	41.45 g	\$26.20
<i>t</i> -butylMgCl	\$474	63 ml (58.65 g)	\$22.52
THF	\$90	224 mL	\$22.40
Ni(dppp)Cl ₂	\$375	6.01 g	\$2.25
Methanol	\$1.91	2.8 L	\$6.685
Hexane	\$9.63	2.8 L	\$26.96
HCl	\$15	70 mL	\$1.05
EDOT	\$260	240 mL	\$62.40
TOTAL			\$170.47 \$7.97/g

Table 6.8 Cost to synthesise P3HT by batch chemistry

Material	Cost per unit (kg or L)	Amount used for 133 g scale of P3HT	Cost (AUD)
2,5-dibromo-3-hexylthiophene	\$632	0.4	\$252.80
<i>t</i> -butylMgCl	\$474	0.6	\$284.40
Ni(dppp)Cl ₂	\$375	0.002	\$0.75
THF	\$90	6 L	\$540.00
Methanol	\$1.91	3	\$5.73
Hexane	\$9.63	3	\$28.89
Chloroform	\$6.60	3	\$19.80
HCl	\$15	0.4	\$6.53
		TOTAL	\$1,138.90 \$8.56/g

6.4 Conclusion

Flow chemistry setup has been updated from small to a large-scale polymer synthesis. The upscale of flow chemistry P3HT production was successfully performed at yield of 1.78 g at 59 %. This polymer was purified using the Soxhlet extraction technique with methanol and n-hexane solvents. Purified P3HT was tested on a small scale BHJ devices, and demonstrated a PCE_{MAX} of 2.04 %, which compared well with the batch synthesised polymer.

A goal of this thesis was to be able to produce high quantities of P3HT by flow chemistry and to be able to produce it continuously. This was achieved in terms of the flow chemistry P3HT upscale. Further experimentations are required to identify the potential maximum output from the system during continuous run. So far, the study was performed on a set of various residence times which affect the quality and quantity of the polymer produced. The apparatus manufactured potentially allows us to generate 8.5 g/day of uninterrupted P3HT, i.e., considering our synthesised P3HT of 1.78 g yield during a 5 hour of continuous flow reaction. Hence, this flow chemistry method allows us to synthesise a total of 60 g/week at a cost lower than that obtained for batch chemistry. As future work it is suggested that we explore and maximise the capability of the upgraded system, as well as exploring molecular weight increase for BHJ solar cells optimisation and further improvements to the purification technique.

References

- [1] Trojanowicz, M., 2016. Flow chemistry vs. flow analysis. *Talanta*, 146, pp.621-640.
- [2] A. Pashkova and L. Greiner, "Towards Small-Scale Continuous Chemical Production: Technology Gaps and Challenges," *Chemie Ing. Tech.*, vol. 83, no. 9, pp. 1337–1342, 2011.
- [3] H. Seyler, D. J. Jones, A. B. Holmes, and W. W. H. Wong, "Continuous flow synthesis of conjugated polymers," *Chem. Commun.*, vol. 48, no. 10, pp. 1598–1600, 2012.
- [4] F. Grenier et al., "Electroactive and photoactive poly [Isoindigo -alt- EDOT] synthesized using direct (hetero) arylation polymerization in batch and in continuous flow."
- [5] Seyler, H., Wong, W.W., Jones, D.J. and Holmes, A.B., 2011. Continuous flow synthesis of fullerene derivatives. *The Journal of Organic Chemistry*, 76(9), pp.3551-3556.
- [6] Myers, R.M., Fitzpatrick, D.E., Turner, R.M. and Ley, S.V., 2014. Flow chemistry meets advanced functional materials. *Chemistry–A European Journal*, 20(39), pp.12348-12366.
- [7] Seyler, H., Subbiah, J., Jones, D.J., Holmes, A.B. and Wong, W.W., 2013. Controlled synthesis of poly (3-hexylthiophene) in continuous flow. *Beilstein journal of organic chemistry*, 9(1), pp.1492-1500.
- [8] Bannock, J.H., Krishnadasan, S.H., Nightingale, A.M., Yau, C.P., Khaw, K., Burkitt, D., Halls, J.J., Heeney, M. and de Mello, J.C., 2013. Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Advanced Functional Materials*, 23(17), pp.2123-2129.
- [9] Seyler, H., Subbiah, J., Jones, D.J., Holmes, A.B. and Wong, W.W., 2013. Controlled synthesis of poly (3-hexylthiophene) in continuous flow. *Beilstein journal of organic chemistry*, 9(1), pp.1492-1500.
- [10] Wiles, C. and Watts, P., 2008. Continuous flow reactors, a tool for the modern synthetic chemist. *European journal of organic chemistry*, 2008(10), pp.1655-1671.
- [11] Kumar, A., Hasan, J., Majji, A., Avhale, A., Gopinathan, S., Sharma, P., Tarange, D., Bajpai, R. and Kumar, A., 2014. Continuous-flow synthesis of regioregular

