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Design, synthesis and characterization of novel low band gap conjugated polymers for use in bulk heterojunction photovoltaic solar cells

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Design, Synthesis and Characterization of Novel Low Band Gap Conjugated Polymers for use in Bulk Heterojunction Photovoltaic Solar Cells:

A thesis submitted to Bangor University in candidature for the degree of

Philosophiae Doctor in Materials Chemistry

by

Athanasius Justin Mānji.

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Dedication:

THIS WORK IS DEDICATED TO MY REVERED PARENTS AND MY YOUNGEST SON ATHANASIUS AKACHA ATHANASIUS

Acknowledgement:

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Abbreviations:

AM	Air mass
APFO-Green1	6,7-diphenyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-
	g]quinoxaline
APFO-Green15	2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline
APFO-Green2	2,3-diphenyl-5,7-di(thiophen-2-yl)thieno[3,4-b]pyrazine
APFO-Green9	2,3,7,8-tetraphenyl-5,10-di(thiophen-2-yl)pyrazino[2,3-
	g]quinoxaline
As	Absorbance of standard
Au	Absorbance of unknown
BDT	Benzodithiophene
BHJ	Bulk heterojunction
BHT	Bromohexylthiophene
BT	2,1,3-Benzothiadiazole
CV	Cyclic voltammetry
D-A	Donor-acceptor
DEBT	4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3-
	benzothiadiazole.
DES	3,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[b,d]
	thiophene 5,5-dioxide.
DPP	Diketopyrrolopyrrole
DSSC	Dye sensitized solar cell
DTBT	Dithienylbenzothiadiazole
DTDPP	Dithiophene(diketopyrrolopyrrole)
E _B	Binding energy
EgEC	Electrical band-gap
E _{FC}	Potential of ferrocene
EgOpt	Optical band-gap
Eox	Onset oxidation potential
Ered	Onset reduction potential
EDOT	3,4-ethylenedioxythiophene
e-h	Electron-hole

E _{HOMO}	Energy of HOMO
E _{LUMO}	Energy of LUMO
EP-PTC	Perylene tetracarboxyl diimide N,N-bis(1-ethylpropyl)-3,4:9,10-
	perylene bis(tetracarboxyl diimide)
EQE	External Quantum Efficiency
FF	Fill Factor
Fs	Integrated fluorescence intensities of standard
F _u	Integrated fluorescence intensities of unknown
GPC	Gel permeation chromatography
GRIM	Grignard metathesis
HMPER	N,N'-bis-2-(1-hydoxy-4-methylpentyl)-3,4,9,10-perylene-bis
	(dicarboximide)
НОМО	Highest occupied molecular orbital
HT	Head-to-tail
ICT	Intra-molecular charge transfer
IPCE	Incident photon-to-current conversion efficiency
I-V	Current-Voltage
J_{pp}	Current at peak power
J_{sc}	Short circuit current density
LBG	Low band gap
LEDs	Light emitting diode
LUMO	Lowest unoccupied molecular orbital
MDMO-PPV	Poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-
	vinylene)
MEH-PPV	Poly(2-methoxy-5(2'-ethylhexyloxy)-p-phenylene vinylene
M _n	Molecular weight number average
M _w	Weight-average molecular weight
NBS	<i>N</i> -bromosuccinimide
nc-TiO ₂	Nano-crystal-titanium oxide
Ni(dppp)Cl ₂	[1,3-Bis(diphenylphosphino)propane]dichloronickel(II)
N-P7	Poly(2-(9,9-dioctyl-9H-fluoren-2-yl)-5(6,7-diphenyl-4-(thiophene-
	2-yl)naphthalene-1-yl)thiophene.
NREL	National renewable energy laboratory

OFET	Organic field-effect transistor
OLED	Organic light emitting diode
OMeTAD	2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-
	spirobifluorene.
OPV	Organic photovoltaics
OSCs	Organic solar cells
P3HT	Poly(3-hexylthiophene)
PA	Polyacetylene
PAA	Palmitate ascorbic acid
PANI	Polyaniline
PBDTTPD	Poly(1-(4,8-bis(2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-
	yl)-5-octyl-4H-thino[3,4-c]pyrolle-4,6(5H)-dione
PBTTT	Poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2b]thiophene)
PC ₆₁ BM	Buckminsterfullerene [(6,6)-phenyl C ₆₁ -butyric acid methyl ester]
PCDEBT	Poly{9-(heptadecan-9-yl)-9H-carbazole-4,7-bis(2,3-
	dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3-benzothiadiazole}
PCDES	Poly{3-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(7-(9-
	(heptadecan-9-yl)-9H-carbazol-2-yl)-2,3-dihydrothieno[3,4-
	b][1,4]dioxin-5-yl)dibenzo[b,d]thiophene-5,5-dioxide}
PCDTBT	Poly(4-(5-(9-(heptadecan-9-yl)-9H-carbazol-2-yl)thiophene-2-yl)-
	7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole
PCE	Power conversion efficiency
PCPDTBT)	Poly(4-(7,7-bis-(2-ethylhexyl)-7H-cyclopenta[1,2-b;4,3-
	b]dithiophen-2-yl)benzo[c][1,2,5]thiadiazole.
PDI	Polydispersity index
PDTSTPD	Poly(1-(4,4-bis(2-ethylhexyl)-6-methyl-4H-silolo[3,2-b:4,5-
	b']dithiophen-2-yl)-3-methyl-5-octyl-4H-thieno[3,4-c]pyrolle-
	4,6(5 <i>H</i>)-dione
PEDOT	Polyethylene dioxythiophene
PEDOT:PSS	Poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate)
PFDEBT	Poly{9,9-dxioctyl-9H-Fluorene-4,7-bis(2,3-dihydrothieno[3,4-
	b][1,4]dioin-5-yl)-2,1,3-benzothiadiazole}

PFDES	Poly{3-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(7-(9,9-
	dioctyl-9H-fluoren-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-
	yl)dibenzo[b,d]thiophene-5,5-dioxide}
PFDTBT	Poly(4-(5-(9-(2-ethylheyl)-9-hexyl-9H-fluoren-2-yl)thiophene-2-
	yl)-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole
PhEDOT	3,4-Phenylene dioxythiophene
PL	Photoluminescence
PLED	Polymer light emitting device
PPEI	Perylene bis(phenethylimide)
PPHT	Poly(3-phenylhydrazonethiophene)
PPP	Poly(<i>p</i> -phenylene)
PPV	Poly(<i>p</i> -phenylene vinylene)
PPy	Polypyrrole
PT	Polythiophene
PTB1	Poly(dodecyl-4(4,8-bis(octyloxy)benzo[1,2-b:5,4-b']dithiophen-2-
	yl)thieno[3,4-b]thiophene-2-carboxylate.
PTT	Poly(thieno[3,4-b]thiophene
PV	Photovoltaic
REPE	Resonance energy per electron
[Ru(bipy) ₃ Cl ₂]	Tri(bipyridine)ruthenium (II) chloride
T_d	Thermal degradation
TGA	Thermogravimetric analysis
TPD	Thieno[3,4-c]pyrrole-4,6-dione
V _{oc}	Open circuit voltage
V_{pp}	Voltage at peak power

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Abstract:

This work details the synthesis of a functionalised all-donor polymer, poly(3-hexylthioacetate thiophene) (P3HTT) [42] along with four new donor-acceptor (D-A) copolymers. Two of the four copolymers are based on fluorene (F) and carbazole (C) as electron donors copolymerised with DEBT to give, PFDEBT [62] and PCDEBT [63] respectively, while the other two are based on the same electron donors, but copolymerised with DES to give PFDES [64] and PCDES [65] respectively.

All the polymers exhibited good solubility in common organic solvents and good thermal stability. The spectrophotometry analysis of polymer [42] in chloroform showed that it emits in the green region with 26% photoluminescence quantum yield (PL Φ). The optical response of copolymers [62] and [63] in chloroform solution and thin films are similar; both have two broad absorption bands with peaks at short and long wavelengths which are within comparable range. In addition, both emit in the deep red region of the emission spectrum and have similar PL Φ values, 28 % and 27 % respectively. In contrast, copolymers [64] and [65] have single broad absorption band and emit in the green region with PL Φ values of 55 % and 51 % respectively.

The electrochemical responses of the polymers were measured using cyclic voltammetry. The results obtained for polymer [42] were different from what was expected; its band-gap was similar to that of P3HT and its energy levels were elevated. In contrast, the band-gaps of the copolymers were tuned in the range of 1.47 to 1.65 eV. The results showed that the acceptor units have exhibited the same effect of band-gap lowering in the two sets of the copolymers, for instance, the LUMO energy level of copolymers [62] and [63] is -3.32 eV and those of copolymers [64] and [65] is -3.57 eV. Conversely, different effect was observed in the values of the HOMO energy levels, for example, the values for [62] and [64] which contain the same donor (fluorene) are -4.86 and -5.07 eV respectively; while those of copolymers [63] and [65] composed of carbazole are -4.97 and -5.04 eV respectively. This may suggest that the acceptor unit reduced the band-gap by lowering the LUMO energy level but at the same time elevated the HOMO energy level probably due to the presence of EDOT.

DSSCs devices based on polymer [42] were fabricated in combination with nc-TiO₂ and ruthenium 535-bisTBA dye to give devices with the configuration, glass/SnO₂:F/nc-TiO₂/dye/polymer/Au. The best device showed a PCE of 0.035 % with V_{oc} , J_{sc} and FF of 610 mV, 1.7 mA/cm² and 34 % respectively. The copolymers were used in combination with $PC_{60}BM$ to make BHJ solar cells having the structure, glass/ITO/PEDOT:PSS/copolymer:PC₆₀BM/Al. The best performance was observed in the device based on copolymer [62] with 1:1 polymer:PC₆₀BM ratio which showed PCE of 1.45 % while the values of V_{oc}, J_{sc} and FF are 647 mV, 5.57 mA/cm² and 40 % respectively.

Chapter One:

1.0: Introduction:

1.1: Thesis Outline:

Chapter one presents an overview to the basics underlying the work presented as a result of this research in relation to conjugated polymers, sources of energy and organic solar cells (OSCs). It will also give the driving force behind this research.

The overall experimental procedure used in this study is presented in chapter two along with the synthesis of monomers and side-chain functionalised derivative of P3HT, poly(3-hexylthioacetate thiophene), P3HTT, an all-donor LBG polymer, and the fabrication of DSSC devices using this polymer. The synthesis of co-monomers and the LBG donor-acceptor copolymers is also outlined in this chapter.

Chapter three will present the results and discussions based on P3HTT, while the results and discussions based on the co-monomers and the LBG copolymers will be presented in chapter four.

Finally, the overall conclusion and recommendations for future work will be given in chapter five.

1.2: Conjugated Polymers:

The first and model example of a semiconducting polymer is polyacetylene (PA). Natta et al. in 1958 polymerized acetylene into insoluble polyacetylene as a gray, infusible and powdery compound using a Ziegler-Natta catalyst. Unfortunately, this product could not be characterized using most of the available methods and did not possess the electrical properties that were expected.¹ Since the electrical properties of this polymer could not be determined, all organic polymers were still considered to be insulators at that time.

Shirakawa et al., were the first to synthesize free-standing PA films having metallic luster using the same Ziegler-Natta catalyst but with different experimental conditions.^{2, 3} While studying the physical properties of the polymer, Shirakawa discovered that its characteristic IR peaks disappeared upon doping with bromine. Ordinarily, these IR peaks represent the local vibrations of bond charge carriers forming dipole moments, a characteristic feature of insulators. It was concluded therefore, that the disappearance of

the peaks could be due to charge delocalization. Consequently, Shirakawa, McDiarmid and Heeger conducted electrical conductivity measurement on a film of the polymer; and they discovered a great increase in its conductivity upon doping.⁴ The conclusion drawn from this work was that the conjugated configuration in this polymer is the basis for its electrical conductivity; and this discovery and the subsequent development of conductive polymers have since dismissed the notion that all organic polymers are insulators. This work led in part to the award of Nobel Prize in Chemistry to Heeger, MacDiarmid and Shirakawa in 2000.⁵

Three generations of conjugated polymers have evolved since the time of this discovery. The *cis*- and *trans*- form of PA (Fig. 1.0 a and b) are the first generation of conjugated polymers. Both forms can be formed during polymerization using the Ziegler-Natta catalyst used in Shirakawa synthesis, but the *trans*- form is the stable form. However, the *cis*- form can be thermally converted to the *trans*- form.⁶



Figure 1.0: Structures of first generation conjugated polymers a) cis- and b) trans- forms of polyacetylene.

Pristine PA is a typical semiconductor, but its electrical conductivity can be varied by over 14 orders of magnitude through chemical doping. The maximum conductivity reported for PA is 10⁵ S cm⁻¹, which is comparable to those of copper and gold. Both forms of PA have planar structures due to strong pi-conjugation between the sp²-hybridised carbon atoms in the polymer chain. Also, because of strong interchain interactions, they have a fibrillar crystals consisting of rigid, pi-stacked polymer chains. This makes PA infusible and insoluble in any kind of solvent.¹ There was therefore the need to develop other forms of conjugated polymers.



Figure 1.1: Structures of some important second generation conjugated polymers a) polyparaphenylene (PPP), b) poly(paraphenylene vinylene) (PPV), c) poly(2,5-dialkoxy)paraphenylene vinylene (e.g. MEH-PPV and MDMO-PPV) d) polythiophene, (PT) e) polypyrrole (PPy), f) polyethylene dioxythiophene (PEDOT), g) poly(3-alkyl) thiophenes (P3ATs), h) polyfluorene (PFO) and i) polyaniline (PANI)

The second generation polymers were then developed; and the structures of some important types are shown in (fig. 1.1 a-i). Poly(2-methoxy-5(2'-ethylhexyloxy)-pphenylene vinylene (MEH-PPV), poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1.4phenylene-vinylene) (MDMO-PPV), and poly(3-hexylthiophene) P3HT (from poly(3alkylthiophene, P3AT) could be described as classic polymer donors (all-donor polymers) and are the most widely studied of the second-generation semiconducting polymers.⁶ The semiconducting form of poly(aniline) (PANI) has not been of major importance in the development of either the physics or the device science of semiconducting polymers. However, the so-called emeraldine salt form of it has been and continues to be one of the most important near-metallic polymers. In the case of poly(ethylenedioxythiophene) (PEDOT), the doped form is far more important than the parent pristine semiconductor.⁶ Conversely, MEH-PPV and MDMO-PPV are said to have strong absorption in the visible light band,⁷ and power conversion efficiency (PCE) up to 4.3% has been reported for bulk heterojunction (BHJ) device of MDMO-PPV and buckminsterfullerene [(6,6)-phenyl C₆₁-

butyric acid methyl ester] (PC₆₁BM) fabricated using screen printing.⁸ rr-P3HT, on the other hand, has demonstrated a PCE as high as 5.2 % as a result of the insertion of nickel oxide (NiO), a *p*-type oxide semiconductor optical spacer, between the active layer and the anode of the BHJ solar cell based on this polymer and PC₆₁BM.⁹

Despite this optimization method, and several others, such as using different solvents to fabricate the active layer, thermally annealing the active layer or the device, film forming speed, additives to the active layer, anode or cathode interfacial layer, nanocrystals and tandem structure; the PCE of devices based on these polymers has not exceeded that reported for rr-P3HT. It is therefore, imperative to significantly enhance the PCE in order to meet the requirements for large-scale commercialization of OPV solar cells as a renewable energy source. One of the routes for such improvements is the design of new polymer donors that have extended absorption edge to match solar terrestrial radiation, higher carrier mobility, and better energy alignment with acceptors to reach high V_{oc} .¹⁰ Thus, the third generation polymers took the centre stage.

The third generation polymers have more complex molecular structures with more atoms in the repeat unit. Important examples include the highly ordered and crystalline poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2b]thiophene) (PBTTT) (Fig. 1.2) and the ever-growing class of donor (electron rich)-acceptor (electron deficient) (D-A) co-polymers introduced by Havinga and coworkers in the early 1990s.¹¹



Figure 1.2: Structure of PBTTT.

As a result of the work of Havinga, several narrow band-gap π -conjugated polymers with improved absorption than the wide band-gap all-donor second-generation polymers have been synthesized. Examples include the bithiophene–acceptor co-polymers, poly(4-(7,7-bis-(2-ethylhexyl)-7*H*-cyclopenta[1,2-*b*;4,3-*b*']dithiophen-2-yl)benzo[*c*] [1,2,5]thiadiazole (PCPDTBT) Fig.1.3a pioneered by Konarka and the polycarbazole–acceptor co-polymers, Fig.1.3b, pioneered by Leclerc and colleagues.⁶



[13]



b) [14]

Figure 1.3: Structures of a) PCPDTBT and b) Polycarbazole-acceptor.

The widely used electron-rich units (donors) to synthesize D-A copolymers include: thiophene dialkoxy benzene and dialkyl benzene; diphenylamine and triphenylamine carbazole, phenothiazine, and fluorene.¹² Others include; cyclopenta[2,1b:3,4-b]dithiophene, dithienosilole, dithieno[3,2-b:2', 3'-d]pyrrole, indolo[3,2-b]carbazole, benzo[2,1-b:3,4-b']dithiophene, benzo[1,2-b:4,5-b']dithiophene.¹³ At the same time, many electron-deficient units, which often contain imine nitrogen (C-N) such as pyridine, bipyridine, pyrazine, quinoline, quinoxaline, benzothiadiazole, benzoselenodiazole, benzotriazole.¹² and 4,7-dithienyl-2,1,3-benzoxadiazole are among the acceptor units widely use.¹⁴ Others are 3,6-bis(thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione,¹⁵ and thieno[3,4-b]thiophene.¹⁶

Conjugated polymers therefore have since found applications in electrical appliances, such as organic light emitting diodes (OLEDs) and solar cells. The conjugation in such polymers affords delocalized pi (π) electron-bonding along the polymer chain. In general, the electronic structure of π -conjugated polymers originates from the sp²p_z hybridised carbon atoms in the repeat unit.

1.2.1: Band-gap in Conjugated Polymers:

An important feature of semiconducting polymers is the energy band that originate from the bonding and anti-bonding energy levels associated with the σ -bonds between adjacent carbon atoms (sp² hybrid orbitals) and the π -bonds that come from the p_z hybrid orbital. The σ -bonds holds the structure together, while the π -bonds give the polymer its semiconducting properties. The π -bonding molecular orbitals and π^* antibonding molecular orbitals form the delocalized valence and conduction band wavefunctions respectively, which support mobile charge carrier.

The energy levels in conjugated polymers are denoted by the molecular orbitals that form the σ - and π -bonds. The lower energy level of the polymer known as the σ - and π -bonding molecular orbitals is the highest occupied molecular orbital (HOMO) and it forms the valence band; while the higher energy level known as the σ *- and π *-antibonding molecular orbitals is the lowest unoccupied molecular orbital (LUMO) and it forms the conduction band. The difference between the two energy levels is called the band-gap (Fig. 1.4). The band-gap governs the intrinsic optical and electrical properties of these organic semiconductors.¹⁷ It is usually within the range of 1.5 - 3 eV and this makes these semiconductors ideally suited for optoelectronic devices since their band gap can be fine-tuned to match the photon flux of the sun which peaks at around 700 nm.¹⁸



Figure 1.4: Energy levels of Conjugated Polymer.

The low band gap (LBG) that characterise these polymers increases the possibility of electron promotion from the HOMO to LUMO, which does not occur in organic insulators where the gap is very large. It also means that the free charge concentration can readily be changed by charge injection from electrodes or by photo-excitation. When these polymers are doped, electrons are removed from the π bonds generating holes. An aromatic polymer undergoes a change in its configuration around the hole, to form the higher energy quinoid arrangement. The structural changes due to formation of the holes are known as polarons (Fig. 1.5a). An increase in the dopant concentration results in the formation of bipolarons, thereby introducing new energy level into the energy gap (Fig. 1.5b).



Figure 1.5: Chemical structure of polythiophene after formation of a) polaron and b) bi-polaron.

1.2.2: Optical Properties of Conjugated Polymers:

The absorption of photons by semiconductors leads to promotion of electrons from the valence band (π -band) to the conduction band (π *-band) forming holes and electrons respectively, in these energy levels as shown in Fig. 1.6. It is expected that these photo-generated holes and electrons are mobile and free to move in response to an applied electric field. However, even in the classical inorganic semiconductors like silicon (Si), germanium (Ge) and gallium arsenide (GaAs), where the bandwidths are larger than the separation of atomic levels, the electron-hole Coulomb attraction results in the formation of bound excited state known as excitons, with a binding energy that is sensitive to the dielectric constant of the material.



Figure 1.6: π - π * inter-band transition leading to generation of a mobile electron in the π *-band and mobile hole in the π -band.⁶

Inorganic semiconductors however, have high dielectric constant of the order of 10, with small exciton binding energy (E_B) (ca. 3 meV for GaAs) and an exciton radius much larger than the interatomic spacing.⁶ As a result, the type of exciton in these semiconductors is the loosely bound e-h pair known as Wannier-Mott exciton, which are delocalised over many atoms.¹⁹

On the other hand, molecular solid such as anthracene, have bandwidths smaller than the separation of the molecular energy levels. Hence, exciton corresponds to an excited state of the molecule with an electron promoted from the HOMO energy level to the LUMO energy level. The E_B is therefore, usually larger than 1 eV. This result in the formation of strongly bound exciton known as Frenkel exciton, which is localised on a single molecule and the constituent electron and hole lose their identity. Although such excitons are localized, they can hop from molecule to molecule due to the weak interactions between molecules.^{6,19}

When semiconducting polymers absorb photons with energy beyond the absorption edge, electron and hole with opposite spins are created, bound by their Coulomb attraction in a singlet exciton state. Because coupling between neighboring molecules in such systems is low, the molecular excitations are localized and there is no band-to-band transition, unlike in inorganic semiconductors. Also, because of the π -electron overlap between closely spaced neighbouring atoms in the repeat units, their interchain bandwidth is larger than those in inorganic semiconductors but they have weak interchain interactions compared to molecular crystals. The E_B for these compounds is therefore, an intermediate between those of Wannier and Frenkel excitons ranging between < 0.1 eV in PPV and PT to several tenths of eV in larger band gap polymers.⁶ In addition, the relative dielectric constant of the order of 3, as compared to 10 in inorganic semiconductors, results in excitons that are more strongly bound than those in inorganic semiconductors.²⁰ It has also been observed that exciton wave-function can extend over a

number of repeat units along polymer chain in organic semiconductors and onto neighboring chains forming multi-chain exciton known as exciplex.⁶ Neutral inter-chain excitons may be formed due to rapid relaxation of the photo-generated electrons and holes towards their respective band edges. If the resulting charge carriers are on separate chains, the carriers will get self-localize to form polarons.⁶ The e-h relaxation, polaron self-localization and formation of neutral excitons can be expressed as follows:

$$e^+ + e^- \rightarrow P^+ + P^- \rightarrow BP^o \rightarrow exciton$$

where e^+ and e^- are holes and electrons, respectively, P^+ and P^- are positive and negative polarons, and BP^o is a neutral bipolaron. A polaron is therefore a charge, that is, an electron or a hole, plus a distortion of the charge's surroundings (a charge + the charge carrier).

Also, because conducting polymers undergo optical transition of electrons from the valence band to the conduction band $(\pi - \pi^*)$ they are generally highly colored in the non-conducting state. Upon doping, two new states are produced within the energy gap between the valence and conduction bands, and the presence of these gives rise to new low-energy transitions in the doped material. These transitions increase in intensity upon increased doping while the original absorptions seen in the un-doped material, decrease in intensity. Thus, by lowering the band gap (as in LBG polymers) the optical transition would be in the long wavelength portion of the visible spectrum (the material would be highly colored). Upon oxidative doping, the new absorptions would still be at longer wavelength, in the near-infrared spectral region, and the original absorption, which produced the color, would be considerably reduced. This, as is the case with a number of LBG polymers, renders the polymer very lightly colored and essentially transparent.²¹

1.2.3: Factors affecting the band-gap:

An important requirement for a semiconductor is that it should absorb significant fraction of the sun's light. The high peak optical absorption coefficient ($\sim 10^5$ cm⁻¹) of many conjugated polymers makes them excellent candidates in this regard. While crystalline Si PV cells must be made $\sim 100 \mu$ m thick to effectively absorb incident light, organic semiconductors have a direct band-gap and generally must only be 100-500 nm thick to absorb most of the light at their peak absorption wavelength.²² The band-gap of a

conjugated polymer determines which wavelengths of light are absorbed and emitted by the material. Conjugation length, solid-state ordering and the presence of electronwithdrawing or donating group are among the factors that influence the band-gap of a polymer.²³ It has been reported that the effective conjugation length, which is dependent on the angle between the repeating units along the polymer chain, can be controlled by introducing bulky side-chain to twist the units out of plane.²³ Varying the heat or vapour treatment have been found to control the solid state ordering, thus modifying the band-gap of conjugated polymers. The introduction of an electron-withdrawing group (trifluoromethyl) in poly(phenylene vinylene) (PPV) has been reported to lower the HOMO and LUMO energies of the polymer. Electron-withdrawing groups have also been found to effectively improve electron injection along the conjugation length.²⁴ The incorporation of alternating donor (D) and acceptor (A) moieties in a polymer main-chain has also been reported to reduce the band-gap of the polymer *via* ICT.¹¹ The main factors which affect band-gap include:

1.2.3.1: Bond length alternation:

The concept of band-gap was long predicted by Peierls before the synthesis of polyacetylene by Shirakawa.²⁵ Peierls band-gap is directly related to the bond length alternation.



Figure 1.7: Structure of a) aromatic and b) quinoid forms of poly(benzo[c]thiophene-1,3-dyl).

Reducing the bond length of the polymer can reduce its band-gap. For instance, while polythiophene with band-gap of 2.0 eV is known to exist in the aromatic form; poly(benzo[c]thiophene-1,3-dyl) with band-gap of 1.0 eV can alternate between the aromatic (Fig. 1.7a) and the quinoid (Fig. 1.7b) form in which the thiophene part loses its aromaticity while, the benzene part gains it.²⁶ This process reduces the potential energy of the compound thus, narrowing the band-gap. Another method is the use of the donor-acceptor approach or the 'push-pull' system.²⁶ Incorporation of alternating donor and

acceptor units in a polymer backbone can stabilise the quinoid form since alternation of donors and acceptors increases the double bond character between repeating units. This stabilises the quinoid form, thus reducing the potential energy and the band-gap. The donor molecules, mostly thiophene-based or 3,4-ethylenedioxythiophene-based, are electron rich and are able to increase the electron density between the repeating units (push). The acceptor units commonly used are the cyano- group; the benzothiadiazole and the thienopyrazine moieties which reduce the electron density (pull).

1.2.3.2: Torsion angle between rings of adjacent units and conjugation length:

Torsion between adjacent rings partially interrupts the conjugation length in polymers and leads to an effective increase of the band-gap. It was generally found that the band-gap decreases with increasing conjugation length. Reducing the tilt angle by using either smaller side groups, non-proton carrying atoms, or bridging *via* covalent bonds or H-bonds, can reduce the torsion angle in a polymer, thereby enhancing the backbone planarity and, consequently, reducing its band gap.²⁷

1.2.3.3: Aromatic resonance energy:

This is obtained from Resonance Energy per Electron (REPE) value. A high value of REPE results in broader band-gap of the aromatic unit, because aromaticity leads to a confinement of the π -electron on the ring and competes with delocalisation.^{28,29} Therefore, a low REPE-value is desirable for a small band-gap. However, this factor is restricted by the chemical stability of the (anti) aromatic unit.

1.2.3.4: Substituent effects:

Substituents can influence the HOMO and LUMO levels of a polymer through mesomeric or inductive effects, thereby altering its band-gap. Electron donating groups raise the energetic position of the HOMO level making the compound stable. Electron withdrawing groups on the other hand lowers the energetic position of the LUMO. This is because the reduction potential is lowered, making it easier to push an electron into the LUMO energy level. A polymer is generally stabilised when an electron is pushed into its LUMO energy level.²⁵

1.2.3.5: Effect of intermolecular interactions:

Conjugated polymers in the solid state generally show a lower band-gap as compared to the solution phase, this is attributed to reduced torsion angle due to π - π interaction between chains. Consequently, the electrons are more delocalized, reducing the band-gap. Supra-molecular ordering induced by alkyl side chains can also enhance the solid-state packing, thereby, reducing the band-gap^{21, 30}

1.3: Sources of Energy:

Electrical energy is a key factor in the achievement of economic growth. It has multiple effects on other economic activities, so that an inadequate supply of electricity puts the economy in a bad shape. At present the major ways of generating electricity is by the use of fossil fuels (oil, gas and coal), nuclear materials or water. While water could be infinite, fossil fuels and nuclear materials are not; so there is the probability of their depletion due to over-dependence as is the case at present. Also, the burning of these fuels emits carbon dioxide (CO₂) gas into the atmosphere. This gas is considered to contribute to "greenhouse effect" which brings about "global warming." Nuclear materials, on the other hand, generate electricity without CO₂ emission. These materials contribute significant amount of the total energy consumed in the world, but they have the risk of emitting dangerous radioactive particles that may contaminate the environment. Therefore, nuclear power stations require special system designs to prevent the release of these radioactive particles during operation, which makes it difficult and expensive for most countries to establish and maintain such power stations. Water, though infinite has its own limitations. Hydropower is dependent on in-flow of water into a dam and this in-flow can be affected up stream by rainfall in the catchment area, or outside the borders of a country by political or other considerations.

Therefore, a nation that depend on fossil fuels and water for power production will suffer a setback should there be a shortage in the supply of these commodities. The future of countries that depend on these resources for energy generation is therefore bleak because supplies are expensive, diminishing and politically regulated as is the experience all over the world in recent times. The per capita energy consumption rate of most developing nations is almost less than half of that of developed nations. The reason could be that the resources used for the conventional method of production of power are in short supply, scarce or exploration and exploitation are limited due to militant activities as is the case in many countries nowadays. For instance, pipe lines supplying thermal power stations with gas or oil are frequently vandalized for political reasons or otherwise, thus creating shortage in power supply. There is therefore the need to generate electrical energy from renewable sources.

The main sources of renewable energy are; the wind, sun, tide and biomass. These are available, cheap and environmentally friendly. The sun for instance, is the largest carbon-free energy source that has not been fully utilized;³¹ it is unlike fossil fuels available just about everywhere on earth. It is free, immune to rising energy prices and can be used in many ways to provide heat, lighting, mechanical power and electricity.

However, there is a wide gap between the costs of energy produced from fossil fuels as compared to renewable sources. Finding a low-cost method for the extraction of energy from renewable sources is therefore a great challenge to scientists.

1.4: Solar energy:

Solar energy, besides fusion, has the largest potential to satisfy the future global need for renewable energy sources. The amount of solar energy that strikes the earth's surface is estimated to be 1.7×10^5 TW from which a practical terrestrial global solar potential value is estimated to be ca. 600 TW. Thus, using 10 % efficient solar farms, about 60 TW power could be supplied. The sun emits light with a range of wavelengths from the ultraviolet and visible to the infrared. It peaks in the visible, resembling the spectrum of a blackbody at a temperature of 5760 K. It is, however, influenced by atmospheric absorption and the position of the sun. Ultraviolet light is filtered out by ozone, and water and CO₂ absorb mainly in the infrared making dips in the solar spectrum at 900, 1100, 1400, and 1900 nm (H₂O) and at 1800 and 2600 nm (CO₂). When skies are clear, the maximum radiation strikes the earth's surface when the sun is directly overhead, having the shortest path length through the atmosphere. The path length is called the air mass (AM) and can be approximated by AM = $1/\cos \theta$, where θ is the angle of elevation of the sun. The standard solar spectrum used for efficiency measurements of solar cells is AM 1.5 G (global), given that $\theta = 45^{\circ}$. This spectrum is normalized so that the integrated irradiance (the amount of radiant energy received from the sun per unit area per unit time) is 1000 W m⁻². The irradiance varies depending on the position of the sun, orientation of the Earth, and sky conditions. One also distinguishes sunlight in direct or diffuse light. The direct

component can be concentrated, which increases the solar cell efficiency by increasing cell voltage outputs. Diffuse light arises by scattering of the sunlight in the atmosphere. This fraction is around 15% on average but larger at higher latitudes and in regions with a significant amount of cloud cover.³²

The best way to tap solar energy is by the use of photovoltaic (PV) devices because they can convert sunlight directly into electricity, second only to photosynthesis.³³ Edmund Becquerel was said to be the first person to note the PV effect in 1839 at the age of 19. While he was working in his father's laboratory, he noted that light incident on a silver coated platinum electrode immersed in an electrolyte produced electric current.³⁴

Despite, the early discovery of PV effect by Becquerel; the ancestor of the modern day inorganic solar cells were not discovered until 1939 by Russell Ohl, while he was testing the resistivity of Si ingots at Bell laboratories in the US.³⁴ Even so, the first truly efficient Si solar cell with sunlight to electrical power conversation efficiency (PCE) of 6% could only be reported fifteen years later by Chapin et al.³⁵ As a result of Chapin's work, an intensive research on the use of inorganic materials for the generation of solar energy has been done; and at present solar energy is mostly harnessed using inorganic PVs. The conventional solar cells are the first and second generation solar cells. While the first generation are based on crystalline silicon, the second generation are based on thin-films of amorphous silicon, III – V compounds, CdTe and chalcopyrite compounds.

1.4.1.: Crystalline Si (c-Si) Solar Cells:

The early material used to fabricate solar cells was c-Si; unfortunately this material has an indirect energy band-gap of ca. 1.1 eV at r.t. resulting in a low optical absorption coefficient, $\alpha \approx 100 \text{ cm}^{-1}$. Thus, the Si layer need to be greater than 200 µm thick to be able to absorb most of the sun's photons.^{36,37} In addition, Si has to be pure enough and its densities of crystal defects minimised before it can be used to produce efficient devices since charge mobility and lifetime of the charge carriers are dependent on material purity and crystallinity.³⁶ Hence the high cost of c-Si based solar cells. Solar cells based on mono- and multi-crystalline Si have shown efficiency up ca. 25 and 20 % respectively.^{37,38}

1.4.2: Amorphous Si (a-Si) Solar Cells:

Thin films of a-Si are usually produced using plasma-enhanced chemical vapour deposition (PECVD) of gases containing silane (SiH₄) to give hydrogenated amorphous Si. The a-Si unlike the c-Si has a direct band-gap of 1.7 eV with optical coefficient, $\alpha > 10^5$ cm⁻¹. Therefore, only a few microns of materials are needed to absorb most of the incident light, thus, reducing materials usage and hence cost compared to c-Si. The a-Si is the most established thin-film technology and the highest efficiency shown by solar cells based on it is 10 %.³⁷ Although the efficiency is lower than those of c-Si, the a-Si has the advantage of lower temperature coefficient for power loss.³²

1.4.3: III - V Solar Cells:

The III – V compounds, such as GaAs, InP and GaSb, have been reported to have direct energy band-gaps, high optical absorption coefficients, and good values of charge mobilities and lifetime of charge carriers. As a result, they have been found to be excellent materials for high-efficiency solar cells. The most widely used of these materials are GaAs and InP, because both have near optimum energy band-gap of 1.4 eV. Single-junction cells of GaAs and InP have shown conversion efficiency of 25.8 and 21.9 % respectively under standard conditions. However, the cost of producing such devices is very high, unwanted impurities are also found in most crystals which reduce device efficiencies. These materials are also easily cleaved and are significantly mechanically weaker than Si.³⁷

Multi-junction (sometimes called tandem) solar cells of the III – V compounds have been developed achieving an efficiency of 30 % for a GaAs/GaSb stacked cell. Much work on the development of stacked cells grown by metal-organic chemical vapour deposition (MOCVD) onto GaAs, InP and Ge substrates has been done and a device grown onto Ge substrate has been reported to give a conversion efficiency > 39 %.³⁷

1.4.4: CdTe Solar Cells:

The compound CdTe like the III - V compounds, has a direct band-gap of 1.5 eV and a high optical absorption coefficient for photons with energies greater than its bandgap. Therefore, only few microns of the material are needed to absorb most of the incident light, thereby minimising material cost. The expenses of material processing can also be avoided since a short diffusion length is adequate for the charge carriers. CdTe solar cells have been reported to have demonstrated efficiency up to 16.5 %.³⁷ The drawbacks of this technology include the toxicity and low abundance of materials, temperature-dependent efficiencies and low light tolerance.³²

1.4.5: Chalcopyrite Solar Cells:

The first chalcopyrite solar cells developed were based on the use of CuInSe₂ (CIS), but the incorporation of Ga to produce the solid solution Cu(In,Ga)Se₂ (CIGS) gave an improved material quality with band-gap of 1.3 eV. The band-gap of such materials is also direct like the III – V and CdTe compounds and they also have high optical absorption coefficient for photons with energies greater than the band-gap, such that only a few microns of material are needed to absorb most of the incident light. The best CIGS solar cells are grown on soda-lime glass and an efficiency of 19.5 % has been reported.³⁷

1.5: Determination of Photovoltaic Performance:

Besides the insight into the overall PCE, there are many other parameters to characterize solar cell devices, for example, the incident photon-to-current conversion efficiency (IPCE), the short circuit current (J_{sc}), the open circuit voltage (V_{oc}) and the fill factor (FF).

1.5.1: The incident photon-to-current conversation efficiency (IPCE):

The photocurrent action spectrum of solar cells is very informative for the characterization of new materials in a device. It represents the ratio of the absorbed photocurrent divided by the incident photon flux as a function of the excitation wavelength and is referred to as the (IPCE). The photocurrent, which is normally measured, is obtained outside the solar cell device; therefore, IPCE can also be referred to as external quantum efficiency (EQE), e.g. the current obtained outside the photovoltaic device per incoming photon:

$$EQE = \frac{\eta_{electrons}}{\eta_{protons}} = \frac{I/e}{P/h\nu} = \frac{I}{P} \times \frac{hc}{e\lambda} = \frac{I}{P} \times \frac{1240}{\lambda(nm)} \qquad 1$$

16

where I is the photocurrent in A m⁻² and P is the incident light power in W m⁻².

By recording the photocurrent response while continuously varying the wavelength of the incident light, the conversion efficiency of photons to electrons, namely IPCE, can be determined. The IPCE value is expressed as a product of three factors:

$$IPCE(\lambda) = LHE(\lambda) \times \varphi_{inj} \times \varphi_{col}$$
 2

where LHE(λ) is the light-harvesting efficiency of active materials, φ_{inj} is the charge injection efficiency between the active materials (in BHJs, the charge injection is mainly from the donor to the acceptor while, in the case of DSSCs, the charge injects *via* the sensitizers into the semiconductors), and φ_{col} is the charge collection efficiency at the external electrodes. IPCE is the ultimate goal of photovoltaic research, this determines the size of the cell required to produce useable current, and thus, the input cost and output power.³⁹

1.5.2: Power conversion efficiency (I-V Curve):

To decide whether a solar cell has the potential to be commercialized or not, the most efficient method is to measure the photocurrent and photo-voltage under a simulated AM1.5 solar light. A typical solar cell I-V curve is shown in Fig. 1.8.



Figure 1.8: Current-voltage characteristics of a photovoltaic device.¹⁷

The overall PCE, η , is calculated according to equation 3:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{(V \times J)_{pp}}{P_{in}}$$
3

where P_{out} is the maximum output electrical power (in W m⁻²) of the device under illumination, P_{in} (in W m⁻²) is the light intensity incident on the device, V_{pp} and J_{pp} are the open circuit voltage and short circuit current at peak power. The maximum rectangular area ($V_{pp} \times J_{pp}$) under the *I-V* curve corresponds to the maximum output power of the device and is defined as:

$$(V \times J)_{pp} = (V_{oc} \times J_{sc})FF$$
 4

where V_{oc} and J_{sc} are the open circuit voltage and short circuit current, respectively and FF is the fill factor. An ideal device would have a rectangular shaped *I-V* curve and therefore a FF \approx 1. Substituting equation 4 into 3,

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$
 5

Thus, high PCEs can be obtained by maximizing the three basic parameters of solar cell, that is, the V_{oc} , J_{sc} and FF.

1.5.3: Open Circuit Voltage (Voc):

Besides experimentally characterizing the performance of the solar cells, some parameters can also be calculated based on the redox potentials of materials in the active layers. In heterojunction solar cells, the V_{oc} is linked to the difference between HOMO level of the donor and LUMO level of the acceptor (Fig. 1.9). Therefore, the HOMO and LUMO energy levels of the donor and acceptor in the active layer need to have an optimal offset to maximize the attainable V_{oc} . For example, in the case of polymer:fullerene based solar cells, the V_{oc} value can be estimated using the following equation:

$$V_{oc} \approx E_{LUMO_{Acceptor}} - E_{HOMO_{Donor}} - 0.3 V$$
 6

where the constant 0.3 V represents the lost energy during the photo-induced chargegeneration process.³⁹ Furthermore, it has been estimated that a minimum energy difference
of 0.3 eV between the LUMO energy of the donor and acceptor is required to facilitate the splitting of exciton and charge dissociation.⁴⁰



Figure 1.9: Schematic diagram of the donor and acceptor energy levels at D/A junction.⁴¹

Fullerene and its derivatives (such as $PC_{61}BM$) are often used as acceptor in BHJ PV cells because of their excellent electron accepting and transporting properties. Since $PC_{61}BM$ has a LUMO energy level of – 4.2 eV, the ideal lowest possible LUMO level of the donor polymer would be about – 3.9 eV. A low value of the HOMO level is essential for a high V_{oc} , however, low HOMO level would lead to increased band-gap in the donor polymer, which in turn will lead to less efficient light absorption.⁴⁰

Similar to multilayer or bulk-junction solar cells, dye-sensitized solar cells (DSSCs) also have similar V_{oc} values, corresponding to the difference between the Fermi level of the n-type material (TiO₂) and the workfunction of the electrolyte or hole-transporting materials. Interestingly in DSSCs, the dye's energy levels are only indirectly responsible for the cell's V_{oc} . However, a dye, which can transfer electrons to inorganic semiconductors and obtain electrons from the hole-transport materials, must have a higher LUMO level than the Fermi level of TiO₂ and a lower HOMO level than the workfunction of the hole-transport materials.³⁹

1.5.4: Short Circuit Current (Jsc):

In solar cells the photocurrent generation is determined by the amount of absorbed photons in relation to the total flux of photons from the solar spectrum; and the internal conversion efficiency defined by the fraction of collected carriers per absorbed photon, that is, the number of excitons created during solar illumination. Generally, low band-gap materials absorb more light, thus increasing the J_{sc} . To lower the band-gap in conjugated polymers used to fabricate BHJ solar cells, the HOMO level will have to be increased since the LUMO level of the acceptor cannot be lower than -3.9 eV and this will lower the value of V_{oc} . Scharber et al.⁴² and Soci et al.⁴³, have proposed an optimal band-gap of 1.5 eV to strike a balance between these two opposing factors.

1.5.5: Fill Factor (FF):

The FF is a measure of how much power is extracted from the cell relative to the theoretical maximum. It is a reflection of the series and shunt resistances in photovoltaic devices. Hence, a limiting factor of the FF of PV is the physical state of the active layer. An inorganic device fabricated with pure material with reduced densities of crystal defects will give a better photovoltaic effect; while organic photovoltaic (OPV) device requires continuous interpenetrating network with small domain to give a similar effect. Optimizing the morphology of the active layer of OPV device can therefore, maximize the attainable FF. It has been observed that a large interface between the donor/acceptor phases, which can be achieved through good morphology, is necessary for efficient charge separation and their subsequent transport within the active layer.^{16,40,} Generally, the higher the mobility, the less voltage is required to extract a charge to create current, thereby maximizing the achievable J_{so} and FF.

Even as the efficiency of inorganic devices have improved over time, this technology is not widely used to generate electricity, because most of the commercial solar cells are manufactured using crystalline (mono- or multi-) Si and the cost of the manufacture of such solar devices is very high. The production of pure Si is cost intensive and the fabrication procedures of the devices involve elevated temperature (400-1400°C), high vacuum and numerous lithographic steps,^{22, 37, 44} thus the high cost of production. Mass production of thin film solar cells based on Si, CdTe and CIGS has been reported, so it is expected that they will achieve the cost reduction needed to compete directly with the

other forms of energy production. Multi-junction solar cells based the III – V compounds, have also proved that by minimising thermalization and transmission losses, very large improvements in efficiency could be achieved over those of single-junction cells. Such devices have found use in generating power for space applications and are used in concentrator systems.³⁷ However, the cost of such devices is still very high relative to conventional ways of generating electrical energy. There is therefore the need to search for materials that can tap solar energy cheaply.

The use of different materials and fabrication techniques has been investigated by many solar cell scientists with the view to develop a highly efficient solar cell at low cost. Among these materials, conjugated polymers (organic semi-conductors) have been found to possess potential properties that can compete with Si. They are flexible and so can fit unto any substrate. In addition, the cost and energy of production of devices based on these compounds are low; therefore they are cheap to produce. Furthermore, they are easily processed from solution and they have large surface-area⁴⁵

1.6: Conjugated Polymers and Photovoltaic Solar Cells:

Organic photovoltaic (OPV) is a new generation low cost solar cell technology usually called 'excitonic' solar cell. The simplest configuration of such solar cell is to have the conjugated polymer sandwiched between two electrodes of different work-functions as illustrated in Fig. 1.10.⁴⁶ The difference in the work-functions of the electrodes or the Schottky barrier formed at the interface between one electrode and the doped polymer influence such device to function as an ideal diode. A brief account of the evolution of excitonic solar cells is given below.