poly (3-hexylthiophene): ultrafast polymerization with high throughput and low polydispersity index. *Journal of Flow Chemistry*, 4(4), pp.206-210.

- [12] Helgesen, M., Carle, J.E., dos Reis Benatto, G.A., Søndergaard, R.R., Jorgensen, M., Bundgaard, E. and Krebs, F.C., 2015. Making Ends Meet: Flow Synthesis as the Answer to Reproducible High-Performance Conjugated Polymers on the Scale that Roll-to-Roll Processing Demands. *Advanced Energy Materials*, 5(9), p.1401996.
- [13] Rossi, E., Carofiglio, T., Venturi, A., Ndobe, A., Muccini, M. and Maggini, M., 2011. Continuous-flow synthesis of an efficient methanofullerene acceptor for bulk-heterojunction solar cells. *Energy & Environmental Science*, 4(3), pp.725-727.
- [14] Pirotte, G., Kesters, J., Verstappen, P., Govaerts, S., Manca, J., Lutsen, L., Vanderzande, D. and Maes, W., 2015. Continuous Flow Polymer Synthesis toward Reproducible Large-Scale Production for Efficient Bulk Heterojunction Organic Solar Cells. *ChemSusChem*, 8(19), pp.3228-3233.
- [15] Bannock, J.H., Xu, W., Baïssas, T., Heeney, M. and de Mello, J.C., 2016. Rapid flow-based synthesis of poly (3-hexylthiophene) using 2-methyltetrahydrofuran as a bio-derived reaction solvent. *European Polymer Journal*, 80, pp.240-246.
- [16] Loewe, R.S., Khersonsky, S.M. and McCullough, R.D., 1999. A simple method to prepare head-to-tail coupled, regioregular poly (3-alkylthiophenes) using Grignard metathesis. *Advanced materials*, 11(3), pp.250-253.
- [17] Iovu, M.C., Sheina, E.E., Gil, R.R. and McCullough, R.D., 2005. Experimental evidence for the quasi- “living” nature of the grignard metathesis method for the synthesis of regioregular poly (3-alkylthiophenes). *Macromolecules*, 38(21), pp.8649-8656.
- [18] Hummelen, J.C., Knight, B.W., LePeq, F., Wudl, F., Yao, J. and Wilkins, C.L., 1995. Preparation and characterization of fulleroid and methanofullerene derivatives. *The Journal of Organic Chemistry*, 60(3), pp.532-538.
- [19] Cooling, N.A., Barnes, E.F., Almyahi, F., Feron, K., Al-Mudhaffer, M.F., Al-Ahmad, A., Vaughan, B., Andersen, T.R., Griffith, M.J., Hart, A.S. and Lyons, A.G., 2016. A low-cost mixed fullerene acceptor blend for printed electronics. *Journal of Materials Chemistry A*, 4(26), pp.10274-10281.
- [20] M. G. Wilson, 2014, *Preparation of Regioregular Poly(3-hexylthiophene) and its Precursor Monomer, 2,5-dibromo-3-hexylthiophene, Using Low Pressure Flow Synthesis Techniques*, PhD Thesis, University of Newcastle, Newcastle.
- [21] Kumar, A., 2014. Continuous-flow synthesis of regioregular poly (3-

hexylthiophene): ultrafast polymerization with high throughput and low polydispersity index. *Journal of Flow Chemistry*, 4(4), pp.206-210.