Figure 1.10: Structure of single layer organic solar cell.⁴⁶

1.6.1: Mono-Layer OPV Cells:

The first organic PV cell was said to be investigated as early as 1959, when an anthracene single crystal was studied.²⁰ This cell showed a photo-voltage of 200 mV with an efficiency of 0.1 % making it unsuitable for photovoltaic applications. Despite, the early investigation of photovoltaic effect in organic materials, the use of conjugated polymers to form PV cells was not reported till after more than two decades. Weinberger et al. in 1982 used polyacetylene to fabricate a homogenous polymer solar cell, which afforded V_{oc} of 0.3 V and charge collection efficiency of 0.3 %.⁴⁷ Following this work, Glenis et al. in 1986 reported a cell based on poly(3-methylthiophene), which showed an external quantum efficiency (EQE) of 0.17 %, Voc of 0.4 V and FF of 3 %.48 The work of Karg and co-workers, in 1993 showed an improvement in the performance of OPV solar cells. They used PPV to fabricate an ITO/PPV/A1 cell which showed an improved Voc of 1 V compared to the earlier two, but a low PCE of 0.1 % under white light illumination.⁴⁹ In the same year Mark and his group measured the photovoltaic effect in a diode structure formed with thin film (100 nm) of PPV sandwiched between electrodes of ITO (indium-tin oxide) and either aluminium, magnesium or calcium (Fig. 1.10). They observed that devices based on Al and Mg showed Voc of 1.2 V, while those with calcium showed larger value of 1.7 V. In addition an EQE of order 1 % were measured at low intensities.⁵⁰

Despite the slightly high value of V_{oc} , the single layer PV cells had low photocurrent, because their EQE at an excitation wavelength of 458 nm was between 0.1 to 1 % depending on the metal used. The low photocurrent was attributed to the formation of excitons. The ITO layer in Fig. 1.10 functions as a transparent electrode and allows the light generated within the diode to leave the device. The top electrode is conveniently formed by thermal evaporation of a metal. Diodes of this type can be readily fabricated by solution-processing of the semiconducting polymer onto the ITO-coated glass. Spin coating from solution has been demonstrated to be capable of producing highly uniform layer, with no more than a few Ångström (Å) thickness spread over several cm². The choice of electrode is determined by its ability to assist with charge injection; ITO has a relatively high workfunction and is therefore suitable for use as a hole-injecting electrode, while, low workfunction metals such as aluminium, magnesium, or calcium are suitable for injection of electrons.⁴⁶

The formation of exciton on absorption of sun's photons by OPV solar cells is illustrated in Fig. 1.11. These excitons resist dissociation into free charge carriers in single layer OPV due to low dielectric constant of the polymers.⁵¹



Figure 1.11: Formation of Exciton by incident Photon.¹⁷,

Therefore, the excitons will diffuse within the polymer matrix and may get dissociated into free charges at the interface between the Schottky contact and the polymer (Fig. 1.12) or they get recombined and decay. The exciton diffusion is what limits the charge carrier generation in such devices, because most of them are lost through recombination due to the short diffusion length of the excitons (the distance over which excitons travel before recombination). The diffusion length in most organic semi-conductors is ca. 3 - 10 nm, which is much shorter than the device thickness.⁵² In addition, the exciton splitting process that occurs at the polymer-electrode interface is not very efficient, which contributed to the low quality of the early polymer photovoltaics.¹⁷

It has also been reported that photovoltaic devices based on homogenous polymer layer have very low fill factor (FF) of 25 % or even less, because of their poor response to light. Consequently, they have poor collection and transfer of charges, which make them to have poor PCE.⁵³ The poor performance was attributed to the high resistance of the organic materials which limits the transport of charge carriers.⁵⁴ The double layer PV cells were therefore, introduced.



Figure 1.12: Excitons dissociate at interfaces between materials having different ionization energies and electron affinities.¹⁷

1.6.2: Bi-Layer PV Cells:

The discovery of heterojunction (device comprising of two materials with differing electron affinity and ionization potential) in 1986 by Tang C. W.⁵⁵ has brought a major breakthrough in organic solar cell technology. The advantage of such devices over the single-layer is that one of the material has a high electron mobility (acceptor) while the other has a high hole mobility (donor); therefore, unlike single-layer cells, there are no electrons trapped in bi-layer solar cells.^{56,57} In addition, the absorption of incident light in bi-layer solar cells is increased because of the difference in energy gaps of the materials involved.

This cell configuration forms the backbone of all types of organic solar cells that currently exist, for example, dye sensitised solar cells, planar organic semiconductor cells and BHJ cells.²⁰ In his work Tang created bi-layer PV cells with organic semiconductors that have offset energy bands, forming a heterojunction of donor (D) and acceptor (A). The cell efficiency increased from around 0.1 % observed in single layer cells to about 1 % and the EQE reached 15 %.^{22,55} From the shape of the EQE spectrum of his cell, Tang

concluded that the improved efficiency was due to exciton dissociation at the interface created by the heterojunction.

Sariciftci et al were the first to discover an ultrafast photo-induced electron transfer from conjugated polymer (MEH-PPV) onto C_{60} . The process was much faster than the recombination of the charges and this opened the door for OPVs. ⁵⁸ The following year Sariciftci et al reported the first two-layer OPV cell based on this polymer.⁵⁹ In this cell, C_{60} was evaporated on top of a spin-cast MEH-PPV layer, which was used to absorb and transport holes to an ITO electrode following exciton dissociation at the interface. The C_{60} on the other hand, was used to accept electrons from the polymer and transport them to the anode since it has electron affinity greater than that of MEH-PPV (about 0.7 eV). The EQE for this device was about 1.2 % at 514 nm, recording a small improvement over pristine polymer films. Halls et al. on the other hand, obtained 9 % EQE using the same materials but optimized the thickness of the active layers.⁶⁰

Polymers and inorganic semi-conductors have also been used to fabricate bi-layer PV cells. The first of such device was made by Savenjie et al.,⁶¹ when they deposited a thin film of titanium dioxide (TiO₂) on a transparent ITO electrode using the sol-gel route and then spin-cast MEH-PPV on top of it. This cell afforded a 1 % EQE and 0.15 % PCE. However, Arango et al ⁶² obtained a higher PCE when they used phenylamino-*p*-phenylene vinylene (PA-PPV) instead of MEH-PPV. Because of the improved hole mobility and exciton diffusion length in PA-PPV, a 25 % EQE was achieved at the absorption maximum of the polymer, which is very impressive considering the flat interface between the two layers. A monochromatic power efficiency of 3.9 % was reported at a wavelength of 435 nm for this device.

From these experiments it could be deduced that for an efficient PV cell to be made from conjugated polymers, an interface need to be created between the polymer and another semiconductor to allow exciton dissociation. The strong potentials at the interface may favour exciton dissociation; and the electrons will be accepted by the material with the larger electron affinity while the holes will be accepted by the material with lower ionisation potential provided that the difference in potential is more than the exciton binding energy.²⁰ However, such devices usually have small interfacial area between the donor and acceptor. Thus, the dissociation of excitons which occurs within ~ 10 nm of the interface is limited, because those formed further from the interface than the diffusion length have a lower chance of being harvested.⁵² Such excitons will otherwise decay yielding luminescence instead of contributing to the photocurrent.²⁰ The active volume of

this type of solar cell is therefore limited to very thin region close to the heterojunction, which is not enough to absorb most of the solar radiation flux. Many devices nowadays use nano-structured interpenetrating network of donor and acceptor materials to form domain size twice the diffusion length so that every exciton formed in the active layer can reach an interface with the acceptor to undergo charge transfer.⁵² This approach has been the focus of researchers in recent years.

1.7: Disperse Heterojunction (HJ) Conjugated Polymer PV Cells:

The introduction of the dispersive heterojunction in designing organic solar cells in 1995 was a great break-through concept that has brought substantial improvement in the PCE of these devices.⁶³ In such devices the donor and acceptor materials are mingled together to form a continuous interpenetrating network of donor/acceptor, which reduces the exciton decay process since in the propinquity of every generated exciton there is an interface with an acceptor where fast dissociation can occur. Consequently, charge generation takes place everywhere in the active layer; and as long as there is a continuous pathway in each material from the interface to the respective electrodes, the IPCE and the photosensitivity are increased.²⁰ A good morphology of such heterojunction devices has been reported to enhance the interfacial area for exciton dissociation into free carriers and enable holes and electrons to be transported and collected.^{64, 65, 66, 67, 68, 69, 70} The use of polymer/inorganic nanocrystal and polymer/polymer are the two approaches used to create an optimal heterojunction to improve the PCE of OPVs.⁷¹

1.7.1: Polymer/Inorganic:

The fabrication of polymer/inorganic nanocrystal composite HJ solar cell was first demonstrated by Greenham et al.⁷² in 1996. This group mixed MEH-PPV with 5 nm diameter spherical cadmium sulphide (CdS) and cadmium selenide (CdSe) nanocrystals. They observed a PL quenching by 95 % in the blends when the organic ligand, trioctylphosphine oxide, used to passivate the surface of the nanoparticles was replaced with pyridine. The PL quenching increased to 98 % when 90 wt % 5 nm diameter CdSe nanoparticles were used. In addition, highly elongated nanocrystals improved the electron transport property of the composites. However, in blends with lower weight fractions of the nanoparticles, incomplete quenching was observed. TEM images revealed that phase

separation in the blends was the primary cause for the incomplete quenching. Devices made on a transparent ITO electrode with an aluminium top electrode produced 12 % EQE under low-intensity light, and a PCE ca. 0.1% under AM1.5G conditions. The device performance improved as the weight fraction of nanocrystals was increased. As a result, they concluded that electron transport was the limiting factor in photovoltaic conversion.

An improvement in polymer-CdSe nanocrystal PV cells came in 1999 with the work of Huynh et al.⁵³ It was reported in this work that electron transport in the composite film could be improved by using larger, slightly elongated nanocrystals that could pack efficiently within the film. In addition, the authors discovered that the use of P3HT improved hole transport compared to MEH-PPV. Devices constructed from thin films of 8 \times 13 nm CdSe blended with P3HT displayed photovoltaic effect with the *I-V* curves in the dark and under monochromatic illumination at 514 nm for a device with 80 % CdSe. When the device was irradiated below 4.8 W/m², a J_{sc} of 0.031 mA/cm² and V_{oc} of 0.57 V were observed. The EQE and FF were 16 % and 49 % respectively. For a similar device constructed from 4 \times 7 nm CdSe particles, the EQE and FF dropped to 4 % and 45 % respectively.

In 2002 Huynh and co-workers⁴⁴ studied further the concept of using elongated nanocrystals to improve electron transport. The nano-rods (CdSe) were co-dissolved with the polymer (P3HT) in a mixture of pyridine and chloroform, a solvent mixture consisting of a good solvent and ligand for CdSe and a good solvent for the polymer too. Device made with 90 wt % of 7×60 nm CdSe nanocrystals in P3HT when tested in simulated sunlight A.M1.5 solar conditions, under argon, showed V_{oc} of 0.7 V, FF of 4 % and PCE of 1.7 %. The maximum EQE of 55 % under 0.1 mW/cm² illumination at 485 nm was obtained for this device. Thus, they concluded that elongation of the nano-rod enhances electron transport.

Zotti et al.⁷³ also reported the use of CdSe for the fabrication of PV cells. They reacted terthiophene and sexithiophene- α , ω -dicarboxylic and α , ω -diphosphonic acids (Fig. 1.13 a and b) and some poly(thiophene-carboxylate)s and -sulfonate)s with hexadecylamine-capped 6 – 7.5 nm CdSe nanoparticles in CHCl₃ to form regular polymeric structures on ITO-glass surfaces via layer-by-layer (LBL) alternation. Based on the result of the cyclic voltammetry, UV-Vis, FTIR and PL spectroscopy, photoelectrochemistry, and photoconductivity, the LBL structures were observed to exhibit optical and electronic properties useful in photovoltaic devices.



Figure 1.13: Structures of a). Terthiophene- α , ω -dicarboxylic and b). Sexithiophene- α , ω -diphosphonic acids.

The use of Titania (TiO_2) in polymer/nanocrystal BHJ has also been widely studied. Arango et al.⁷⁴ were the first to fabricate HJ based on MEH-PPV and TiO₂; however, the EQE of the device was only 4 %, which they attributed to insufficient penetration of the polymer into the pores of the TiO₂. In 2003 Coakley and McGehee⁷⁵ reported higher EQE ca. 10 % with an estimated PCE of 0.5 % for cells made by infiltrating P3HT into films of meso-porous TiO₂.

Kwong et al.⁷⁶ instead of infiltrating P3HT into films of TiO₂; blended the polymer with different concentrations of the TiO₂. The best device composing of 60 % TiO₂ exhibited a V_{oc} of 0.44 V, J_{sc} of 2.76 mA cm⁻², FF of 36 %, PCE of 0.42% and EQE greater than 10 %.

In an effort to improve the performance of $P3HT/TiO_2$ solar cell, Gunes et al.⁷⁷ modified the surface of the nanocrystals using 6-palmitate ascorbic acid (6-PAA). Despite the surface modification, the general performance of the cells was still very low.

Sharma et al.⁷⁸ studied the optical and electrical properties of hybrid photovoltaic devices formed from a blend of poly(3-phenylhydrazonethiophene) (PPHT) as an electron donor and TiO₂ particles as an electron acceptor. The devices were made by sandwiching the blend between ITO and Al electrodes and were annealed at 50 °C for a day. A strong fluorescence quenching was observed in the devices, which indicates that exciton dissociation and charge separation occurred successfully at PPHT:TiO₂ interfaces formed in the bulk. This also showed the possibility that the separated charges reached the electrodes before any possible recombination. The authors observed that the thermal

annealing process formed separate percolation paths for electrons and holes, which led to increased mobility of charge carriers thereby increasing the photocurrent and overall efficiency of the devices. The best performance was observed in the device with 55 % TiO₂ in the blend showing J_{sc} of 0.65 and 2.1 mA/cm² for the unannealed and annealed respectively, V_{oc} of 0.65 and 0.71 V for the unannealed and annealed respectively, FF of 61 % and 64 % for the unannealed and annealed respectively and PCE of 0.37 % which increased to 0.95 % after thermal annealing.

1.7.2: Polymer/Polymer:

The other approach to improve PCE through HJ is the use of polymer/polymer blend. Yu et al.⁷⁹ and Halls et al.⁸⁰ independently introduced this technology in 1995, in their attempt to tackle the glitch of poor exciton dissociation. The two groups mixed together MEH-PPV, as donor and CN-PPV, as acceptor. The electron affinity of CN-PPV is greater than that of MEH-PPV due to the presence of the cyano– (–CN) group, which makes it more electronegative than MEH-PPV, thus, favouring electron transfer from MEH-PPV to CN-PPV. In both experiments the quenching of photoluminescence from each of the polymers was observed, a phenomenon the groups attributed to dissociation of excitons at interface formed between the two polymers before recombination could occur. Only about 6 % EQE at low light intensity was generated by PV cells made from such HJ, but optimization of the device morphology through lamination technique and the choice of polymers with better electron and hole transport; resulted in PV cells with 29 % EQE at 500 nm and 1.9 % PCE under the AM1.5 solar spectrum.⁸¹

1.8: Bulk Heterojunction (BHJ) Polymer/Fullerene:

Following the discovery of polymer:polymer HJ, Yu et al.⁶³ formulated the first fully organic BHJ cell based on a blend of MEH-PPV with a soluble form of PCBM. Luminescence quenching of the polymer as well as improved carrier transport in the device were observed. In 2001 Shaheen et al.⁷ reported the first promising results for BHJ solar cell when they mixed MDMO-PPV and PC₆₁BM and optimized the morphology to yield PCE of 2.5 % under AM1.5G conditions. They discovered that the choice of solvent and blending ratio greatly affected the performance of the cells. For instance, when toluene was used as the common solvent, PC₆₁BM formed domains that were more than 100 nm in size,

which acted as dead zones because they do not contribute to the photocurrent, a phenomenon also observed by Martens et al.⁸² and Hoppe et al.⁸³ The use of chlorobenzene on the other hand, formed fine phase segregation because it is a good solvent for both PPV and $PC_{61}BM$.⁷ Mihailetchi et al.⁸⁴ and Mihailetchi et al.⁸⁵ in separate works reported that the hole mobility in PPV is also another problem associated with such systems. The mobility is ten times lower than the electron mobility in PC₆₁BM, which lead to a build-up of holes and a field that opposes the built-in field, a condition known as space-charge limited photocurrent. However, when the amount of $PC_{61}BM$ was increased the hole mobility increased and they attributed it to increased ordering in the PPV phase.⁸⁵ When the polymer was replaced with P3HT, EQE above 70 % at the absorption maximum and 3.5 % PCE under white light illumination were observed.⁸⁶ Shaheen and other co-workers in another work, fabricated a solar cell based on MDMO-PPV and PC₆₁BM using screen-printing technique and obtained a PCE of 4.3 %, which is the highest value reported for this polymer.⁸

1.8.1: History of BHJ Solar Cells:

The most important limiting factor for optimizing the PCE is the properties of the polymer that forms the active layer of the solar cell devices.^{16,87} An ideal polymer that may give an improved PCE is one that has a better overlap with solar spectrum, that is, have broad absorption with high coefficient to effectively harvest solar energy. In addition, a good polymer should be able to have bi-continuous network with domain width within double that of the exciton diffusion length. It should also have high donor-acceptor interfacial area to enhance exciton diffusion and dissociation and efficient transport of the separated charges to external electrodes. A reasonable offset energy (exciton binding energy) to facilitate exciton dissociation for good charge generation and separation in a donor-acceptor blend is also another quality of a good conducting polymer.^{16, 88} Finally, a good polymer should have low lying HOMO to provide a large (V_{oc}).¹⁶

The rather brief history of BHJ solar cells based on polymer donor and $PC_{61}BM$ acceptor blends can be divided into three phases.⁴⁰ Phase one is centred on PPVs, in which structural modification and optimization of BHJ morphology has afforded efficiency as high as 3.3 % for MDMO-PPV. The low HOMO (– 5.4 eV) of this polymer afforded V_{oc} as high as 0.82 V; unfortunately, its large band gap limited the J_{sc} to between 5 and 6 mA/cm². Another polymer with smaller band gap, rrP3HT, came to the limelight in phase

two. Devices based on this polymer provided a higher J_{sc} (> 10 mA/ cm²), because of its relatively LBG (1.9 eV) and its increased crystallinity, which yields a higher hole mobility. Improved methods of fabrication and design of devices, such as control of morphology of the BHJ blend through thermal or solvent annealing and the use of optical spacers; had led to PCE of 5.2 %. Unfortunately, the high HOMO (- 5.1 eV) of this polymer has restricted the Voc to 0.6 V, which has limited the overall efficiency. A smaller band-gap polymer, which can absorb more of the solar spectrum and generate a higher photocurrent, was therefore required. In phase three two approaches have been adopted to improve the efficiency. Approach one places prominence on the V_{oc} by designing polymers with a low HOMO. Gadisa et al.⁸⁹, Zang et al.⁹⁰ and Anderson et al.⁹¹ had achieved V_{oc} greater than 1 V using polymers that were designed based on this approach, but the overall efficiency has been less than 4 % because of the low value of their J_{sc}. The second approach is to develop LBG copolymers, which can harvest more influx photons and boost the J_{sc}.⁴⁰ This has been achieved through the design of copolymers with alternating electron-rich (donor) and electron-deficient (acceptor) units along the same polymer backbone, first introduced in early 1990s by Havinga et al.¹¹ The formation of the LBG in these copolymers has been attributed to intra-molecular charge transfer (ICT) which occurs between the donor and acceptor moieties along the polymer backbone.

Different types of D-A copolymers have been synthesized since they were first introduced, and the most widely studied are; poly(2,7-fluorene)s, poly(2,7-dibenzosilole)s, poly(2,7-carbazole)s, poly(1,4-diketopyrrolopyrrole)s, poly(thieno[3,4-b]thiophene)s and poly(thieno[3,4-c]pyrrole-4,6-dione)s. These copolymers have shown promising photovoltaic properties, with PCE ranging between $5.4 - 8 \%^{92,93}$ when used in BHJ solar cells.

1.8.1.1: Poly(2,7-fluorene)s and Fluorene based Copolymers:

The poly(2,7-fluorene)s were initially studied for their good light-emitting properties. In 2001 Leclerc⁹⁴ reported that they can emit colors spanning the entire visible range with high efficiency and low operating voltage, making them the first family of conjugated polymers to exhibit such properties.

The first BHJ solar cell based on a copolymer consisting of fluorene as the donor and 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole as the acceptor known as PFDTBT (Fig. 1.14a), was reported in 2003 by Andersson et al.⁹⁵ The cell showed a J_{sc} of 4.66

mAcm⁻², V_{oc} of 1.04 V, FF of 46 % and PCE of 2.2 %, when it was illuminated with simulated solar light AM1.5G.



Figure 1.14: Structures of a) PFDTBT and b) N-P7.

Several types of acceptor units have been copolymerized with fluorene and have been applied in BHJ solar cells. Among these are, 6,7-diphenyl-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (APFO-Green1), 2,3-diphenyl-5,7-di(thiophen-2yl)thieno[3,4-b]pyrazine (APFO-Green2), 2,3,7,8-tetraphenyl-5,10-di(thiophen-2yl)pyrazino[2,3-g]quinoxaline (APFO-Green9) and 2,3-bis(3-(octyloxy)phenyl)-5,8di(thiophen-2-yl)quinoxaline (APFO-Green15).92 Despite the numerous copolymers of fluorene that have been synthesized and used to fabricate solar cells; it is only the N-P7 derivative (Fig. 1.14b) that has been reported to have a PCE up to 5.5 % with $J_{sc} = 9.72$ mA cm⁻², $V_{oc} = 0.99$ V and FF = 57.4 % under simulated solar light AM1.5G (100 mW/cm²) illumination; when it was used in conjunction with phenyl C71 butyric acid methyl ester (PC71BM) to fabricate BHJ solar cell.96

1.8.1.2: Poly(2,7-dibenzosilole)s and Dibenzosilole based Copolymers:

Just like poly(2,7-fluorene)s, poly(2,7-dibenzosilole)s have found vast application in the area of light-emitting diodes, blue light emission in particular. In fact, they are considered a substitute to the polyfluorenes, which are limited in this area due to formation of unwanted green emission band.⁹² Copolymers based on dibenzosiloles have also been used in polymer PVs. Leclerc et al.⁹⁷ synthesized poly(4-(5-(5,5-dioctyl-5*H*-dibenzo[*b*,*d*] silol-3-yl)thiophen-2-yl)-7-(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (Fig. 1.15) with molecular weight of 15 kDa and optical band-gap of 1.89 eV. From the preliminary PV tests they obtained PCE of 1.6 %, V_{oc} of 0.97 V, J_{sc} of 2.80 mA/cm² and FF of 55 %.



Figure 1.15: Structure of copolymer based on dibenzosilole.

1.8.1.3: Poly(2,7-carbazole)s and Carbazole based Copolymers:

Several types of the poly(carbazoles) have been reported; the first being poly(vinylcarbazole)s known as the PVKs and was first used in the development of photoreceptors for photocopiers.^{93, 98} The other forms are poly(3,6-carbazole)s, poly(1,8-carbazole)s and poly(2,7-carbazole)s. The 2,7-derivative was found to show features that make them attractive for photovoltaic applications.⁹³ Li et al.⁹⁹ reported the use of 2,7-carbazole-based polymer in photovoltaic solar cell in 2006. They blended poly-(N-(2'-decyltetradecyl)-2,7-carbazole) (Fig. 1.16) with perylene tetracarboxydiimide as the acceptor and reported a PCE of 0.6 %. In a bid to have a better harvest of the sun's photons, Leclerc et al. introduced series of carbazolevinylene polymers that were synthesized using the metal-free Horner's-Emmons polymerization reaction. The molecular weights of these polymers were below 5 kg mol⁻¹, which according to them was responsible for the low maximum PCE of 0.8 % recorded for the polymers.¹⁰⁰



[24]

Figure 1.16: Structure of poly- [N-(2'-decyltetradecyl)-2,7-carbazole].

The introduction of branched alkyl side chains on the carbazole unit was found to increase the molecular weight of poly(2,7-carbazole) derivatives and improved their solubility. Leclerc's group was the first to report such copolymers when they copolymerized *N*-alkyl-2,7-carbazole and 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole acceptor moiety using the Suzuki cross-coupling reaction to give poly(4-(5-(9-(heptadecan-9-yl)-9*H*-carbazol-2-yl)thiophen-2-yl)-7-(thiophen-2-yl)benzo[*c*] [1,2,5] thiadiazole (PCDTBT) (Fig. 1.17). The chloroform-soluble fraction gave high molecular weight number average (*M_n*) and weight-average molecular weight (*M_w*) of 37 and 73 kg mol⁻¹ respectively. This polymer gave a PCE of 3.6 %, V_{oc} of 0.86 V, J_{sc} of 6.8 mA/cm² and FF of 56 % when mixed with PC₆₀BM.¹⁰¹



Figure 1.17: Structure of PCDTBT.

Leclerc et al¹⁴ also investigated several alternating polymeric structures using theoretical models and calculations, to develop optimized poly(2,7-carbazole)s containing other acceptor moieties for solar cell applications. These acceptor moieties include; 5,8-di(thiophen-2-yl)quinoxaline, 5,8-di(thiophen-2-yl)pyrido[3,4-*b*]pyrazine, 4,7-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine,4,7-di(thiophen-2-yl)benzo[*c*][1,2,5] oxadiazole, and 4,7-di(thiophen-2-yl)-[1,2,5]oxadiazolo [3,4-*c*]pyridine. The polymers with a pyridine core, however, showed low molecular weights (4 to 11 kg mol⁻¹), which they attributed to the pyridine acting as a ligand for the palladium catalyst used for the Suzuki cross-coupling

reaction. In addition, none of these copolymers showed a PCE as high as PCDTBT. The PCE of PCDTBT was further increased to 4.6 $\%^{102}$ and 5.7 %,¹⁰³ when the solution concentration, the acceptor ratio, and the thickness of the active area were varied. Heeger et al.¹⁰⁴ on the other hand, have reported a PCE of 6.1 % for the copolymer without the use of thermal annealing or processing additives. A highly encouraging PCE of 7.1 % was reported for this polymer by Chu et al.¹⁰⁵

Encouraged by this work, Gendron et al.¹⁰⁶ copolymerized 2,7-carbazole with series of pyridazine based acceptor moieties *via* the Suzuki method. The introduction of the pyridazine was hoped to lower both LUMO and HOMO energy levels. However, the pyridazine core just like the pyridine core was thought to have a strong interaction with the palladium catalyst, which resulted in polymers with very low M_n . These copolymers showed very low PCE, V_{oc}, J_{sc}, and FF with values ranging between 0.13 – 0.47 %, 0.66 – 0.91 V, 0.55 – 1.52 mA/cm² and 35 – 44 % respectively, which was partly attributed to the low molecular weight of the copolymers.

Great progress has been recorded with the poly(2,7-carbazole) derivatives in the area of PCE of solar cells. Nonetheless, it appears the PCE of 7.1 % is about the maximum that can be reached with the presently known poly(2,7-carbazole)s. Therefore, to obtain the target PCE of 10 %, there is the need to develop new LBG poly(2,7-carbazole) derivatives.

1.8.1.4: Poly(1,4-diketopyrrolopyrrole)s:

The 1,4-diketopyrrolopyrrole (DPP) ring was first mentioned in the literature in 1974, when Farnum et al.¹⁰⁷ accidentally synthesized it instead of the 2-azetidinones they wanted to synthesize. Despite, the early discovery of this compound, the first DPP based polymer (PDTDPP) (Fig. 1.18) used in organic electronics with substantial result was reported just recently (2008) by Janssen's group.¹⁰⁸ The polymer showed an optical band gap of 1.4 eV with a M_n of 20 kg mol⁻¹ and obtained PCE of 4.0 %, V_{oc} of 0.61 V, J_{sc} of 11.3 mA/cm² and FF of 58 % on active area of 9 mm² when chloroform/*o*-DCB mixture (4:1) was used as the cast solvent and PC₇₀BM as the acceptor.



Figure 1.18: Structure of PDTDPP.

Several DPP based copolymers containing benzene ¹⁰⁹ carbazole¹¹⁰, fluorene¹¹¹, N-alkyldithienopyrrole¹¹¹, dithienosilole.¹¹², benzo[1,2-b:3,4-b]dithiophene¹¹², benzo[2,1-b:3,4-b]dithiophene¹¹² and cyclopentadithiophene as donors¹¹³; have also been synthesized and characterized. The best photovoltaic performance for this new class of copolymer in the area of organic electronics was reported for the benzene-containing derivative, which has shown PCE as high as 5.5 %. Based on the low band-gap, high hole/electron mobilities and good HOMO/LUMO energy levels of these copolymers; there is the possibility of obtaining much better PCEs in the near future.

1.8.1.5: Poly(thieno[3,4-b]thiophene) derivatives:

Copolymers based on thieno[3,4-*b*]thiophene derivative were first reported in the late 1990s and early 2000s; when Neef et al. ¹¹⁴ reported the synthesis of poly(2-phenylthieno-[3,4-*b*]thiophene) in 1999. The polymerization was done by repetitive oxidative electrochemical cycles of a saturated solution of the monomer, 2-phenylthieno-[3,4-*b*]thiophene yielding a polymer with optical band gap of a 0.85 eV. This was followed by the work of Pomerantz et al.²¹, who synthesized poly(2-decylthieno-[3,4-*b*]thiophene-4,6-diyl) in 2001; using FeCl₃ oxidative polymerization method producing a polymer with M_n of 52 kg mol⁻¹ and a band gap of 0.92 eV. This was closely followed by the work of Lee and Sotzing¹¹⁵ who synthesized poly(thieno[3,4-*b*]thiophene) using electrochemical

polymerization. The polymer showed LBG of 1.2 eV and good electrical properties. From the results of the polymerization, the authors noticed that the monomer have low oxidation potential for polymerization, so in 2005 they studied it for OLEDs and electrochromic devices.¹¹⁶

The first photovoltaic study involving the poly(thieno[3,4-*b*]thiophene) derivatives was reported by Yang's group¹¹⁷ when they synthesized an ester-functionalized poly(thieno[3,4-*b*]thiophene), (PTT) (Fig. 1.19) using the Stille polycondensation reaction and studied its optical and electrochemical properties. Functionalizing the polymer with an ester at the 2- position stabilized it and the long alkyl group improved its solubility. The M_n of the polymer was found to be 11.8 kg mol⁻¹ and showed absorption maximum at 750 nm with an onset of absorption at 970 nm, thus an optical band-gap of 1.3 eV. It has also shown near IR photo-detection properties with EQE exceeding 38 % and under illumination, photovoltaic effect was observed with an overall PCE of 1 %.





Figure 1.19: Structure of ester-functionalized PTT.

Yu et al.¹¹⁸ reported another thieno[3,4-*b*]thiophene based polymer in which the thiophene group in PTT was replaced with benzodithiophene (BDT) unit to give PTB1 (Fig. 1.20). Its photovoltaic response when mixed with PC₆₁BM in 1:1 weight ratio was encouraging with PCE of 4.76 %, V_{oc} of 0.58 V, J_{sc} of 12.5 mA/cm² and FF of 65 %. Upon modifying the active layer with the weight ratio of PBT1:PC₇₁BM at 1:1.2, a remarkable PCE of 5.3 % with higher J_{sc} of 15.0 mA/cm² was observed, while the V_{oc} remained at 0.58 V and FF reduced to 63 %.



[28]

Figure 1.20: Structure of PTB1.

Several copolymers based on the skeleton of PTB1 with modifications in the groups attached either to the thieno[3,4-*b*]thiophene or the benzodithiophene have been synthesized with some showing PCE close to or slightly higher than those of PTB1.⁹³ However, when a fluorine atom was introduced in the thieno[3,4-*b*]thiophene ring of PTB1 and all the alkyl groups were replaced with ethylhexyl a PCE as high as 7.4 % was obtained in BHJ solar cell using PC₇₀BM, chlorobenzene as solvent and di-iodooctane (DIO) as processing additive.³¹ In another development, a massive improvement in the overall photovoltaic effect was observed with a polymer similar to the one that afforded the 7.4 % PCE, but instead of the ester group a ketone was introduced. A BHJ solar cell based on this polymer gave a PCE of 7.7 %, V_{oc} of 0.76 V, J_{se} of 15.2 mA/cm² and FF of 67 %.⁹³ Solarmer has however, reported an NREL-certified PCE of 8.3 \pm 0.3%, V_{oc} of 0.82 V, J_{se} of 14.46 mA/cm² and FF of 70 %.^{119,120}

1.8.1.6: Poly(thieno[3,4-c]pyrrole-4,6-dione) derivatives:

According to Gendron and Leclerc, the thieno[3,4-*c*]pyrrole-4,6-dione (TPD) based polymers were first reported in the late 1990s.⁹³ However, the first application of TPD based copolymers in solar cells came in 2010 with the work of Leclerc et al.¹²¹This group copolymerized TPD and BDT by Stille coupling to give PBDTTPD (Fig. 1.21) with M_n of 13 kg mol⁻¹. The ethylhexyloxyl chain on the BDT was thought to enhance the solubility of the polymer.



Figure 1.21: Structure of PBDTTPD.

The optical band gap of the polymer was found to be 1.81 eV in the solid state and it gave good photovoltaic properties when blended with $PC_{70}BM$ as the acceptor. The overall PCE of 5.5 % with a V_{oc} of 0.85 V, J_{sc} of 9.81 mA/cm² and FF of 66 % were observed for a BHJ solar cell based on this polymer with an active area of 100 mm² and a 1:2 polymer/acceptor ratio under AM1.5G illumination.

Other workers have synthesized other copolymers similar to PBDTTPD with minor structural modifications, but the overall PCE of these copolymers did not show significant improvement compared to Leclerc's polymer. The introduction of thiophene spacer between the BDT and TPD did not improve the PCE either.⁹³ However, when Chu et al. ¹²² synthesized PDTSTPD (Fig. 1.22), by copolymerizing TPD and dithieno[3,2-b:2,3-d]silole (DTS) an impressive PCE of 7.3 % was obtained.





This copolymer was synthesized using the Stille coupling polymerization and when it was blended with PC₇₀BM, V_{oc} of 0.88 V, J_{sc} of 12.2 mA/cm² and FF of 68 % were obtained. With this noteworthy performance by this new class of conjugated polymers, the PCE target for commercialization of OPVs may soon be reached, though many derivatives will have to be designed and tested. Recently Mitsubishi Chemical reported the development of an OPV material showing a record-breaking PCE of 10 ± 0.3%, V_{oc} of 0.899 V, J_{sc} of 16.75 mA/cm² and FF of 66 %,³⁸ therefore, there is an indication that the OPV technology will soon be commercialized.

1.8.2: Physical Processes in Polymer: Fullerene BHJ Solar Cells:

The basic principles of operation of BHJ device can be viewed as follows: a) The active layer of the device absorbs sunlight photons and get excited leading to the creation of excitons in the conjugated polymer. b) The excitons start to diffuse within the donor phase and if they encounter an interface with the acceptor, then charge dissociation occur leading to charge separation. The resulting metastable e-h pairs diffusing across the D/A interface may still be held by Coulombic force and an electric field is needed to separate them into free charges. c) The separated charges are transported with the help of internal electric field, caused by the use of electrodes with different work-functions, towards the external electrodes where they are collected and driven into the external circuit. Nevertheless, the excitons may fail to reach an interface and so they will decay yielding luminescence. Therefore, the excitons should be generated within the diffusion length of the interface.²⁰

1.8.3: Morphology, Charge Transport and Mobility in BHJ Solar Cells:

The conducting properties of conjugated polymers are mainly determined by the conjugation length (the number of continuous defect free polymer units), that is, the measure of the degree of free movement of electrons along a continuous polymer backbone. A principal factor that governs the mobility of charges in conjugated polymers therefore is the effect of the morphology of the polymer on charge and energy transfer. This property also determines how the polymer chains constituting the sample can interact. Such inter-chain interactions can result in charge transfer between polymer strands, which is essential to charge transport across a macroscopic distance as the length of one polymer

strand is limited.¹²³ Studies have shown that the overall charge mobility in conjugated polymers is controlled by the inter-chain charge transport,¹²⁴ since mobility within one single chain is much higher than over an entire amorphous film.¹²⁵

Understanding and controlling the nano-scale morphology is therefore crucial to the performance of polymer BHJ and polymer inorganic nanocrystals solar cells. In these photovoltaic devices, optimum blend morphologies must be commensurate with the nanometer length scales of exciton diffusion and charge separation.¹²⁶ The domain size of the materials, therefore play vital role in the actual J_{sc} measured in a device. Large domain size may lead to exciton loss due to decay; whereas too small domain sizes can enhance recombination of the charge carriers.¹²⁷ A balance must therefore be attained to optimize device efficiency. This can be done using polymer domains that are small enough for efficient migration of excitons to an interface, yet large enough to promote efficient longrange geminate charge separation.¹²⁶ This can be achieved through good device morphology. The morphology of photoactive polymer/fullerene blend can be affected by controlling several production parameters during the film formation or by postproduction treatment. Large range of solvents, polymer:fullerene ratios, annealing effects, additives.¹²⁸ solution concentration and the chemical structure of the materials are the parameters required to induce the correct morphology. Single polymer chain in solution has shown some similarities to common metals in terms of electrical charge mobility.¹²⁵ However, in the films that form the active layer of conjugated polymer-based devices; the polymer strands are not mobile. Therefore, conjugation is broken due to twists along the backbone hampering mobility.

To achieve an organic solar cell with a reasonable PCE and stability, the materials have to be designed carefully in order to fulfill the parameters, such as redox energies, range of light absorption, and self-organization.³⁹

Though scientists and engineers have over the years, been working round the clock in the area of morphology control, electrode modification and the incorporation of dielectric layers in organic solar cell devices to further improve their photovoltaic performance, the technology is yet to be commercialized due to the poor PCE.

1.9: Dye Sensitised Solar Cells (DSSCs):

DSSCs like polymer photovoltaic solar cells are another promising technology that is highly promising and cost-effective alternative for the photovoltaic energy sector. In 1991 ORegan and Grätzel¹²⁹ introduced the first DSSC based on ruthenium(II)-polypyridyl complex as the active material in conjunction with Γ/I_3^- liquid electrolyte and nanocrystalline TiO₂ (nc-TiO₂) affording an overall PCE approaching 11 % under standard AM1.5G illumination. This high PCE was attributed to the wide absorption range of the ruthenium(II)-polypyridyl complex, which extends from the visible to the near-infrared (NIR) regime. Therefore, a lot of effort has been devoted to the synthesis and investigation of materials for DSSCs. The synthesis can be grouped into two broad areas: a) functional ruthenium(II)-polypyridyl complexes like, N3 [31], N719 [32], Z907 [33] and black dye [34] (Fig. 1.23 a) and b). metal free organic donor-acceptor (D-A) dyes such as oligoenes [35] containing dialkyamino-phenyl groups as donor and cyanoacrylic acid as acceptor and oligothiophene with difluorenyl-phenylamine [36] (Fig. 1.23 b). The former class contains expensive ruthenium metal and requires careful synthesis and tricky purification steps. On the other hand, the second category can be prepared cheaply, and their absorption and chemical properties can easily be tuned through suitable molecular design.¹³⁰













b).

Figure 1.23: Structures of a). ruthenium(II)-polypyridyl complexes N3, N719, Z907 and Black dye and b). metal free organic donor-acceptor dyes.

In DSSCs the incoming light is absorbed by the sensitizer, which is attached to the surface of the semiconductor nc-TiO₂. Charge separation takes place at the interface through photo-induced electron injection from the excited dye into conduction band of nc-TiO₂. Holes are created at the dye ground state, which is further regenerated through reduction by the electrolyte (the hole-transport material, HTM), which itself is regenerated at the counter-electrode by electrons through an external circuit. In principle, for efficient DSSCs the regeneration of the sensitizer by the HTM should be much faster than the recombination of the conduction band electrons with the oxidized sensitizer.¹³⁰ Despite the relatively high PCE of DSSCs, they suffer from operational drawback. The electrolyte and its solvent are prone to degradation and evaporation, which has posed a problem with long-term performance. As a result, there have been several research efforts to replace the liquid electrolyte with semi-conducting polymers or other organic materials with the aim to solving these problems. For instance, Bach along with Grätzel and other co-workers¹³¹.

reported a promising solid-state dye-sensitized solar cell based on heterojunction of nc-TiO₂ with an amorphous organic HTM 2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (OMeTAD). They reported an IPCE of 33 % and PCE of 0.74 % for the devices to which additives [N(PhBr)₃SbCl₆ and Li(CF₃SO₃)₂N)] were added.

Dittmer et al.¹³² have also reported the effect of perylene bis(phenethylimide) (PPEI) dye in DSSC based on MEH-PPV. They investigated the PL quenching in a blend of MEH-PPV/PPEI. The PL efficiency quenching they observed for PPEI/MEH-PPV blends was more efficient than in blends of MEH-PPV and CN-PPV. From the efficient PL quenching they deduce that virtually all excitons generated in MEH-PPV were affected by the presence of PPEI. This then indicated that a continuous interpenetrating network of the polymer/dye with interface within the exciton diffusion range was formed. Therefore, charge separation was improved by introducing PPEI into MEH-PPV thin film devices. It was also observed that the EQE of the blend was more than fourfold for a 1:60 PPEI:MEH-PPV blend when compare to pristine MEH-PPV as a monolayer in a sandwich photovoltaic cell which shows an EQE of 0.04% under similar conditions.

In 2000 Dittmer et al⁷¹ did a similar work, they blended P3HT (as a donor and hole conductor) with perylene dye [perylene tetracarboxyl diimide N,N-bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide) (EP-PTC)] (as an acceptor and electron transport material). This dye can form crystals within a polymer matrix, and such crystals are expected to have higher electron mobilities than amorphous composites and should allow much higher exciton diffusion ranges as a result of the higher degree of order in the crystals. Films of the pristine polymer and that of the dye and their blends with different weight ratios were investigated in a sandwich structure between an Al top electrode and ITO coated glass. The EQE in the pristine materials lie below 0.2 %, whereas in the blend devices it reached maximum of ca. 7 % at 495 nm for device containing 80 wt % of EP-PTC. Thus, there is an improvement in the EQE by a factor of 40 compared to the pristine dye and 250 compared to the pristine polymer device. This device had also shown V_{oc} of 350 mV and FF of 41% under illumination at a wavelength of 540 nm through the ITO contact at an incident light intensity of 0.16 mW/cm². This afforded a PCE ca. 0.4 % at 540 nm. Furthermore, the photoluminescence (PL) was quenched by a factor of more than 10³ for a 30:70 EP-PTC:P3HT blend with respect to pristine dye and more than 200 with respect to pristine P3HT. According to them the observed EQE enhancement was due to additional charge separation and the possibility of energy transfer followed by radiative

recombination was ruled out. They concluded that photo-induced charge transfer took place between the polymer and the dye.

Gebeyehu et al. ¹³³ have also demonstrated the effect of dye on the performance of hybrid solar cell based on nano-porous TiO_2 and conjugated polymers; [poly(3-octylthiophene), P3OT] and three different thiophene-isothianaphthene based copolymers. The photovoltaic properties of devices which did not contain the dye cis-bis[(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)bis-tetrabutyl-ammonium, and those that contain it were compared. It was observed that the devices based on P3OT that contained the dye showed a PCE of 0.16 %, which is two-fold higher than those without it, while the PCE of the devices based on the copolymers depended on the band gap of the respective copolymers.

Zafer et al.¹³⁴ have also reported solid-state dye sensitized nc-TiO₂ solar cells based on perylenediimide (PDI) derivative dye; N,N' -bis-2-(1-hydoxy-4-methylpentyl)-3,4,9,10-perylene bis (dicarboximide) (HMPER) with P3OT and P3HT polymers. Devices containing both polymers gave similar values of J_{sc} , V_{oc} , FF and PCE; ca. 80 mA/ cm², 0.7 V, 0.26 and 2 % respectively at 80 mW/cm² AM 1.5 light intensity.

Tsekouras et al.¹³⁵ have reported the doping of poly(terthiophene) with anionic dyes during electro-deposition for the fabrication of solid-state dye sensitized solar cells. The device based on sulforhodamine B dye doped polymer showed the best result with $J_{sc} = 178 \text{ mA/cm}^2$, $V_{oc} = 318 \text{ mV}$, FF = 29.6 % and PCE = 0.033 % under white light illumination with an intensity of 500 Wm⁻².

Komiya et al.¹³⁶ have reported a highly efficient quasi-solid state dye-sensitized solar based on ion conducting polymer electrolyte, ruthenium dye [Ru (2,2'-bipyridine-4,4'-dicarboxylic acid)2] and porous TiO₂. Poly(ethylene-oxide-co-propylene oxide)trimethacrylate, (oligomer) having three polymerizable reactive groups was used to form a stable quasi-solid three-dimensional polymer structure, which acted as the ion conducting polymer. According to the authors, the conductivity values of the polymer electrolyte in different organic solvents showed that the ionic conductivity increased with decreasing viscosity of the solvent and a high ionic conductivity of 9 mS/cm was observed for the polymer electrolyte. The cells were fabricated by sandwiching these materials between fluorine doped SnO₂ conducting glass and platinum coated counter electrode. By optimizing the electrolyte composition, polymer concentration and thickness of the porous TiO2, efficiency close to the highest value reported for liquid DSSCs was achieved. A Jsc of 14.8 mA/cm², V_{oc} of 0.78 V, a FF of 70 % and an overall PCE of 8.1 % under AM1.5 irradiation (100 mW/cm²) were reported for the best cell. It was also observed that this cell showed higher V_{oc} than that of the liquid cells, a phenomenon the authors attributed to the possibility of the suppression of the back electron transfer between the conduction band of the TiO₂ electrode and the triiodide ion in the electrolyte of liquid DSSC.

1.10: Motivation:

The continuous search for materials with good photovoltaic properties has been the driving force for embarking on this research. The invention of DSSCs in 1991 by Grätzel and co-workers¹²⁹ has attracted considerable interest because of the encouraging performance of the cells. The excellent power conversion performance of these cells and the efficiently low cost of production have made them appear to be good alternative to Si solar cell. For example, DSSCs based on nc-TiO₂ coated with light absorbing dye have shown very high performance because of the large surface area of the TiO₂ structure. Upon illumination, the dye injects an electron into the surface of the inorganic nanocrystal. Complete pathways to the electrode then allow electron collection while the hole charge is carried to the anode by an electrolyte usually based on an Γ/I_3^- redox couple. However, one of the problems in the commercial applications of the DSSC is the stability of the cell.