- [22] Bannock, J.H., Treat, N.D., Chabiny, M., Stingelin, N., Heeney, M. and de Mello, J.C., 2016. The influence of polymer purification on the efficiency of poly (3-hexylthiophene): fullerene organic solar cells. *Scientific Reports*, 6(1), pp.1-8.
- [23] Griffith, M.J., Cooling, N.A., Vaughan, B., Elkington, D.C., Hart, A.S., Lyons, A.G., Quereschi, S., Belcher, W.J. and Dastoor, P.C., 2015. Combining printing, coating, and vacuum deposition on the roll-to-roll scale: a hybrid organic photovoltaics fabrication. *IEEE Journal of Selected Topics in Quantum Electronics*, 22(1), pp.112-125.
- [24] Dissanayake, D.S., Sheina, E., Biewer, M.C., McCullough, R.D. and Stefan, M.C., 2017. Determination of absolute molecular weight of regioregular poly (3-hexylthiophene) by ^1H -NMR analysis. *Journal of Polymer Science Part A: Polymer Chemistry*, 55(1), pp.79-82.

Chapter 7: Conclusions and Future Work

7.1 Conclusions

This thesis aimed to explore the economic viability of flow and batch synthesis of selected high performance materials and address upscale issues, examine device physics and more importantly investigate both performance improvements and fabrication cost reductions. Mass manufacturing methods of P3HT, PDCBT and ITIC by batch or flow chemistry and their respective cost control is still a relatively unexplored area of OPV research. Almost no work has been conducted on this subject, with publications focusing on small-scale device manufacturing, and especially small-scale device efficiency, only. A recent target of solar research is expanding eco-friendly processing technologies for solar cells, to take advantage of the sustainable “green” possibilities the technology. Organic solar cells are an excellent emerging technology in this regard. One of fundamental requirements for the development of efficient large-scale OPV device (both BHJ and NPs) mass production is low-cost upscale of organic photovoltaic materials. This thesis has explored the link between economic aspect of these selected materials and their upscale potential, looking at material costings for both flow and batch chemistry. The thesis also examined these material’s nanoparticle device fabrication and performance to achieve the safest, less toxic way for both performance and commercialisation.

7.2 Optimisation of PDCBT and ITIC synthesis

Firstly, a thorough study of the donor:acceptor literature was conducted to identify potentially commercially viable materials pairings. From this study PDCBT and ITIC

were chosen as materials with merit. Then to prove that PDCBT and ITIC is a good combination of donor:acceptor for a large scale organic solar cells application, an intrinsic cost study was performed and the costing were compared to other benchmark materials. In Chapter 3 the cost analysis of active layer materials was successfully conducted and confirmed commercially feasibility of PDCBT and ITIC for OPVs. This economic modeling of the levelised cost of electricity for OPVs concluded, that there exists a trade-off among three key factors - cost, efficiency, and lifetime. Synthesis step by step costing studies were fully assessed and the synthesis cost of high performing materials, focusing on PDCBT and ITIC. The theoretical cost for PDCBT was found to be AUD \$63.78/g and the actual synthesized cost was AUD \$92.70/g and the theoretical cost for ITIC was AUD \$225.42/ g with the actual cost AUD \$214.91/g. In addition, the cost of device fabrication for these materials was presented, as well as a cost comparison with benchmark photoactive materials based on reported literature publications (P3HT, PCBM, ICxA, ICBA).

Secondly, the synthesis of PDCBT and ITIC materials was explored in Chapters 4 and 5 on a small laboratory scale and their synthesis upscale methods were assessed in detail. These chapters demonstrate the use of a range of low budget purification methodologies (recrystallisation, distillation etc.) to improve manufacture costs and alternative synthesis procedures and significant improvements to improve the safety of large scale PDCBT and ITIC material mass production. Much more knowledge and work to optimise these syntheses for material upscale are required to fully explore the development of new high-performance materials.

7.3 Optimisation of PDCBT and ITIC OPV devices

7.3.1 BHJ organic solar cells

Chapter 6 explored PDCBT and ITIC OPV device fabrication and their performance in BHJ organic solar cells. Devices with a maximum power conversion efficiency (max) of 5.27 % were observed. This value is lower than the reported maximum (10.16%; see Chapter 3, Table 3.3), due to existing morphology issues in the device, but sets an excellent basis for further optimisation. These devices require further improvements to achieve higher efficiency in terms of internal morphology optimisation. Also, apart from the efficiency of bulk heterojunction devices it is also important to consider the lifetime of the solar cells that are exposed to changing weather conditions. By introducing a UV blocking external layer it should be possible to protect the solar cell to achieve longevity.