The electrolyte and solvent are prone to evaporation and degradation, thus, limiting the long-term performance of such devices. Therefore, recent efforts in DSSCs research are focusing on replacing the liquid electrolyte with solid-state hole conductor to eliminate practical problems with sealing and degradation. Semiconducting polymers are of practical interest as replacements for the liquid electrolyte as a hole conducting material. Unfortunately, the efficiency of cells based on these new hole transport have not exceeded 4 %.¹³⁷

BHJ solar cells based on conjugated polymer donor and fullerene acceptor blend, have also received enormous attention for more than a decade and half now; and almost all the researches done within these years have been directed towards improving the PCE. Significant success has been achieved because the PCE of devices based on MDMO-PPV evolve from less than 1 % in 1995⁶³ to as high as 4.3 % in 2001, which is the highest recorded for this system. Sean et al.⁸ recorded this achievement, from a device fabricated using screen-printing and illuminated by monochromatic light with a wavelength of 488 nm and an intensity of 27 mW/cm². The improved PCE according to the authors was as a

result of good morphology afforded by the use of the screen-print method. As a result of its relatively low HOMO energy level of -5.4 eV, the V_{oc} was as high as 0.84 V; however the J_{sc} was very low (3.16 mA/cm²), due to possibly the large band gap of the polymer. ⁴⁰ This has prevented further improvement of the PCE of devices based on this polymer.

A polymer with smaller band gap, regioregular poly(3-hexylthiophene) (rr-P3HT), therefore, came into the limelight. Devices based on this polymer gave a much higher J_{sc} (> 10 mA/cm²), due to its LBG (1.9 eV) as well as its increased crystallinity, which gives it a high hole mobility.^{138, 139, 140} Irwin M. D. et al.⁹ reported a 5.2 % PCE of BHJ solar cell based on rr-P3HT as a result of modification in the cell configuration. In their device, the traditionally used poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) electron-blocking layer was replaced with NiO. This afforded a device with $V_{oc} = 0.638$ V $J_{sc} = 11.3$ mA/cm² and FF = 69.3 %. The low value of the V_{oc} was attributed to the high HOMO energy level (- 5.1 eV) of this polymer. This factor has hampered the overall efficiency of devices based on this polymer to the regime of 5 %.⁴⁰

Despite, these optimization methods, and numerous others, such as using different solvents to deposit the active layer, thermal annealing of the active layer or the device, film forming speed, adding some additives to the active layer, electrode interfacial layer and tandem structure, adopted to improve the PCE of devices based on MDMO-PPV, MEH-PPV and P3HT, the performance of devices based on these polymers has not improved beyond 5 %.

The first motivation, therefore, is the search for material with LBG to fabricate DSSCs in conjunction with nc-TiO₂. Lowering the band gap of the polymer is envisaged to boost the absorption of the influx photons since LBG polymers absorb at wavelength that overlaps with the solar spectrum. Studies have shown that introducing electron-withdrawing side groups in the polymer backbone of P3HT lowered its HOMO energy level.¹⁴¹ The introduction of electron-withdrawing group at the ω -position of the hexyl side chain, was therefore, envisaged to lower the HOMO energy level of this polymer.¹⁴²

The second part of this research was motivated by the new approach adopted to improve the overall efficiency of BHJ photovoltaic solar cells. LBG polymers are necessary to achieve OPV that can reach commercial and widespread use level, because they will match the solar spectrum better and produce high J_{sc} . However, lowering the band gap hoists the HOMO energy level, thereby lowering the V_{oc} . The construction of D-A having electron-rich and electron-deficient units in the backbone of the same polymer has

been an efficient tool used to design LBG polymers with the HOMO energy level lowered through ICT.^{11, 143} The desire to develop new materials that possess such quality is therefore, the driving force for the second part of this thesis.

The choice of materials to synthesize the LBG polymer was informed by their features. The use of poly(2,7-carbazole)s in polymer light emitting devices (PLED) and organic field-effect transistors (OFET), has revealed the potential for these polymers in BHJ photovoltaic cells. For instance, carbazole the donor moiety in carbazole copolymers was found to be a good hole transporting material and the absorption spectrum of polymers based on it could be fine-tuned for optimal solar spectral match *via* selective copolymerisation. ^{92, 144} It can also keep the HOMO reasonably low, which may provide good air stability and possibly high V_{oc} .⁹² Furthermore, with proper manipulation of structure, carbazole-based materials can have strong intermolecular interactions in the solid state, with its aromatic structure giving a better stability.^{144, 145, 146}

Fluorene is another donor moiety that has been studied extensively and poly(fluorene)s (PFs) have been widely studied for PLED because of their easy processability, high quantum yield, and good charge transport properties.¹⁴⁷ Hou, et al., ¹⁴⁸ synthesized the first dithienyl-benzothiadiazole (DTBT) containing polyfluorenes *via* Suzuki coupling for use in red light-emitting diodes. Later in 2004¹⁴⁹ it was applied as a donor phase for BHJ cells in which PCE of 1.95 % was achieved. Slooff, et al.¹⁵⁰, achieved a higher PCE of 4.2% when they used a polymer containing two decyl groups. It is therefore, worth exploiting the photovoltaic properties of fluorene using different types of acceptor.

The co-monomer that will be used to synthesize the copolymers is a strong electron-acceptor, 2,1,3-benzothiadiazole (BT).⁴⁰ It is a heterocyclic compound used extensively to construct LBG polymers due to its ability to lower the band gap through ICT. Such polymers have shown high electron mobility in addition to high hole mobility and good solar photon absorption.^{10, 101, 151, 152, 153, 154}

However, studies have shown that coupling BT with donor aromatic units caused steric hindrance, less planarity and reduced chain-to-chain interactions, thereby lowering charge carrier mobility along the polymer backbone. Conversely, according to model study by van Mullekom H.A.M. et al.¹⁵⁵ and the work of Zhou H. et al.,¹⁵⁶ the combination of electron releasing unit like thiophene with the BT unit improved the electronic and physical properties of the D-A polymer. This arrangement mitigates the severe steric hindrance between the BT and the donor material, which improves planarity. As a result,

the desirable chain-to-chain interaction among polymers is improved, which in turn will enhance charge carrier mobility. Furthermore, an intermolecular S***N contact may be established, which might provide strong inter-chain interactions that may further improve planarity.¹⁵⁷

Finally, it has been observed that inner electron D-A interactions promote intermolecular π - π stacking, a condition necessary for high charge mobility. A rigid coplanar fused aromatic ring efficiently enhances this interaction and improves charge transport of conjugated polymers.¹⁵⁴ For instance, poly(2,7-carbazoledithiophene-2,1,3benzothiadiazole) (PCDTBT) has recently yielded a significant PCE of 6.1% when combined with PC₇₀BM in modified configuration of BHJ solar cell containing TiOx cathode interlayer.¹⁰⁴ Another electron acceptor that will be used to synthesise the copolymers is dibenzothiophene-S,S-dioxide, which has coplanar benzene rings. Moreover, the acceptor character of the SO₂ group is expected to decrease the LUMO energy level of the copolymers thereby improve their electron transport properties. Such qualities have already been exploited in OLEDs by Perepichka et al.¹⁵⁸

Chapter Two:

2.0: Introduction:

The first part of this chapter will give an overall experimental methods used in this research; the second part will outline the synthetic route to the polymer P3HTT, while part three will explain the fabrication of DSSCs using this polymer. The fourth part will outline the synthesis of the co-monomers and the donor-acceptor (D - A) copolymers.

2.1: Experimental:

2.1.1: General Procedure:

Unless otherwise stated, reactions were magnetically stirred and monitored by TLC. The chromatograms were visualised with iodine or under UV light. All anhydrous reactions were conducted under a constant flow of nitrogen using oven dried (120 °C) glassware that had previously been cooled under a stream of nitrogen.

2.1.2: Materials:

Starting materials and reagents were purchased from commercial suppliers and were used without further purification unless otherwise stated. 2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)trimethylstannane **[53]**, 3,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[b,d]thiophene-5,5-dioxide **[56]** and benzo[b]thieno[3,4-e][1,4]dioxane **[58]** were donated by Professor Igor F. Perepichka, while 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) **[61]** was purchased from Sigma Aldrich. All anhydrous solvents used were distilled over sodium wire and benzophenone or obtained from a solvent distiller manufactured by Innovative Technology PS-MD-3 Newburyport MA, USA. Flash chromatography was performed on Davisil[®] silica gel (35-70 microns) with the eluent specified in each case. TLC was conducted on pre-coated E.Merck silica gel 60 F_{254} glass plates.

2.1.3: Instrumentation:

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 500 spectrometer using an internal deuterium lock at ambient temperature or otherwise stated, at 500 MHz and 125 MHz with internal references of $\delta_{\rm H}$ 7.27 and $\delta_{\rm C}$ 77.0. Melting points were determined using a Gallenkamp MF370 instrument and are uncorrected. High resolution Atmospheric Pressure Chemical Ionisation (APCI) mass spectra were recorded on LTQ Orbitrap XL at the EPSRC National Mass Spectrometry Service Centre based in Swansea, while Time of Flight (TOF) mass spectra were recorded on Micromass GCT CA-091 based in Bangor. Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity index (PDI) were determined using gel permeation chromatography (GPC) analysis with a polystyrene standard calibration and were recorded on Agilent PL-GPC Plus Integrated GPC System. Thermal properties were evaluated using Thermogravimetric Analysis (TGA) recorded on SDT Q600 V4.1 Build 59.

Electron absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis NIR spectrophotometer in quartz cells with 10 nm path-length (solution) or as spin-coated films on glass slides. The photoluminescence spectra were recorded on Horiba Scientific Fluoromax-4 Spectrofluorometer in 10 nm path-length quartz cells (solution).

Electrochemical properties were recorded on a Nova AutoLab PGSTAT302N potentiostat-galvanostat using platinum disk (d = 1.6 mm) as the working electrode, platinum wire as counter electrode and quasi-reference Ag/Ag⁺ electrode (0.01 M AgNO₃ with 0.1 M Bu₄NPF₆ in acetonitrile). The samples were prepared as thin films by drop-cast from chloroform solution, air dried and scanned in an anhydrous and nitrogen saturated solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) in acetonitrile at a scan rate of 100 mV s⁻¹. The reference electrode was calibrated by a ferrocene/ferrocenium (Fc/Fc⁺) redox couple (-4.8 vs. vacuum level).

Photoresist Spinner Model 4000, Electronic Micro Systems Ltd was used to spin coat compound [42] onto glass slides and Edwards AUTO 306 Turbo Evaporation System was used to apply the external electrode. The photovoltaic (I-V) measurement of the fabricated DSSCs was measured using an Abet Technologies, Function Focused Sun 2000 Solar Simulator, with light intensity of 1 kW/m² equivalent to 1 Sun and AM1.5 at Technium OpTic, Centre for Solar Energy Research, St Asaph Business Park, North Wales UK.

Finally, the fabrication and characterisation of BHJ solar cells based on the D-A

copolymers were done in Russia by the group of Dr. Pavel A. Troshin of Institute for Problems of Chemical Physics of Russian Academy of Sciences.

2.2: Synthetic Routes:

2.2.1: Synthesis of 1-(6-Bromohexyloxy)-4-methoxybenzene)¹⁵⁹



Potassium hydroxide (33.78 g, 0.6 mol) was dissolved in methanol (100 mL) and added drop-wise to 4-methoxyphenol (62.01 g, 0.50 mol) also dissolved in methanol (25 mL) in a 250 mL two necked round bottomed flask. The resulting solution was added drop-wise to 1,6-dibromohexane (244.30 g, 1.0 mol) dissolved in acetone (200 mL) in a 500 mL two necked round bottomed flask over 1.5 h. The mixture was then refluxed (70 °C) for 1 h, cooled and diluted with water (250 mL) and diethyl ether (400 mL) was added and kept overnight in a freezer. The mixture was filtered to remove precipitated potassium bromide and the organic layer was separated, washed with NaOH (1 N, 3 x 100 mL) and water (3 x 50 mL), then dried (MgSO₄). Removal of the solvent gave colourless oil, from which the pure compound was crystallized by dissolving the oil at room temperature in diethyl ether (150 mL) and storing overnight in a freezer to give compound [37] as a white solid, (107.52 g, 75 %). R_f 0.35 (10 % diethyl ether in petroleum ether 40 – 60 °C) m.p. 45 °C.

¹H NMR 500 MHz, CDCl₃), δ (ppm): 7.26 (s, 4H), 4.35 (t, J = 6.4 Hz, 2H), 4.20 (s, 3H), 3.86 (t, J = 6.8 Hz, 2H), 2.33 (t, J = 6.5 Hz, 2H), 2.20 (t, J = 5.9 Hz, 2H), 1.94 (m, 4H). This result is in agreement with literature work.¹⁵⁹
2.2.2: Synthesis of 3-[6-(4-methoxyphenoxy)hexyl]thiophene¹⁶⁰



[38]

Compound [37] (26.50 g, 0.092 mol) in anhydrous ether (35 mL) was added to magnesium turnings (2.34 g, 0.096 mol) in ether (5.90 mL) in a three-necked 500 ml round bottomed flask under an inert atmosphere. This was refluxed for 6 h (40 °C) and the resulting Grignard solution was transferred *via* cannula over 1 h to another apparatus containing 3-bromo thiophene (12.70 g, 0.078 mol) and Ni(dppp)Cl₂ (52 mg, 0.096 mmol) dissolved in cold (0 °C) ether (16 ml). The mixture was refluxed for 15 h, cooled and hydrolysed with HCl (1M, 40 mL) and ice water (115 mL). The mixture was extracted with diethyl ether (3 x 25 mL) and the combined organic portions washed with saturated NaHCO₃ (3 x 15 mL) to neutrality and dried (MgSO₄). Removal of the solvent gave a dirty yellowish white solid from which an analytically pure solid was obtained by recrystallization in n-hexane (300 mL). The crystals were removed by filtration, washed with small portion of cold (0 °C) n-hexane and dried to give compound [38] as a white solid, (14.81 g, 65.47 %). R_f 0.42 (10 % ether in petroleum ether) m.p. 35 °C.

¹H NMR 500 MHz, CDCl₃), δ (ppm): 7.25 (dd, 4.8, 3.0 Hz, 1H), 6.94 (dd, J = 6.9 Hz, 3.4, 1H), 6.84 (s, 4H), 3.91 (t, J = 6.5 Hz, 2H), 3.78 (s, 3H), 2.65 (t, J = 7.7 Hz, 2H), 1.77 (m, 2H), 1.66 (m, 2H), 1.51 (m, 2H), 1.41 (m, 2H). The result is in agreement with those published in literature.¹⁶⁰

2.2.3: Preparation of 3-(6-bromohexyl)thiophene¹⁶⁰



A mixture of hydrogen bromide (48%, 20.50g, 0.121 mol) and acetic anhydride (20.5g, 0.200 mol) (CAUTION EXOTHERMIC REACTION! MIX the HBr and Ac₂O at 0 °C) was added to compound **[38]** (5.90 g, 0.02 mol) under inert atmosphere and the reaction mixture was refluxed for 25 h (100 °C). The mixture was then cooled, diluted with water (30 mL) and extracted with ether (4 x 30 mL). The combined organic portions were washed with saturated NaHCO₃ (ca. 30 mL) solution to neutrality. After drying (MgSO₄), the removal of solvent yielded brown-yellow oil from which hydroquinone was precipitated by addition of n-hexane. The solution was filtered and the filtrate was transferred to a short column of silica gel and eluted with n-hexane. Removal of the solvent gave compound **[39]** as colourless oil (3.92 g, 79.51 %). R_f 0.28 (n-hexane).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 7.28 (d, J = 5.0 Hz, 1H), 6.96 (d, J = 5.0 Hz, 2H), 3.45 (t, J = 6.8 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 1.86 (m, 2H), 1.68 (m, J = 7.5 Hz, 2H), 1.51 (m, 2H), 1.4 (m, 2H). This result is in agreement with those published in literature.¹⁶⁰

2.2.4: Preparation of 2,5-dibromo-3-(6-bromohexyl)thiophene¹⁶¹



Compound [39] (3.74 g, 15.1 mmol) was dissolved in THF and acetic acid (24:24/v:v) in a 250 mL flask equipped for stirring. *N*-Bromosuccinimide (5.4 g, 30 mmol) was added and the mixture was stirred for 1.5 h in the dark. The mixture was then cooled; water (50 mL) was added and the mixture extracted with diethyl ether (3 x 50 mL). The organic portions were combined and washed with water (3 x 50 mL) and saturated NaHCO₃ solution (3 x 50 mL). After drying (MgSO₄) the removal of the solvent gave an orange-yellow (5.39 g) liquid which on column chromatography over silica gel using petroleum ether 40 – 60 °C as the eluent gave compound [40] as a colourless oil, (4.24 g, 67 %) R_f 0.39 (petroleum ether).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 6.79 (s, 1H), 3.41 (t, J = 6.8 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.87 (m, 2H), 1.57 (m, 6H). The result is in agreement with those published in literature.¹⁶¹

2.2.5: Preparation of HT-Poly[3-(6-bromohexyl)thiophene]¹⁶¹



Compound [40] (1.5 g, 3.7 mmol) was dissolved in freshly distilled THF (30 mL) in a two necked 250 mL flask equipped for stirring under an inert atmosphere. Methylmagnesiumchloride (1.25 mL, 3.750 mmol) was added to the flask *via* a syringe and the solution was refluxed for 2 h. [Ni(dppp)Cl₂] (10 mg, 0.018 mmol) was then added to the mixture and stirred for 1 h 50 min at reflux under argon. Methanol/water (10:1, 10 mL) was added to the mixture to quench the reaction and to precipitate out the polymer. The polymer was filtered and washed with methanol, acetone and chloroform (150 mL) in that order in a Soxhlet extractor overnight. The chloroform fraction was evaporated over rotary evaporator to give compound [41] as a reddish-purple solid (0.33 g, 36.3 %).

 1 H NMR 500 MHz, CDCl₃), δ (ppm): 6.98 (s, 1H), 3.43 (t, J = 5.0 Hz 2H), 2.82 (t, J = 5.0 Hz, 2H), 1.89 (m, 2H), 1.72 (m, 2H), 1.49 (m, 4H). The result is in agreement with those published in literature.¹⁶¹

2.2.6: Preparation of HT-Poly[3-hexylthioacetate thiophene)[42]¹⁶¹



The product of the previous reaction, compound [41] (300 mg, 1.22 mmol) was dissolved in dry THF (35 mL) and the solution was heated to reflux. Potassium thioacetate (0.70 g, 6 mmol) was added in one portion and the mixture was stirred overnight at reflux temperature of THF. The polymer was obtained by precipitation in methanol/water (10:1, 10 mL), filtered and washed with methanol (150 mL) in a Soxhlet extractor and then dried to give compound [42] as a dark brown solid (280 mg, 93.33 %).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 6.90 (s, 1H), 2.78 (m, 4H), 2.24 (s, 3H), 1.49(m, 8H). The result is in agreement with those published in literature.¹⁶¹

2.3: Fabrication of DSSC using compound [42]:

The DSSCs were fabricated on glass substrate coated with a transparent conducting layer of fluorine-doped tin dioxide (SnO₂:F), which was cover with a layer of compact TiO₂ ~500 nm thick. Ruthenium 535-bisTBA dye (same structure as [32] on page 43) was used as sensitizer, while a porous layer of nano-crystalline titanium dioxide (nc-TiO₂) served as the n-type semiconductor and the polymer served as the p-type semiconductor and light absorber. Gold electrode was deposited on the active (polymer) layer through shadow mask evaporation method to form a solar cell of the type SnO₂:F/nc-TiO₂/dye/polymer/Au.

The substrate, nc-TiO₂ and the dye were all purchased from Solaronix SA and the dye and the nanocrystals were used without further treatment, while the substrate was cleaned before use.

2.3.1: Substrate Preparation:

The substrate was obtained as a 5 cm by 2 cm glass slide with a thickness of about 1 mm. This slide is composed of aluminoborosilicate glass coated on one face with SnO_2 :F layer having a resistance of $10\Omega/sq$ (supplier). The substrate was cut to 2.5 cm by 2 cm and cleaned as outlined below (supplier's specifications). The cut piece was rinsed under running ultrapure and hot water for 2 minutes each; the surface was then cleaned with cotton wool soaked in Decon 90[®] (Scientific Service Ltd, UK) to remove any organic materials. The substrate was then held with a pair of tweezers and kept again under running ultrapure and then hot water for 2 minutes each. It was then dried under stream of warm air for 3 minutes and held under running ethanol for 3 minutes. The slide was finally dried under warm air for 5 minutes to remove all traces of water or ethanol.

2.3.2: Porous Layer of nc-TiO2:

The nc-TiO₂, which comes in the form of sol-gel, was stirred (1 minute) using a clean glass rod before use. The doctor blade method¹⁶² was used to deposit a porous layer of the sol-gel on the substrate. A 3M Scotch Magic tape (50 μ m thick) was used to define the area of the substrate to be coated with the sol-gel. The tape is easily removed from the

substrate without leaving trace of the adhesive material. The sol-gel (50 μ L) was deposited on the edge of the substrate using a micropipette and was uniformly spread out with a clean glass rod over the surface defined by the tape to make a 3 μ m thick layer. The substrate was dried in the air for 10 minutes and the tape was removed. The substrate is now ready for the next stage.

2.3.3: Sintering:

The dried substrate was transferred to a hot plate pre-heated to 100 °C for 30 minutes, and was held at this temperature for 15 minutes. The temperature was then increased to 150 °C and was kept for another 15 minutes. Further, the temperature was ramped to 250, 350 and 450 °C and was maintained for 15, 30 and 30 minutes respectively. During the heating process, the substrate was observed to first turn brownish and later yellowish-white due to the temperature dependent band-gap narrowing in the pure titanium dioxide (anatase) (supplier). The sintered substrate was then cooled to 70 °C in 3 minutes.

2.3.4: Sensitizer Impregnation:

The sensitizer (10 mg) was dissolved in pure ethanol (50 ml), which gave a winered colour. The sintered substrate, kept at 70 °C was slowly put into the sensitizer solution with its face-up. This was stored in the dark for two days for proper impregnation. After this period the substrate was removed, rinsed with pure ethanol and dried with stream of nitrogen for 3 minutes. The substrate was then ready for the next step.

2.3.5: Spin Coating of Polymer Layer:

Various concentrations of P3HTT [42] (10mg, 20mg and 30mg/L) were prepared in anhydrous chloroform. The solutions were sonicated at 50 °C for 30 minutes to enhance the solubility of the polymer. The solutions were filtered through a 0.45 μ m syringe filter into clean vials. The treated substrate was placed on the vacuum chuck of a spinner and enough drop of the polymer solution was placed on it. The coating was done at 1000 rpm for 60 seconds. The substrate was removed and spilled polymer solution was cleaned off the conducting surface of the substrate that was not covered with the porous nc-TiO₂ and the dye using cotton wool soaked in chloroform. The substrate was then kept in the dark until a gold electrode was deposited on the active layer to complete the device.

A gold wire was cleaned with Decon 90[®] and rinsed with hot and ultrapure water and then dried in a stream of hot air. The clean gold wire was then placed in a tungsten boat in an Edwards AUTO 306 Turbo Evaporation System. A shadow mask was placed on the substrate held in place with tape and the set up was placed above the tungsten boat in the evaporation system. The evaporator was pumped to $\sim 10^{-6}$ torr and a gold film, 50 nm thick was deposited through the shadow mask to form $\sim 2 \text{ mm}^2$ circular electrodes, Fig. 2.1, and the current-voltage characteristics of the device were recorded.



Figure 2.1: Cross section of a complete DSSC device.¹⁶³

2.4: Synthesis of building blocks (co-monomer) for LBG copolymers:

2.4.1: Synthesis of 4,4'-Dibromo-2-nitrobiphenvl.¹⁶⁴



To a 500 mL two necked round-bottomed flask equipped for stirring were added 4,4'-dibromobiphenyl [43] (20.00 g, 64 mmol) and glacial acetic acid (300 mL). The flask was heated at 100 °C until compound [43] was completely dissolved. Fuming nitric acid (90 mL) was then added drop-wise over a period of 30 minutes at the same temperature. The formation of yellow precipitate was observed towards the end of the addition of the acid. The resulting mixture was stirred vigorously for 1 h and the precipitate disappeared. The mixture was cooled to room temperature and was added to ice water resulting in the formation of yellow precipitate in large quantity. This was filtered, washed exhaustively with water and dried. The crude product was re-crystallized from absolute ethanol to give compound [44] as a yellow solid (21.35 g, 93 %).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 8.05 (d, J = 1.85 Hz, 1H); 7.79, 7.77 (dd, J = 1.9 Hz, J = 8.2 Hz, 1H); 7.59 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.15 Hz, 1H); 7.18 (d, J = 8.2 Hz, 2H). The result is in agreement with those published in literature.¹⁶⁴ m.p. 110 – 115 °C Lit. mp not available.

2.4.2: Synthesis of 2,7-Dibromocarbazole^{.165}



A solution of [44] (10.00 g, 28.01 mmol) and PPh₃ (18.36 g 69.99 mmol) in *o*dichlorobenzene (55 mL) was refluxed in a 250 mL round-bottomed flask for 12 h. After cooling to room temperature, the excess solvent was removed by high vacuum distillation and the residue was purified by column chromatography (silica gel) using hexane/chloroform (1:1 to 1:2) as eluent to give compound [45] as an off-white solid (6.40 g, 70 %).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 8.08 (br 1H); 7.91 (d, J = 8.5 Hz, 2H); 7.61 (d, J = 1.55Hz, 2H); 7.39, 7.37 (dd, J = 1.6 Hz, J = 8.2, 2H). The result is in agreement with those published in literature.¹⁶⁵

m.p. 218 - 220 °C, Lit. mp not available.

2.4.3: Synthesis of Heptadecan-9-ol.¹⁶⁴



In a 1000 mL oven dried (120 °C) two-necked round-bottomed flask equipped for stirring, magnesium turning (8.43 g, 346.77 mmol) was suspended in dry THF (150 mL) under nitrogen. The flask was cooled to 0 °C and 1-bromo-octane (54.47 g, 282.06 mmol, 48.90 mL) was added drop-wise to the suspension over 1.5 h (**caution! exothermic reaction**). The mixture was stirred for 3 h and the Grignard reagent thus formed, was transferred through a cannula over a period of 3 h into a 500 mL two-necked round-bottomed flask containing [46] (7.42 g, 100.16 mmol, 8.10 mL) cooled to -78 °C. The mixture was stirred at room temperature overnight and the reaction was quenched by the addition of methanol (MeOH) (40 mL) followed by saturated aqueous ammonium chloride (NH₄Cl) (40 mL). The resulting mixture was extracted with ethyl acetate (3 x 50 mL) and the organic fractions were dried over MgSO₄ and filtered. Removal of the solvent by rotary and high vacuum afforded a solid, from which the pure compound was obtained by recrystallizing from ethyl acetate to give compound [47] as a white solid (21.50 g, 84 %).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 3.61 (s, 1H); 1.45 (m, 8H); 1.32 (m, 21H), 0.90 (t, J = 6.6, 6H). The result is in agreement with those published in literature.¹⁶⁴ m.p. 30 - 32 °C, Lit. m.p. 28 - 31 °C.

2.4.4: Synthesis of Heptadecan-9-yl-4-methylbenzenesulfonate:¹⁰¹



Compound [47] (10.00 g, 39.06 mmol), triethyl-amine (Et₃N) (9.87 g, 97.54 mmol, 13.59 mL) and trimethyl-ammonium hydrogen chloride (Me₃N.HCl) (3.73 g, 39.03 mmol) were dissolved in dry DCM (40 mL) in a 250 mL two-necked round-bottomed flask and cooled to 0 - 5 °C. A solution of *p*-Toluenesulfonyl chloride (9.30 g, 48.78 mmol) in dry DCM (39 mL) was added drop-wise over a period of 1.5 h and the reaction was warmed to room temperature and stirred for 2 h. Water (40 mL) was added to the reaction mixture and the mixture obtained was extracted several times with DCM. The combined organic fractions were washed with water (3 × 50 mL) and brine (3 × 50 mL) then dried over MgSO₄. The solvent was removed by rotary vacuum evaporation and a yellow liquid was obtained from which some solid precipitated. This mixture was purified using silica gel column chromatography with hexane/ethyl acetate (9:1) as eluent to give [48] as a colourless viscous oil, which slowly crystallized to give a white solid (14.77 g, 92 %).

¹H NMR 500 MHz, CDCl₃), δ (ppm): 7.81 (d, J = 8.20 Hz, 2H); 7.34 (d, J = 7.85 Hz, 2H); 4.55 (q, J = 5.95 Hz, 1H); 2.46 (s, 3H); 1.59 (m, 4H); 1.29 (m, 24); 0.89 (t, J = 6.9 Hz, 6H). The result is in agreement with those published in literature.¹⁰¹ m.p. 32 – 34 °C, Lit. m.p. 31 – 32 °C.

2.4.5: Synthesis of 2,7-Dibromo-9-(heptadecan-9-yl)-9H-carbazole¹¹¹



Compound [45] (1.95 g, 6.00 mmol) and freshly powdered potassium hydroxide (1.70 g, 30.30mmol) were dissolved under nitrogen in anhydrous DMSO (20 mL) in a 100 mL two-necked round-bottomed flask. After compound [45] was completely dissolved, a solution of compound [48] (3.54 g, 8.62mmol) in anhydrous DMSO (10 mL) and dry THF (10 mL) was added drop-wise over a period of 1.5 h at room temperature and the mixture was stirred overnight. The reaction mixture was then poured into de-ionised water (50 mL). This mixture was extracted with hexane (3×40 mL) and the combined organic layers were dried (MgSO₄). The solvent was removed by rotary vacuum evaporation and the residue was purified by column chromatography (silica gel) using hexane as eluent, to give compound [49] as a white solid (2.15 g, 64 %).

¹H NMR (500 MHz, CDCl₃), δ (ppm): 7.94 (br, 2H); 7.72 (br, 1H); 7.56 (br, 1H); 7.35 (br, 2H); 4.44 (br 1H); 2.24 (br, 2H) 1.93 (br, 2H); 1.25 (br 22H) 1.03 (br, 2H); 0.86 (t, J = 6.95 Hz, 6H). The result is in agreement with those published in literature.¹¹¹ m.p. 61 – 63 °C, Lit. m.p. 59 – 61 °C.

2.4.6: Synthesis of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole:¹¹¹



Compound [49] (1.00 g, 1.78 mmol) was dissolved in dry THF (18 mL) under nitrogen in a 100 mL two-necked round-bottomed flask. The solution was cooled to -78°C and n-BuLi (1.5 mL, 3.75 mmol, 2.5 M) was added drop-wise *via* a syringe over 4 min. The solution was then stirred for 1 h at this temperature and 2-isopropoxy-4,4,5,5tetramethyl-1,3,2-dioxaborolane (1.1 g, 5.91 mmol) was added rapidly to the solution. After an additional hour at -78 °C, the mixture was warmed to room temperature and stirred overnight. The mixture was poured into water (40 mL) and the aqueous layer extracted with diethyl ether (3 × 40 mL). The combined organic fractions were dried (MgSO₄) and the solvent was removed vacuum. The crude product was purified using column chromatography (silica gel) and 7 % ethyl acetate in hexane as the eluent to give compound [50] as a sticky solid (0.8 g, 45 %)

¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.15 (d, J = 7.8 Hz, 2H); 8.04 (s, 1H); 7.90 (s, 1H); 7.68 (d, J = 7.8 Hz, 2H); 4.71 (m, 1H); 2.35 (m, 2H); 1.95 (m, 2H); 1.41 (s, 24H); 1.13-125 (m, 24H); 0.83 (t, J = 8 Hz, 6H). The result is in agreement with those published in literature. ¹¹¹

m.p. 130 - 132 °C, Lit. 128 - 130 °C.

2.4.7: Synthesis of 4,7-Dibromo-2,1,3-benzothiadiazole:166



To a 250 mL two-necked round-bottomed flask were added [51] (5 g, 36.72 mmol) and HBr (70 mL, 48%). A solution containing bromine (17.6 g, 110.13 mmol) in HBr (50 mL) was added drop-wise 1.5 h. The solution was then heated to reflux for 6 h then cooled to room temperature. A solution of NaHSO₃ (100 mL) was then added to consume any excess bromine and the mixture was filtered and the solid obtained washed exhaustively with water then once with cold ether to give [52] as an off-white needles (5.11 g, 47 %).

 1 H NMR (500 MHz, CDCl₃), δ (ppm): 7.75 (s, 2H). The result is in agreement with those published in literature. 166

m.p. 187 - 189 °C, Lit. m.p. 189 - 190 °C.

2.4.8: Synthesis of 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3-benzothiadiazole (DEBT):



Compound [54] was prepared according to the procedure described by Yang, et al.¹⁶⁷ A dried 100 mL two-necked round-bottomed flask was charged with [52] (1 g, 3.40 mmol), [53] (2.6 g, 8.53 mmol) and $[Pd(PPh_3)Cl_2]$ (48 mg, 2 mol%) and purged with nitrogen for 30 minutes. Dry THF (20 mL) was then added and the solution obtained was refluxed for 4.5 h. After stirring overnight at r.t., the solvent was removed using a rotary evaporator and the residue was purified by column chromatography on silica gel using DCM/Hexane (1:1) as eluent to give compound [54] as red crystals (1.20 g, 85 %).

¹H NMR (500 MHz, CDCl₃), δ (ppm): 8.32 (s, 2H), 6.49 (s, 2H), 4.33 (q, 4H), 4.25 (q, 4H).

APCI MS: $m/z 417 (100 \% [M^+ + H^+])$.

The decomposition temperature range is 168 - 170 °C, but there are no literature data available. The ¹³C NMR spectra of the compound could not be obtained because of its low solubility in most organic solvents. Also the elemental composition of the compound could not be determined because of lack of instrument.

2.4.9: Synthesis of 4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3-benzothiadia-zole.



This compound was prepared according to the procedure described by Li, et al.¹⁶⁸ Compound [54] (0.22 g, 0.53 mmol) was dissolved in chloroform (40 mL) and heated to 50 $^{\circ}$ C in a 100 mL round bottomed flask with exclusion of light. NBS (0.2 g, 1.12 mmol) was then added to the solution and the mixture was stirred vigorously at this temperature for 24 h under a nitrogen atmosphere. After cooling, the mixture was poured into water, separated-and the aqueous layer extracted several times with chloroform. The combined extracts were washed with water and dried (MgSO₄). Removal of solvent gave compound [55] as a dark brown solid (0.30g, 99 %).

 $^{1}\mathrm{H}$ NMR 500 MHz, DMSO 50 °C), δ (ppm): 8.34 (d, J = 2.2 Hz 2H), 4.43 (m, 8H).

TOF MS: m/z 571 (40 % [M⁺], ⁷⁹Br/⁷⁹Br), 573 (100 %, [M⁺], ⁷⁹Br/⁸¹Br), 575 (40 %, [M⁺], ⁸¹Br/⁸¹Br).

This is a new compound and the decomposition temperature could not be obtained because it is not easy to notice colour change. In addition, the ¹³C NMR spectra of the compound could not be obtained because of its low solubility in most organic solvents. Also the elemental composition of the compound could not be determined because of lack of instrument.

2.4.10: Attempted synthesis of 4,7-bis(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno[3,4-b] [1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole: Route 1:



Compound [54] (0.11 g, 0.264 mmol) was dissolved in dry THF (30 mL) and cooled (– 45 °C). n-BuLi [2.5 M in hexanes (0.25 mL, 0.625 mmol., 2.4 eq.)] was added and the mixture allowed to warm to room temperature over 30 minutes then stirred at this temperature for 1 h. The flask was re-cooled (– 45 °C) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.12 mL, 0.591 mmol,) was added rapidly *via* a syringe. The solution was stirred at this temperature for 1 h then allowed to warm to r.t. and stirred overnight. The reaction was poured into ice-cold water then extracted with dichloromethane (3×40 mL). The combined organic layers were washed with water (2×50 mL) and dried (MgSO₄). The solvent was removed by rotary evaporation and the residue purified by column chromatography (silica gel) using DCM:Hexane (1:1). Removal of solvent gave reddish-brown solid which according to the ¹H NMR and mass spectra is not the desired 4,7-bis(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole and we were not able to identify it.

¹H NMR 500 MHz, CDCl₃), δ (ppm): 8.39 (s, 2H), 7.72 – 7.70 (q, 3H), 7.55-7.53 (q, 4H), 6.57 (s, 2H), 4.42 – 4.40 (m, 4H), 4.32 – 4.31 (m, 4H), 4.26 – 4.19 (m, 6H). APCI MS: m/z 417 (100 % [M⁺ + H⁺]).

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2.4.11: Attempted synthesis of 4,7-bis(7-(4,45,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno[3,4-b] [1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole: Route 2:



Compound **[55]** (0.05 g 0.0871 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'bi(1,3,2-dioxaborolane (0.055 g, 0.217 mmol. 2.5 eqv.), potassium acetate (0.035 g, 0.357 mmol. 4.1 eqv.) and Pd(PPh₃)₄ (13.5 mg, 0.012 mmol)) were added to an oven dried two necked flask in the sequence indicated and the mixture flushed with nitrogen for 20 min. Anhydrous dioxane (1.5 mL) was then added and the mixture heated under reflux (110 °C) for 7 h. The flask was allowed to cool to r.t. and the mixture was poured into de-ionised water and extracted with DCM (3 × 50 mL). The combined extracts were washed with water (2 × 50 mL) and dried (MgSO₄).

The solvent was removed on rotary vacuum leaving behind reddish brown solid which according to the ¹H NMR and mass spectra is not the desired 4,7-bis(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c] [1,2,5]thiadiazole and we were not able to identify it.

¹H NMR 500 MHz, CDCl₃), δ (ppm): 8.45 (t, J = 4.45, 3.45 Hz, 1) 8.41 (t, J = 4.4, 3.5, 2H), 7.72 – 7.66 (m, 6H), 7.56 – 7.53 (m, 4H), 7.49 – 7.47 (m, 4H), 6.58 (d, J = 4.75, 2H), 4.42 (m, 4H), 4.33 (q, 4H), 4.26 – 4.19 (m, 4H). APCI MS: m/z 417 (100 % [M⁺ + H⁺]).

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2.4.12: Synthesis of 3,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo-[b,d]thioph-ene 5,5-dioxide.



This compound was prepared according to the method described by Li, et al.¹⁶⁸ 3,7-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)dibenzo[*b*,*d*] thiophene 5,5-dioxide (DES) **[56]** (0.22 g, 0.443 mmol) was dissolved under nitrogen in chloroform (40 mL) in a 100 mL flask covered with aluminium foil and heated to 50 °C. At this point *N*-Bromosuccinimide (0.17 g, 0.955 mmol), was added and the mixture was stirred at this temperature for 24 h. After cooling the reaction was poured into water (40 mL) and the mixture was extracted with chloroform (4 × 50 mL). The organic layers were combined and washed with water (2 x 50 mL) and then dried (MgSO₄) and the evaporated to give compound **[57]** as a yellow solid (0.28 g, 97 %).

APCI MS: m/z 652 (48 % [M⁺], ⁷⁹Br/⁷⁹Br), 654 (100 % [M⁺], ⁷⁹Br/⁸¹Br), 656 (60 % [M⁺], ⁸¹Br/⁸¹Br).

¹H and ¹³C NMR spectra could not be obtained because of low solubility of the compound in most organic solvents. The elemental composition of the compound could not be determined also because of lack of instrument.

2.4.13: Synthesis of 4,7-bis(benzo[b]thieno[3,4-e][1,4]dioxin-1-yl)benzo[c][1,2,5]thiadiazole.



This reaction was carried out according to the procedure described by Yang, et al.¹⁶⁷ 3,4-phenylene-dioxythiophene (PhEDOT) **[58]** (0.5 g, 2.63 mmol) was dissolved in dry THF (20 mL) and cooled to -78 °C and 2.5M BuLi in hexane (1.1 mL, 2.75 mmol) was added drop-wise over 4 minutes. The mixture was stirred for 1 h and then warmed up to 0 °C over 1.5 h and stirred for another 1 h. After cooling (-78 °C) Bu₃SnCl (0.75 mL, 2.76 mmol) dissolved in dry THF (1.5 mL) was added drop-wise over 4 minutes. The mixture was then kept between -60 and -20 °C for 4 h and then evaporated under reduced vacuum at r.t. The residue was dissolved in dichloromethame (30 mL) and water (25 mL) was added to the solution. This was stirred for 30 minutes, separated and the aqueous layer further extracted with dichloromethane (2×25 mL). The combined organic fractions were washed with water (20 mL), dried MgSO₄ and evaporated to give crude **[59]** as yellow oil (2.12 g, > 100 %) which was used in the next reaction without further treatment.

Compounds [52] (0.35 g, 1.19 mmol), [59] (1.46 g, 3.05 mmol) and $Pd(PPh_3)_2Cl_2$ (17 mg, 0.024 mmol) were combined in a 25 mL flask and was purged with nitrogen for 30 min. At this point dry THF (10 mL) was added the refluxed for 6 h and stirred overnight at

r.t. the mixture was evaporated and the residue purified by column chromatography (silica gel) using hexane:dichloromethane (1:1) as eluent. Two products were obtained and the removal of solvent gave [60a] as reddish-brown solid (0.22 g, 37 %) and [60b] as dark brown solid (0.18 g, 30 %).

[60a] ¹H NMR 500 MHz, CDCl₃), δ (ppm): 8.25 (d, J = 8, 1H), 7.94 (d, J = 8, 1H), 7.06 (m, 2H), 6.99 (m, 2H), 6.68 (s, 1H).

[60a] APCI MS m/z: 404 (100 % [M⁺ + H⁺]).

[60b] TOF MS m/z: 511 (100 % [M⁺]).

¹³C NMR spectra could not be obtained because of low solubility of these compounds in most organic solvents. The elemental composition of the compounds could not be determined also because of lack of instrument.

2.5: Synthesis of Copolymers:

The synthesis of the novel copolymers [62], [63], [64] and [65] presented below was carried out according to literature procedure as described by Blouin et al.¹⁰¹

2.5.1: Synthesis of poly{9,9-dioctyl-9H-Fluorene-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3-benzothiadiazole} [62].



Co-monomers [61] (0.1 g, 0.179 mmol) and [55] (0.103 g, 0.179 mmol) and three drops of Aliquat 336 were combined in a 2-necked flask and purged with nitrogen for 30 minutes. Degassed dioxane (4 mL) was then added and the mixture heated to 90 °C. At this point a solution of tetrakis(triphenylphosphine)palladium(0) (6.20 mg, 3 % mmol) in degassed dioxane (1 mL) and 2 M K_2CO_3 (0.5 mL) were added and the mixture was refluxed (110 °C) under inert atmosphere for 72 h. Bromobenzene (28 mg, 0.0179 mmol) was then added and after 1 h phenylboronic acid (22 mg, 0.0179 mmol) was added and the mixture was refluxed overnight. The mixture was cooled to r.t. and the crude copolymer

was precipitated out by adding the cooled mixture to cold MeOH (10 mL). The precipitate was filtered and washed in succession with MeOH (150 mL) and hexane (150 mL) in a soxhlet apparatus for 24 h. The residue in the apparatus was then extracted with chloroform (150 mL) and the extract was concentrated to ca. 30 mL from which the copolymer PFDEBT [62] was re-precipitated in MeOH, filtered and air-dried (yield 0.1 g, 71 %).

GPC: Mn, 32 kDa, Mw, 98 kDa, PDI, 3, degradation temperature (T_d), 370 °C.

2.5.2: Synthesis of poly{9-(heptadecan-9-yl)-9H-carbazole-4,7-bis(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)-2,1,3-benzothiadiazole} [63].



i) Aliquat, ii) K₂CO₃, iii) Pd(PPh₃)₄ iv) Dioxane, 110 °C/72 h, v) Bromobenzene vi) Phenylboronic acid



[63] PCDEBT

Co-monomers [50] (0.1 g, 0.152 mmol) and [55] (0.087 g, 0.152 mmol) and three drops of Aliquat 336 combined in a 2-necked flask and purged with nitrogen for 30 minutes. Degassed dioxane (4 mL) was then added and the mixture heated to 90 °C. At this point a solution of tetrakis(triphenylphosphine)palladium(0) (5.27 mg, 3% mmol) in degassed dioxane (1 mL) and 2 M K_2CO_3 (0.5 mL) were added and the mixture refluxed (110 °C) under inert atmosphere for 72 h. Bromobenzene (0.0024 g 0.0152 mmol) was then added and after 1 h phenylboronic acid (0.0019 g, 0.0152 mmol) was added and the mixture was refluxed overnight. The mixture was cooled to r.t. and the crude copolymer was precipitated out by adding the cooled mixture to cold MeOH (10 mL). The precipitate was filtered and washed in succession with MeOH (150 mL) and hexane (150 mL) in a soxhlet apparatus for 24 h. The residue in the apparatus was then extracted with chloroform (150 mL) and the extract was concentrated to ca. 30 mL from which the

copolymer PCDEBT [63] was re-precipitated in MeOH, filtered and air-dried (yield 0.09 g, 75 %).

GPC: Mn, 6 kDa, Mw, 11 kDa, PDI, 1.8, degradation temperature (Td), 370 °C.

2.5.3: Synthesis of poly{3-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(7-(9,9-dioctyl-9H-fluoren-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[b,d]thiophene-5,5-dioxide} [64]



Co-monomers [61] (0.1 g, 0.179 mmol) and [57] (0,117 g, 0.179 mmol) and three drops of Aliquat 336 were combined in a 2-necked flask and purged with nitrogen for 30 minutes. Degassed dioxane (4 mL) was then added and the mixture heated to 90 °C. At this point a solution of tetrakis(triphenylphosphine)palladium(0) (6.20 mg, 3% mmol) in degassed dioxane (1 mL) and 2 M K₂CO₃ (0.5 mL) were added and the mixture refluxed (110 °C) under inert atmosphere for 72 h. Bromobenzene (28 mg, 0.0179 mmol) was then added and after 1 h phenylboronic acid (22 mg, 0.0179 mmol) was added and the mixture was refluxed overnight. The mixture was cooled to r.t. and the crude copolymer was precipitated out by adding the cooled mixture to cold MeOH (10 mL). The precipitate was filtered and washed in succession with MeOH (150 mL) and hexane (150 mL) in a soxhlet apparatus for 24 h. The residue in the apparatus was then extracted with chloroform (150 mL) and the extract was concentrated to ca. 30 mL from which the copolymer PFDES, [64] was re-precipitated in MeOH, filtered and air-dried (yield 0.14 g, 87 %). GPC: *Mn*, 3 kDa, *Mw*, 5 kDa, PDI, 1.6, degradation temperature (T_d), 400 °C.