7.3.2 Aqueous solar nanoparticle devices (upscale)

In Chapter 6 we investigated the use of PDCBT and ITIC materials for preparing and optimising the nanoparticle inks for use in OPV devices. This is the first time NPs of these materials have been produced and consequently, the first report of PDCBT:ITIC NP OPV devices. The main focus of this study was through optimisation to transfer NP device preparation from the laboratory scale to R2R printing scale. STXM characterisation of the PDCBT:ITIC binary NPs showed no clear evidence of the core shell particle morphology common to most NP material blends, with an intermixed particle morphology predominating. The main finding from this study is that the performance of these devices achieved a maximum PCE of ~2.11 %. However, by further optimisation of these NP devices we should be able to eliminate the efficiency difference with BHJ and fulfill the commercial viability for the pilot scale.

7.4 Developments to P3HT upscaled flow chemistry apparatus and its synthesis

A new flow chemistry setup was manufactured to transition the flow synthesis of P3HT from the small- to large-scale polymer synthesis and this was demonstrated in Chapter 6. Successful upscale of P3HT production via the new flow chemistry apparatus performed at a yield of 1.78 g (59 %). Yielded polymer was carefully purified by a Soxhlet extraction technique by using methanol and n-hexane as solvents. The resulting P3HT polymer was tested in BHJ devices and exhibited a PCE_{MAX} of 2.04 %. Further experimentations are required to identify the potential maximum output from the system during continuous run. So far, the study was performed on a set of various residence times which affect the quality and quantity of the polymer produced. The current flow chemistry setup potentially allows us to generate 32.04 g/day of uninterrupted P3HT flow chemistry synthesis, which is 224.28 g/week. Variations in the residence times of the P3HT synthesis by flow, suggests further study of upscaling P3HT with the lowest residence time permitted as a possible route for better yields.

7.5 Future work

This research project successfully met project aims and focused on organic electronic materials for the large-scale development of OPV's with high efficiency, good device lifetime and low cost by their incorporation within the active layer of bulk heterojunction and nanoparticles solar cells. Upscale of material synthesis was achieved and optimised by both flow chemistry and batch chemistry methods. Our selected donor-acceptor materials were characterised and upscaled in terms of their synthesis and application in OPVs.

In Chapter 3, the cost overview is outlined to achieve target of mass application of the new high efficiency donor:acceptor materials in devices. Cost breakdown by using our developed cost modelling method allowed us to compare and assess large-scale synthesis of different materials. However, new donor and acceptor molecules are being produced constantly and future work should use the presented costing methodology to continue to assess new materials as they become available to ascertain commercial viability.

Optimisation and upscaling by flow synthesis for P3HT allows us to probe commercial viability of OPV at a reasonable price, however at relatively low efficiency for P3HT material solar cells. Therefore, the potential for commercial-scale synthesis of new target materials PDCBT and ITIC was examined in the Chapters 4. It was expected that PDCBT and ITIC synthesis will allow us large-scale application in devices with a low cost. Addressing the synthetic issues by substituting expensive column chromatography clean up methods with different purification methods might aid this target and reduce the overall synthesis costs. However, overall. This material combination proved excellently

amenable to large-scale synthesis and work continues in the COE at the University of Newcastle to produce these materials at 100 g scale for use in OPV modules.

Successful work was introduced in Chapter 5, around preparation and incorporation of the PDCBT and ITIC materials as nanoparticle and bulk heterojunction active layers. Further experiments optimise device manufacturing would be desirable. This method could be upscaled large-scale nanoparticle production which could be used R2R processing without the use of toxic organic solvent. There is a wide range of further optimisations to the device manufacture and architecture which can be undertaken to improve performance, such as adjusting layer thicknesses and material ratios, changing annealing conditions, adjusting NP size and morphology by varying initial material concentrations. A thorough investigation of these parameters, which were beyond the scope of this thesis, will result in improved device performance and suitability for R2R printing.

In Chapter 6, upscaling of flow chemistry synthesis for P3HT was explored. The chapter explained the details of upscale synthesis using a new manufactured apparatus design. This design allows us to produce larger amounts of the polymer comparing to the old flow chemistry apparatus. Also, this system is controlled by installed software in order to control the process allowing it to run continuously. The current equipment used for flow chemistry would be efficient to use for further optimisation of the synthesis for P3HT polymer simply by running in continuous mode, a large scale batch under a careful monitoring by the computer software. Finally, as a future work it is suggested that in this research, the possibly of molecular weight increase for BHJ solar cells optimisation and the purification technique for further improvements.