2.5.4: Synthesis of poly{3-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(7-(9-(heptadecan-9-yl)-9H-carbazol-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[b,d]thiophene-5,5-dioxide} [65].



Co-monomers [50] (0.1 g, 0.152 mmol) and [57] (0.0995 g, 0.152 mmol) and three drops of Aliquat 336 were combined in a 2-necked flask and purged with nitrogen for 30 minutes. Degassed dioxane (4 mL) was then added and the mixture heated to 90 °C. At this point a solution of tetrakis(triphenylphosphine)palladium(0) (5.27 mg, 3% mmol) in degassed dioxane (1 mL) and 2 M K₂CO₃ (0.5 mL) were added and the mixture refluxed (110 °C) under inert atmosphere for 72 h. Bromobenzene (0.0024 g 0.0152 mmol) was then added and after 1 h phenylboronic acid (0.0019 g, 0.0152 mmol) was added and the mixture was refluxed overnight. The mixture was cooled to r.t. and the polymer precipitated by adding the cooled mixture to cold MeOH (10 mL). The crude copolymer was filtered and washed in succession with MeOH (150 mL) and hexane (150 mL) in a soxhlet apparatus for 24 h. The residue in the soxhlet apparatus was then extracted with chloroform (150 mL) and the extract was concentrated to ca. 30 mL from which the copolymer PCDES, [65] was re-precipitated in MeOH, filtered and air-dried (yield 0.09 g, 65 %).

GPC: Mn, 5 kDa, Mw, 7 kDa, PDI, 1.4, degradation temperature (Td), 400 °C.

Chapter Three:

3.0: Results and Discussion Based on P3HTT:

3.1: Synthesis of side-chain Functionalized Poly(3-hexylthiophene):

Studies have shown that 3-alkylthiophenes having a terminal leaving group in the alkyl chain are central intermediates for the synthesis of the functionalized poly(3-hexylthiophenes).¹⁶⁰ The preparation of the intermediates and polymer **[42]** was therefore carried out as reported in literature^{160,161,} and is illustrated in Scheme 1.

The first intermediate, 4-(p-methoxyphenoxy)hexylbromide [37] obtained by reacting potassium 4-methoxyphenolate (previously prepared by reacting methanolic KOH with 4-methoxyphenol) with 1,6-dibromohexane (107.52 g, 75 %), reacted readily with magnesium to give a Grignard compound which was coupled with 3-bromothiophene in the presence of [Ni(dppp)Cl₂] catalyst to give a terminally protected hexylthiophene [38] (14.81 g, 65 %). This product was then converted to 3-(6-bromohexyl)thiophene [39] (3.92 g, 80 %) by reacting it with 48 % HBr in acetic anhydride. The side-chain functionalized poly[3-(6-bromohexyl)thiophene] was then synthesized using the Grignard Metathesis method (GRIM) and post-polymerization functionalization. Compound [39] was reacted with N-Bromosuccinimide (NBS) which gave a colourless oil [40], this was subjected to nickel catalysed Head-to-Tail (HT) coupling via GRIM to give regioregular poly[3-(6bromohexyl)thiophene (rrP3BHT) [41] (0.33 g, 36 %). It has been reported that this polymer is stable to post-polymerisation treatments, which makes it easy to replace the terminal group with different functional groups.¹⁶¹ Therefore, polymer [41] was reacted with potassium thioacetate to produce P3HTT [42] (280 mg, 93 %). The thioacetate group was introduced for two reasons: a). to lower the band-gap of the polymer and b). the initial objective of this research was to fabricate P3HTT:FeS2 nano-crystal photovoltaic devices. It was envisaged that in such a material combination, the polymer will supplement the sulphur deficiency suffered by the pyrite, thereby improving its Voc, which is reported to be only 200mV at room temperature; though its band-gap is within the range for good solar cell material. However, we were not able to synthesize the pyrite nano-crystals.



Scheme 1: Synthesis of monomer and side-chain functionalised polymer: i a) alc. KOH, b) acetone. 1.6dibromohexane/reflux, 1 h; ii a) Mg/Et₂O, 40 °C, 6 h, b) Et₂O, 0 °C, 3-bromothiophene, Ni(dppp)Cl₂/reflux (50 °C); iii) 48% HBr in Ac₂O, 100 °C, 24 h; iv) THF:AcOH, NBS, r.t.; v a) Dry THF, CH₃MgCl/reflux, 2 h; b) Ni(dppp)Cl₂/reflux, 2 h; vi) Dry THF/reflux, C₂H₃OSK/reflux overnight

The synthesis of compound [41] from which compound [42] was obtained was carried out using the Grignard metathesis (GRIM) method. Compound [40] (scheme 1) was treated with 1 equivalent of CH₃MgCl to form the corresponding Grignard compound; which was polymerised to compound [41] using [Ni(dppp)Cl₂] catalyst. This polymer has been reported to be stable to post-polymerisation treatments; which had made it possible to replace the bromine atom with different functional groups.^{142,161} Therefore, compound [41] was reacted with potassium thioacetate to produce compound [42].

The mechanism for the nickel-initiated cross-coupling polymerisation proposed by Yokozawa et al.¹⁶⁹ is shown in Scheme 2. The first step is to react two equivalents of the Grignard compounds [66] and [67] with [Ni(dppp)Cl₂] catalyst to form an organonickel compound [68]. Reductive elimination occurs immediately to form an associated pair of the head-to-tail coupled dimer [69] and the reduced catalyst [70].





The dimer undergoes fast oxidative addition to the nickel centre to form a new organo-nickel compound [71]. Another monomer reacts with the organo-nickel compound *via* transmetalation followed by another reductive elimination to give associated pair of the reduced catalyst and a terthiophene [73]. The growth of the polymer chain occurs by an insertion of one monomer at a time at the site where the Ni(dppp) moiety is incorporated into the polymer chain as end group *via* the formation of a π -complex. Thus, the polymerisation proceeds *via* a chain-growth mechanism.¹⁶⁹ It has also been proposed that this polymerisation system is not only a chain-growth system but also a living system.¹⁷⁰

3.2: Characterisation of compound [42]:

The instrumental characterisation of compound [42] and the photovoltaic response of DSSCs based on this polymer are discussed below.

3.2.1: ¹H NMR of compound [42]:

The ¹H NMR spectra of 3-bromohexylthiophene [**39**] show signals at δ 7.28 and 6.96 ppm for the 2 α and γ -hydrogen atoms on the thiophene ring (inset Fig. 3.1), while those of compounds [**41**] and [**42**] show only one signal at δ 6.98 ppm for the γ -H (inset Fig. 3.2 and Fig. 3.3). This could suggest that coupling had occurred on the α -carbon of the thiophene ring giving rise to HT regioregular polymer (inset b, Fig. 3.2). The protons of the side chain (6-hexylbromide) in compound [**41**] had remained unchanged in compound [**42**] suggesting that the side chain is stable to the post-polymerisation conditions. This result is similar to those reported by other workers. ^{161, 171}



Figure 3.1: ¹H NMR Spectra of compound [39] (inset showing signals for α and γ -hydrogens).



Figure 3.2: ¹H NMR Spectra of compound [41] inset a) showing signal for γ -hydrogen b) showing HT coupling.

The presence of a singlet at δ 2.32 ppm due to 3-hydrogen atoms in the spectra of compound **[42]** could indicate the presence of methyl group attached to a carbonyl group (Fig. 3.3). Thus, the bromine atom at ω -position in compound **[41]** has been successfully replaced by the acetate group. The HT or the regioregularity of P3HTT **[42]** was found to be 98% based on the ratio of the peaks at δ 2.58 and 2.83 ppm (inset b fig.3.2). Other workers have published similar result for P3HT which has similar structure with compound **[42]**.¹⁷²



Figure 3.3: ¹H NMR Spectra of compound [42].

3.2.2: Polymerisation and Thermal Stability of compound [42]:

The spectrum of the molecular weight and polydispersity index (PDI) of the polymer determined using gel permeation chromatography (GPC) in THF is shown in appendix A, while the signals for the thermal analysis are shown in Fig. 3.4. Table 1 shows a summary of the results of the GPC and the TGA, and it can be inferred from these values that compound [42] has relatively high molecular weight and good thermal stability.



Figure 3.4: TGA Thermo-gram of compound [42] with heating rate of 20 °C/min.

le 1: Polymerisation and thermo-stability of compound [42].				
Yield (%)	Mn	Mw	PDI	T _d
2027 - 2246	(kDa)	(kDa)		(%/°C)
94	32	36	1.13	5/270

3.2.3: Optical Properties of compound [42]:

The UV-Vis spectra of compound [42] were acquired in chloroform solution and solid state as thin films cast from chloroform onto ITO glass (Fig. 3.5). The absorption spectrum of the film showed a red-shift of 86 nm compared to the spectrum of the polymer in solution. This bathochromic shift suggests that the polymer exhibits more ordered molecular configuration in the solid state than in the liquid state. The optical band-gap (E_g^{opt}) was calculated from the band-edge of the absorption spectrum of the film. The emission maxima of the polymer lay in the green region of the emission, suggesting that it is a green emitter. The optical and photoluminescence properties of this polymer are summarised in Table 2.


Figure 3.5: Normalised UV-Vis Spectra of compound [42] film spin cast on ITO glass from CHCl₃, in chloroform and normalised photoluminescence (emission) in chloroform.

UV-Vis					PL
CH	Cl ₃		Film		CHCl ₃
λ _{max} (nm)	λ_{onset} (nm)	λ _{max} (nm)	λ _{onset} (nm)	$ \begin{array}{c} E_g^{Opt} \\ (eV) \end{array} $	λ _{max} (nm)
450	560	536	650	1.9	579

The photoluminescence was calculated based on a method described by Ishida et al. ¹⁷³ When a fluorophore absorbs a photon of light, an energetically excited state is formed. The fluorophore will eventually be deactivated (loss of energy) and return to ground state. The main deactivation processes which occur are fluorescence (loss of energy by emission of a photon), internal conversation and vibrational relaxation (non-radiative loss of energy as heat to the surroundings), and intersystem crossing to the triplet manifold and subsequent non-radiative deactivation. The efficiency of the fluorescence process is determined by the fluorescence quantum yield (Φ) defined as the ratio of the number of photons emitted to the number of photons absorbed.

$$\Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$$
7

The maximum fluorescence quantum yield is 1.0 (100%); that is, every photon absorbed results in a photon emitted while compounds with quantum yields of 0.10 are still . considered quite fluorescent. The Φ of fluorophores is often determined using the comparative method; which involves the use of well characterised standard samples with known Φ values. Essentially, solutions of the standard and test samples with identical absorbance at the same excitation wavelength are assumed to be absorbing the same number of photons. Hence, a simple ratio of the integrated fluorescence intensities of the two solutions (recorded under identical conditions) will give the ratio of the quantum yield values.

The Φ of compound [42] was therefore determined as follows. The UV-Vis absorbance spectra of tris(bipyridine)ruthenium (II) chloride [Ru(bipy)₃Cl₂] (standard) in water and compound [42] in chloroform were recorded and the absorbances (A_s and A_u) for the standard and the polymer respectively; at the excitation wavelength were noted. The fluorescence spectra of the same solutions were recorded at these excitation wavelengths and the integrated fluorescence intensities (F_s and F_u) for the standard and the polymer respectively; from the fully corrected fluorescence spectra were determined. A summary of the results of the spectrophotometry studies are recorded in Tables 3 a and b.

	As	Fs	n_s	$\frac{A_s}{F_s}$	$\Phi_{\rm s}$
			(water)		
Ru(bpy)Cl ₂	0.033	1933020	1.33	52885932	0.041
	0.042	2406910			
	0.053	3014220			
	0.061	3440260			
	0.072	4011690			

Table 3b	: Absorbance and	Area of Fluorescen	nce Spectra of	compound [42].	
	A_u	$\mathbf{F}_{\mathbf{u}}$	n _u	$\frac{F_u}{A_u}$	Φ_{u} (%)
			(CHCl ₃)	an u i	
[42]	0.038	12486200	1.45	291084579	26
	0.047	15075000			
	0.057	17852600			
	0.069	21516600			
	0.079	24388900			

The integrated fluorescence intensities of the standard and the polymer were plotted against the absorbance (Fig. 3.6 a and b) and the gradients of the plot were used to calculate the Φ of the polymer using the relationship:

$$\Phi_{\rm u} = \Phi_{\rm s} \left(\frac{{\rm Grad}_{\rm u}}{{\rm Grad}_{\rm s}} \right) \left(\frac{{\rm n}_{\rm u}^2}{{\rm n}_{\rm s}^2} \right) \tag{8}$$

or

$$\Phi_{\rm u} = \frac{A_{\rm s}}{F_{\rm s}} \times \frac{F_{\rm u}}{A_{\rm u}} \times \frac{n_{\rm u}^2}{n_{\rm s}^2} \times \Phi_{\rm s}$$

where Φ_u , Φ_s , $Grad_u$, $Grad_s$, A_u , A_s , F_u , F_s , n_u , and n_s are the quantum yields, gradients, absorbance, areas and refraction indices of compound **[42]** and the standard respectively. The PL Φ of the polymer was found to be similar to that of all thiophene homo-polymers ($\leq 25 \%$),¹⁷⁴





Figure 3.6: Plot of integrated Fluorescence Intensity vs. Absorbance of a) $[Ru(bipy)_3Cl_2]$ and b) compound [42]

3.2.4: Electrical Properties of polymer compound [42]:

The electrochemical data of LBG polymer can give valuable information regarding the intrinsic material stability and allow the estimation of the relative positions of its HOMO and LUMO energy levels. The knowledge of these values is required for compiling the energetically compatible donor-acceptor pairs in BHJ devices. Cyclic voltammetry (CV) is the method used to calculate these energy levels. Therefore, the cyclic voltammograms of thin film of compound [42] drop-cast from chloroform solution were obtained and the energy levels were calculated from the values of the onset oxidation potential (E_{onset}^{ox}) and the onset reduction potential (E_{onset}^{red}) *vs.* half-wave potential of ferrocene (E_{FC} , 0.098 eV) using equations 10 and 11 respectively.

$$HOMO = -4.8 - (E_{onset}^{oxi} - E_{FC})$$
 10

$$LUMO = -4.8 - (-E_{onset}^{red} - E_{FC})$$
 11

The electrochemical band-gap (E_g^{CV}) was calculated as the difference between the HOMO and LUMO energy levels. Fig. 3.7 a and b show the cyclic voltammograms, while (Table 4) presents a summary of the electrical data of the polymer.





b)

Figure 3.7: Cyclic Voltammogram of the film of compound [42] on Pt. electrode in MeCN solution of Bu_4NPF_6 (0.1 M) at a scan rate 100 mV/s a) several scans and b) second scan showing onset of oxidation and reduction

	CV	
E_{onset}^{ox} / H (eV)	OMO E_{onset}^{red} /LUMO (eV)	E_g^{CV} (eV)
0.35/- 5	.05 - 1.8/ - 2.9	2.15

The values of the E_g^{Opt} and E_g^{CV} are in close agreement and are within the experimental error limit of 0.2-0.5 eV. The E_g^{Opt} of the polymer is similar to that of P3HT (1.9 eV),⁹¹ (Table 2). This may suggest that the thioacetate functional group attached to the hexyl side chain did not effectively reduce the band-gap of the polymer.

3.2.5: Photovoltaic Properties of DSSC devices based on compound [42]:

The photovoltaic properties of the devices were investigated using a Sun 2000 Solar Simulator, with light intensity of 1 KW/m² equivalent to 1 Sun and AM1.5 which was used to illuminate the devices. Connecting the testing device electrodes to a Keithley

2400 and sweeping the applied bias from -1 to 1 V, measured the *I-V* characteristics. All measurements, both in the dark and under illumination were done in air. Linear plots of typical current *vs.* voltage (*I-V*) characteristic of the cells are shown in Fig. 3.8 a, b and c. The devices showed good rectification in the dark and photovoltaic properties were exhibited when illuminated.







Figure 3.8: I-V Characteristics of DSSC devices based on compound [42] at a) 10 mg, b) 20 mg and c) 30 mg concentration in chloroform.

The devices were fabricated using 10, 20 and 30 mg polymer solutions and the *I-V* characteristics data is given in Table 5. A slight increase in the values of J_{sc} and FF, thus the PCE, was observed as the polymer concentration increased from 10 mg to 20 mg. This could be due to increased photon absorption by the polymer layer or an increased polymer/nanocrystal contact; which may have enhanced the dissociation of excitons at the polymer/nanocrystal interface. The decrease in these properties in the devices based on 30 mg polymer solution could be due to increased shunts and defects as a result of increased polymer thickness. These might have led to decreased charge mobility and transport, thus, the decreased efficiency.

The overall photovoltaic performance of these devices is less than what has been reported for similar devices based on P3OT and P3HT by other workers.^{133, 163} The poor performance of these devices may be as a result of poor penetration of the polymer into the nc-TiO₂ mesopores due to the bulky nature of the thioacetate functional group, in addition, the polymer and the dye-absorbed surface might not have established a good contact, thus reducing charge separation and subsequent transport.⁹² However, Tsekouras et al¹³⁵ have reported similar result in solid-state dye sensitized solar cells using sulforhodamine B dye.

Fable 5: Pl	notovoltaic Pro	perties of DSSC d	levices based on	compound [42].
Conc.	V_{oc}	J _{sc}	FF	η
(mg)	(mV)	(mA/cm^2)	(%)	(%)
10	710	1.4	30	0.034
20	610	1.7	34	0.035
30	560	1.8	30	0.030
50	500	1.0	50	0.030

Chapter Four:

4.0: Results and Discussions Based on Copolymers:

4.1.: Introduction:

The work of Havinga et al.¹¹ has shown that the donor-acceptor approach is useful in the synthesis of broadly absorbing OSCs with useful photovoltaic and electrochromic properties. This method affords copolymers with LBG and low lying HOMO *via* ICT; therefore, they may give high J_{sc} and V_{oc} . In addition, the copolymers usually have crystalline and rigid coplanar structure due to π - π stacking for efficient charge transport. Such copolymers have been synthesised and they have demonstrated encouraging performance in BHJ solar cells. For instance, LBG copolymers [25] and [78] (Fig. 4.1) have already been reported in literature with PCE values of 7.1 %¹⁰⁵ and 2.1 %¹⁷⁵ respectively. The good photovoltaic performance demonstrated by these copolymers has therefore, informed our decision to design copolymers with DEBT and DES in place of DTBT to study the effect of the structural changes.



Figure 4.1: Structure of [25] and [78].

This chapter is divided into two parts, part one will discuss the synthesis and characterisation of the building blocks for the synthesis of the LBG copolymers. While, part two will discuss the synthesis, characterisation and the photovoltaic responses of the copolymers.

Part One:

4.1.1: Synthesis of Donor (D) based on 2,7-Substituted Carbazole:

Carbazole-based materials both natural and synthetic are widely distributed and have been investigated for their optical and electronic properties and their synthetic methods in particular. These materials have a good electronic and charge transport properties, as well as high thermal stability; therefore, they have been used as building blocks for small molecules and polymeric optoelectronic materials.¹⁷⁶ To fine-tune the properties of carbazole-based materials and incorporate them into complex molecular structures, the carbazole nucleus (Fig.4.2) has to be functionalized or a cheap and available starting material will have to be used.



[79]

Figure 4.2: Carbazole nucleus.

Owing to its highly electron-rich nature, the carbazole nucleus can undergo electrophilic substitution. The most reactive positions for such substitution are therefore, the 3- and 6- positions, and to a lesser extent, the 1- and 8- positions, which often require more forcing reaction conditions. As a result, direct oxidative polymerization or electropolymerization of carbazoles only results in oligomeric materials linked at the 3,6-positions.¹⁴⁴ However, not many 3,6-carbazole-based solar cells have been reported and those available have shown very low PCE. Moreover, the use of small molecule 3-substituted carbazoles in DSSCs has not shown good performance either.⁹² Therefore, the desire to obtain poly(carbazole) with a better property has led to the search for methods that can produce the 2,7-substituted derivative.

Since the electronic rich nature of carbazole inhibits direct and explicit substitution at the 2,7-positions, this derivative has been obtained from the indirect approach. This approach involves the use of a 4,4'-functionalized biphenyl unit, which is a cheap and readily available reagent. The 2(-2') position(s) in this compound are electron rich, which makes the introduction of an electrophile for subsequent ring-closing reaction to either position very easy leading to the 2,7-functionalised carbazoles.¹⁴⁴

Smith and Brown, ¹⁷⁷ were the first to exemplify this method when they converted azide derivatives into 2,7-functionalised carbazoles by thermal cyclization reactions. In 1953, Heinrich ¹⁷⁸ developed a more practical method where the 2,7-functionalised carbazole was directly obtained from 2,2'-diamino-biphenyls under acidic conditions at high temperatures.

A more practical method was introduced by Cadogan et al, ¹⁷⁹ which is today known as the Cadogan cyclization. This method involves the reductive cyclization of 2-nitro-biphenyl derivatives refluxed in organo-phosphorus reagents especially triethylphosphite, P(OEt)₃. Despite the success recorded with this method, it had some drawbacks. After series of investigations, it was discovered that N-ethyl derivative contaminates the carbazole and this becomes common when either long reaction times or substrates bearing electron-donating substituents are involved. In addition, it was hard to obtain the pure product because it requires a careful and tedious chromatographic process, thereby, limiting large-scale synthesis.¹⁷⁹

In 2005 Freeman et al,¹⁷⁶ developed an efficient and cheap method for the synthesis of the 2,7-functionalised carbazoles. They explored the use of alternative reducing reagents, solvents and reaction temperature and found triphenylphosphine (PPh₃) to be a convenient substitute to organo-phosphorus because it is easy to handle, inexpensive and a stable solid. Among the solvents investigated, o-dichlorobenzene (o-DCB) was found to be more effective compared to toluene and chloro-benzene, which share common features (polarity, high solvent power, high boiling points and availability) with o-DCB. The reaction using o-DCB was completed in 16 h, while those in the other solvents required longer time. Removal of the solvent, followed by simple column chromatography afforded the desired product in 83% yield, without any unwanted N-alkylcarbazole by-products. The primary by-product, 2 equivalents of PPhO, was readily removed by either chromatography or precipitation from hexane.

2,7-Dibromocarbazole [45] was therefore, synthesized from 4,4'-dibromo-2nitrobiphenyl [44] based on Freeman's method as described by Lee et al.¹⁶⁵ to give 70 % yield (Scheme 3). Meanwhile, compound [44] was obtained by reacting the commercially cheap and available 4,4'-dibromobiphenyl [43], with fuming nitric acid in glacial acetic acid at 100 °C; to give [44] in 93 % yield. To enhance the solubility and other properties of the resulting 2,7-functionalized carbazole (and subsequent copolymers), there is a need to introduce an alkyl group on the nitrogen atom position. Heptadecan-9-ol [47] was thus prepared from ethyl formate [46] (Scheme 3), by treating it with freshly prepared Grignard reagent to give the required product in 84 % yield. Compound [47] was then reacted with p-toluenesulfonyl chloride (TsCl) in the presence of triethyl amine (Et₃N) and trimethyl ammonium hydrogen chloride (Me₃N.HCl) to give heptadecan-9-vl 4methylbenzenesulfonate [58] in 92 % yield.¹⁶⁴ Compounds [45] and [48] were then reacted as outlined by Zhou et al.¹¹¹ to give 2,7-dibromo-9-(heptadecan-9-yl)-9H-carbazole [49] in 64 % yield.



Scheme 3: Synthesis of donor co-monomer based on carbazole: i).Glacial acetic acid, fuming nitric acid, 100 °C. ii). *o*-DCB, PPh₃, reflux. iii). Dry THF, C₈H₁₇Br/Mg, 0 °C. iv). Dry DCM, Et₃N, Me₃N.HCl/TsCl, 0-5 °C. v). KOH, DMSO:THF, r.t. iv). Dry THF, 2.5M n-BuLi in Hexane, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

Finally, the synthesis of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole **[50]** was attempted to take advantage of the Suzuki polycondensation coupling.¹⁰¹ Thus, compound **[49]** was lithiated using n-BuLi in hexane and then treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give compound **[50]** in 45 % yield.

4.1.2: Synthesis of Acceptors (A) Co-monomers:

The PCE of BHJ solar cells based on all-donor polymer like P3HT (the most promising of these type of polymers) in combination with PCBM has remained relatively low (5.2%), despite the effort of industrial and academic research laboratories to optimize

it. This may then suggest that the intrinsic limit of this polymer is reached. It is therefore, imperative to search for new materials that can afford higher efficiency. From materials perspective, donor polymers should not only be able to match the solar spectrum to increase the J_{sc} (LBG), but should also have high, V_{oc} (low lying HOMO). These conditions can only be met *via* the D-A approach. The ICT between the D-A moieties lowers the band gap by reducing the LUMO level while maintaining a low lying HOMO level. For example, a LBG polymer (PCDTBT), synthesized from a copolymerization of alkylated carbazole and 4,7-di-2-thienyl-2,1,3-benzothiadiazole, recently demonstrated a record high efficiency of 6.1 % when it was blended in a BHJ composite with PC₇₁BM.¹⁰⁴

The success of such copolymers has been attributed to the use of either 4,7di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DTBT) or benzo[c][1,2,5]thiadiazole (BT) as the acceptor unit. The DTBT unit has been found to have some advantages over the BT unit. Firstly, the thienyl units in DTBT help to relieve the possible steric hindrance between the acceptor BT unit and the aromatic donor unit, especially, when benzene based aromatics are used. This gives a planar structure, thereby reducing the band gap by enhancing the D-A conjugation. Also, a planar conjugated backbone would improve the charge carrier mobility due to chain-chain interactions among the copolymers. Secondly, the hole mobility of the polymer is improved by the thienyl units since thiophene-based polymers have shown very high hole mobility.¹⁵⁶These features have led to the choice of DTBT as the acceptor unit. In this study, we decided to replace the thienyl units in DTBT with EDOT to give 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3benzothiadiazole (DEBT) [54]; since EDOT has better electronic qualities than thiophene.

The synthetic route followed is outlined in Scheme 4. BT [51] was brominated in 48% HBr to afford 4,7-Dibromo-2,1,3-benzothiadiazole [52] in 47 % yield.¹⁶⁶ Compound [52] was then cross coupled with (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)trimethylstannane [53] under Suzuki coupling conditions to give 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3-benzothiadiazole [54] in 85 % yield;¹⁶⁷ which was dibrominated with NBS in chloroform at 50 °C to give 4,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,1,3 benzothiadiazole [55] in 99 % yield.¹⁶⁸



[55]

Scheme 4: Synthesis of acceptor co-monomer based on DEBT: i) HBr, Br, reflux. ii). Dry THF, Pd(PPh_3)₂Cl₂, reflux. iii). CHCl₃/50 °C, NBS.

The ¹H NMR spectra of compound [54] (Fig. 4.3) and the result of its MS showing an m/z 417 (100 % $[M^+ + H^+]$) have indicated the formation of the DEBT. However, due to solubility issues the ¹³C NMR could not be obtained. Compound [55] has shown very poor solubility in most organic solvents at room temperature, consequently, only its mass was determined showing m/z of 571 (40 % $[M^+]$, ⁷⁹Br/⁷⁹Br), 573 (100 %, $[M^+]$, ⁷⁹Br/⁸¹Br), 575 (40 %, $[M^+]$, ⁸¹Br/⁸¹Br) (Fig. 4.4).



Figure 4.3: ¹H NMR spectrum of compound [54]



Figure 4.4: MS of co-monomer [55].

We assumed the poor solubility of [55] would affect the polymerization process, as such, we attempted to improve its solubility by trying to synthesise 4,7-bis(7-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c] [1,2,5]thiadiazole *via* two routes as illustrated in Scheme 5. In the first route [54] was reacted with BuLi at – 45 °C and the lithiated compound was reacted with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Whereas, in the second route, [55] was reacted with 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) in the presence of potassium acetate and tetrakis(triphenylphosphine)palladium(0) [Pd(PPh_3)_4] catalyst.



Product not desired compound





Scheme 5: Synthesis of [60]: Route 1: i). Dry THF/BuLi, -45 °C, to 0 °C over 1 h, ii). -45 °C, iii). warm to r.t. Route 2: iv). Potassium acetate, v). Pd(PPh₃)₄ vi) Dry dioxane, 110 °C.

The ¹H NMR of the product of route 1 showed that it is the starting material [54] (Fig. 4.5) (compare with Fig. 4.3); in addition, its m/z value is similar to that of compound [54] (417, 100 % $[M^+ + H^+]$). Route 2 was then adopted; however, the product again turned out to be [54] based on the value of its MS (417, 100 % $[M^+ + H^+]$).



Figure 4.5: ¹H NMR spectrum of route 1.

When our effort to synthesise soluble derivative of compound [54] did not yield the desired result we decided to co-polymerise the co-monomer [55] with the donors (Scheme 9 pp. 116), since the reaction conditions used in the attempt to produce the soluble derivative are similar to the conditions for the copolymerisation reactions.

Another acceptor co-monomer was synthesised using (DES) [56] Scheme 6. Compound [56] was treated with NBS in chloroform at 50 °C to afford 3,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[b,d]thiophene 5,5-dioxide [57] in 97 % yield.

The ¹H NMR spectra of the starting material **[56]** are shown in Fig. 4.6. This compound, like compound **[54]** has solubility problem, as a result the ¹³C NMR could not be obtained. Compound **[57]** has also shown very poor solubility in most organic solvents at room temperature, consequently, only its mass was determined showing m/z of 652 (48 % [M⁺], ⁷⁹Br/⁷⁹Br), 654 (100 % [M⁺], ⁷⁹Br/⁸¹Br), 656 (60 % [M⁺], ⁸¹Br/⁸¹Br) (Fig. 4.7).



[57] Scheme 6: Synthesis of acceptor co-monomer based on DES: i) CHCl₃/50 °C, NBS.



Figure 4.6: ¹H NMR Spectrum of compound [56].



Figure 4.7: MS of co-monomer [57].

This acceptor was also copolymerised with the donors using the Suzuki method (Scheme 10 pp. 117).

We have attempted to synthesise another acceptor co-monomer based on BT, in which the EDOT fraction was replaced with 3,4-phenylene-dioxythiophene (PhEDOT) [58] (Scheme 7). Compound [58] was reacted with BuLi in dry THF at -78 °C and the mixture was treated with tributylchlorostannane at this temperature to produce benzo[b]thieno[3,4-e][1,4]dioxin-1-yltributylstannane [59] in more than 100 % yield. This product was then treated with compound [52] giving two fractions, compound [60a] in 37 % and compound [60b] in 30 % yield.

The ¹H NMR and MS spectrum of compound **[60a]** with m/z of 404 (100 % [M⁺ + H⁺]) (Fig. 4.8 a and b) suggests that it is 4-(benzo[*b*]thieno[3,4-*e*][1,4]dioxin-1-yl)-7-bromobenzo[*c*][1,2,5]thiadiazole; while the MS spectra of compound **[60b]** with m/z of 511 (100 % [M⁺]) (Fig. 4.9) suggests that it is 4,7-bis(benzo[*b*]thieno[3,4-*e*][1,4]dioxin-1-yl)benzo[*c*][1,2,5]thiadiazole.

The trimer [60b] could not be used to synthesize copolymers because the yield was very low (0.18 g, 30 %), and it is only sparingly soluble in common organic solvents.



[58]





[60a]

[60b]

Scheme 7: Synthesis of 4,7-bis(benzo[b]thieno[3,4-e][1,4]dioxin-1-yl)benzo[c][1,2,5]thia-diazole: i). BuLi/dry THF, -78 °C, 0 °C over 1.5 h, stir 1 h, ii). -78 °C, Bu₃SnCl/THF, stir -60 to -40 °C, 4 h, iii). Pd(PPh₃)₂Cl₂, dry THF.



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Figure 4.9: MS of compound [60b]

Part Two:

4.2: Synthesis of the Copolymers:

The first soluble fluorene-based polymer synthesized through ferric chloride oxidative polymerisation was reported in 1989¹⁸⁰ and was used for electroluminescence (EL). The polymer had a relatively low molecular weight and contained structural defects because of the synthetic method used. The palladium catalysed synthesis discovered by Suzuki and co-workers¹⁸¹ has been the most useful method used to synthesize the polyfluorenes and in the early 1990s, researchers at Dow used a modified Suzuki method, to produce a wide range of high molecular weight (50,000 to 600,000Da) and low PDI fluorene-based homo- and copolymers in high yield and purity.¹⁸²

The Suzuki coupling reaction is based on coupling boronic acid with halide in the presence of palladium (0) complex catalyst, its mechanism is illustrated in Scheme 8.



Scheme 8: Illustration of Suzuki-Miyaura catalytic cycle.

The oxidative addition of palladium [80] to aryl halide [81] produces an organopalladium halide [82]. This species reacts with an aqueous solution of base such as $(Na_2CO_3 \text{ or } K_2CO_3)$ to form an intermediate [83]. The boronic acid [84] reacts with the aqueous solution of the base to form boronate complex [85], which undergoes transmetalation with [83] to form the diaryl-palladium species [87]. This undergoes reductive elimination to give the polymer [88] and regenerate the original palladium complex [80].¹⁸³

The polymerisation of the copolymers was done based on the Suzuki coupling reaction and is outlined in Schemes 9 and 10.

The electron acceptor [55] was coupled separately with donors 2,2-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) [61] and [50] *via* the Suzuki coupling to produce the copolymers, PFDEBT [62] in 71 % and PCDEBT [63] in 75 % yield respectively (Scheme 9).



Scheme 9: Synthesis of copolymers [62] and [63]: i). Aliquat 336, ii). Pd(PPh₃)₄, iii). K₂CO₃, iv) Dioxane, 110 °C/72 h, v). Bromobenzene, vi). Phenyl boronic acid.

Similarly, the electron acceptor [57] was coupled with donors [61] and [50] to give the copolymers PFDES [64] in 88 % and PCDES [65] in 66 % yield respectively (Scheme 10).



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Scheme 10: Synthesis of copolymers [64] and [65]: i). Aliquat 336, ii). Pd(PPh₃)₄, iii) K₂CO₃ iv). Dioxane, 110 °C/72 h, v). Bromobenzene, vi). Phenyl boronic acid.

4.3: Characterisation:

4.3.1: Polymerisation and Thermal Stability:

The yield of the copolymers is relatively high, ranging between 66 to 88%. However, their molecular weight varied considerably, with copolymers [62] and [63] showing relatively higher values compared to [64] and [65]. The thermal stability, an important quality of polymers for device fabrication, was also analysed. The results showed that the copolymers have good thermal stability, losing only about 5 % of their total weight at between 370 to 400 °C. These high values of degradation temperature (T_d) may suggest that the thermal stability of these polymers is adequate to retard deformation of the active layer morphology at high temperature; which is desirable for BHJ solar cells. The thermal response of the copolymers is shown in Fig. 4.10, while Table 6 gives a summary of their yield, molecular weight and thermal stability. Appendices A and B show the GPC spectra and thermal spectrum of the individual copolymers respectively.



Figure 4.10: TGA of copolymers [62] to [65].

Table 6: H	Polymerisation	and Thermal Stat	oility of copolym	ers [62] - [65	
	Yield	Mn	Mw	PDI	T _d
Polymer	(%)	(kDa)	(kDa)		(%/°C)
[62]	71.43	31.94	98.09	3.07	5/370
[63]	75.21	6.11	11.57	1.89	5/370
[64]	87.52	3.41	5.16	1.52	5/400
[65]	65.78	5.29	6.72	1.27	5/410

4.3.2: Optical Properties:

The UV-Vis spectra of these copolymers were acquired from chloroform solution and a thin film cast on ITO glass from chloroform. The copolymers having the same acceptor moiety have demonstrated significant similarities in their optical response. For instance, copolymers [62] and [63] have two broad absorption bands with peaks at short and long wavelengths (Fig. 4.11). The peak at the shorter wavelength, is thought to corresponds to the $\pi - \pi^*$ transition of the conjugated main chains of the polymer while that at the longer wavelength could be attributed to the strong ICT interaction between the donor and acceptor.^{184, 185} The absorption bands of the films exhibited a bathochromic shift compared to those in solution and both have also shown similarity in the onset of absorption. The red-shift exhibited by these polymers may suggest that they have more ordered molecular conformation in the solid state than in the liquid state. The spectrofluorometry analysis of a chloroform solution of the polymers when excited at their absorption maximum gave similar values of PL Φ vs. [Ru(bipy)₃Cl₂]. In addition, their emission maxima lay in the deep red region of the emission spectrum with the spectra approaching the near infrared (NIR) region. It has been suggested by Kim et al.¹⁸⁶ that the emission of deep red fluorescence could be due to a very efficient energy transfer from the donor (fluorene and carbazole in present case) unit to the acceptor (DEBT in present case) unit. These results are similar to those already published for some fluorene and carbazole containing co-polymers.^{101, 150, 187,188} Table 7 gives a summary of the optical properties of the copolymers.

In contrast, the copolymers [64] and [65] have shown one broad absorption band with the absorption bands of the films showing no significant bathochromic shift compared to those in solution and both have demonstrated similarity in their onset of absorption (Fig. 4.12). The lack of bathochromic shift in the absorption of the films of these copolymers may suggest that they have similar molecular orientation in both liquid and solid states. The values of their PL Φ vs. [Ru(bipy)₃Cl₂] are within a close range with their emission maxima lying in the green region of the emission spectrum. A summary of the optical properties of the copolymers is given in Table 7. The plots of integrated fluorescence intensity *vs.* absorbance used for the calculation of the values of the PL Φ of the copolymers are available in appendix C.



Figure 4.11: Normalised UV-Vis Spectra in $CHCl_3$ and solid state and Photoluminescence in $CHCl_3$ of Copolymers [62] and [63].



Figure 4.12: Normalised UV-Vis Spectra in CHCl₃ and solid state and Photoluminescence in CHCl₃ of Copolymers [64] and [65].

	UV-Vis Absorption					PL	Φ
	CHC	213		Film		CHCl ₃	CHCl ₃
Copolymer	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ _{onset} (nm)	$ \begin{bmatrix} E_g^{Opt} \\ (eV) \end{bmatrix} $	λ _{max} (nm)	(%)
[62]	578	660	591	730	1.69	709	28
[63]	568	670	593	730	1.69	713	27
[64]	489	539	465	548	2.25	517	55
[65]	461	531	467	563	2.19	518	51

4.3.3: Electrochemical Properties:

The copolymers have demonstrated remarkable difference in their response to electrochemical treatment. Copolymers [62] and [63] in their neutral state have shown a good reversible behaviour under cyclic voltammetry process (Fig. 4.13 a and b). This may suggest that the polymers have a high degree of stability under electrochemical conditions. Copolymers [64] and [65] on the other hand, seem to be unstable because they have not shown significant reversible cyclic voltammograms (Fig. 4.14a and b). This could suggest that the films of these materials unlike those of copolymers [62] and [63] may undergo

degradation when subjected to electrical treatment. The difference in response to electrical conditions of the two sets of polymers could be attributed to their structural difference.

The HOMO and LUMO energy levels of the copolymers were estimated from the values of the onsets oxidation potential (E_{onset}^{oxi}) and reduction potential (E_{onset}^{red}) respectively using equations 10 and 11 and 0.084 eV as the value of the E_{FC} for the copolymers. The difference between the E_g^{EC} and E_g^{opt} for copolymers [62] and [63] is within experimental error limit, while copolymers [64] and [65] have shown a very wide difference possibly due to their low stability to electrical treatment. These copolymers have also shown some differences in the values of their HOMO and LUMO energy levels in relation to the acceptor moiety present. The copolymers [62] and [63] which contain DEBT acceptor unit have HOMO energy value of – 4.86 and – 4.97 eV respectively, while their LUMO is – 3.32 eV. In contrast, the values of HOMO of copolymers [64] and [65] are – 5.07 and – 5.04 eV respectively; which is relatively low lying compared to those of the former. The value of the LUMO energy level of this copolymers is also the same (– 3.57 eV), just like copolymers [62] and [63]. Table 8 gives a summary of the results of the electrochemical properties of the polymers.



a).



b)

Figure 4.13: Cyclic Voltammogram of the films of a) copolymer [62] and b) copolymer [63] on Ag electrode in MeCN solution of Bu_4NPF_6 (0.1 M) at a scan rate of 100 mV/s.





b)

Figure 4.14: Cyclic Voltammogram of films of a) copolymer [64] and b) copolymer [65] on Ag electrode in MeCN solution of Bu_4NPF_6 (0.1 M) at a scan rate of 100 mV/s.

	Cvclic Voltammogram				
Copolymer	Eonset/HOMO (eV)	E ^{red} _{onset} /LUMO (eV)	E_g^{ec} (eV)		
[62]	0.14/- 4.86	- 1.4/- 3.32	1.54		
[63]	0.25/-4.97	- 1.4/- 3.32	1.65		
[64]	0.35/- 5.07	- 1.15/- 3.57	1.53		
[65]	0.32/- 5.04	-1.15/-3.57	1.47		

The HOMO energy level of D-A copolymers according previous studies by other workers such as, Zhou, et. al.¹¹¹ Blouin, N. and Leclerc, M.¹⁴⁴ and Zhang, L. et al.¹⁸⁹; is mainly determined by the electron donor. For instance, the values of the HOMO of carbazole and fluorene based copolymers in the work of Zhou were -5.35 and -5.42 eV respectively, despite both being copolymerised with 2,5-bis(2-ethylhexyl)-3,6-di(thiophene-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione [**89**] (Fig. 4.15) as the electron acceptor. Likewise, the work of Zhang showed a similar pattern, the value of the HOMO of carbazole copolymer was -5.54 eV, while that of fluorene copolymer was -5.67 eV when these were copolymerised with the same electron acceptor [**90**] (Fig. 4.16).



Figure 4.15: Structure of 2,5-bis(2-ethylhexyl)-3,6-di(thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione [89].





Figure 4.16: Structure of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole [90].

Blouin, N. and Leclerc, M. however, studied the effect of various electron acceptors on the HOMO energy level of carbazole. They found that the HOMO of the copolymers ranged between -5.45 to -5.61 eV; which is in close agreement with that of the homo-polymer which they obtained as -5.6 eV. These results suggest that electron acceptor moieties in D-A copolymers have little effect on the HOMO energy level and that the energy level for carbazole and fluorene is low-lying (-5.35 to -5.67 eV) relative to the vacuum level.

The values of the HOMO energy levels determined for the copolymers [62] and [63] used in this study are -4.86 and -4.97 eV respectively, thus, HOMO of both copolymers is high-lying. This could account for the low values of the V_{oc} observed in the devices fabricated using these polymers (tables 12). It was expected that this energy level would be low-lying since the copolymers are based on carbazole and fluorene used in the studies by other workers explained above. This anomaly might be due to the effect of EDOT that was attached to BT. Hou, and co-worker¹⁹⁰ have observed similar effect when

they copolymerised 4,8-bis-alkoxy-benzo[1,2-b:4,5-b']dithiophene [91] (Fig. 4.17) with different electron acceptors. They observed high-lying HOMO energy levels in the copolymers compared to that of the homo-polymer. For example, the value for the copolymer containing EDOT was – 4.56 eV, while that of the homo-polymer was –5.16 eV. Hence, there is the possibility that the acceptor moiety has a role in determining the HOMO energy levels of D-A copolymers.



[91]

Figure 4.17: Structure of 4,8-bis-alkoxy-benzo[1,2-b:4,5-b']dithiophene [91].

The LUMO energy levels of the copolymers [62] and [63], on the other hand, is same (-3.32 eV); which suggests that this energy level is mainly dominated by the electron acceptor. In addition, the low-lying LUMO could be due to the ICT between the donor and the acceptor; which is thought to lower the band-gap by reducing the LUMO while maintaining a low-lying HOMO level.¹⁵⁶

The data of the electrochemical analysis of [64] and [65] have also shown similar pattern to those of [62] and [63]. The HOMO energy level calculated for copolymer [64] is -5.07 eV, while that of copolymer [65] is -5.04 eV. Thus, the HOMO for these compounds is low-lying compared to [62] and [63] yet higher than the usual values for carbazole and fluorene copolymerised with other acceptor moieties. It was expected that the values of the HOMO of all the four copolymers would be similar, while the LUMO energy levels of [62] and [63] would be the same or similar but differ significantly from those of [64] and [65] since the two sets have different acceptor units. While the values of the LUMO have shown the expected pattern for both sets, -3.32 eV for [62] and [63] and -3.57 eV for [64] and [65]; the values of the HOMO seem to suggest that the HOMO energy level is influenced to some extent by the acceptor moieties.
4.3.4: Photovoltaic Properties:

A blend of the respective copolymers with PC₆₀BM in a polymer:PC₆₀BM ratio of 1:1, 1:2, 1:3 and 1:4 was used to fabricate BHJ solar cells with device architecture similar to those reported by Pavel et. al.¹⁹¹ All the polymers have shown photovoltaic response under illumination and since the copolymers have similar HOMO energy levels and E_g^{cv} (Table 8) it was expected that they will show similarity in the values of their V_{oc} and J_{sc}. Conversely, a remarkable variation has been observed (Table 9). Devices based on copolymers [62] and [64] have demonstrated V_{oc} in the regime of 600 to 650 mV and J_{sc} of 4 to 6 mA/cm², affording them PCE of 1.45 and 1.10 % respectively. The performance of the copolymers [63] and [65] is however, limited by the low values of their V_{oc} and J_{sc}. Since factors like morphology of the active layer and the devices, solvent and temperature effects were not studied; the overall low PCE of the copolymers could be attributed to the level of radical impurities they contain (Table 10), because the performance seem to be proportional to amount of impurities present. Linear plots of current *vs.* voltage (*I-V*) characteristic of the best device of the respective polymers at given polymer:PC₆₀BM ratio are shown in Fig. 4.18.

Table 9: Photovoltaic Properties of BHJ devices based on copolymers [62] - [65].					
	Voc	Jsc	FF	η	
[62]:PC ₆₀ BM	(mV)	(mA/cm^2)	(%)	(%)	
1:1	695	4.19	34	0.99	
1:2	647	5.57	40	1.45	
1:3	631	5.24	41	1.36	
1:4	643	5.40	40	1.40	
[63]:PC ₆₀ BM					
1:1	315	1.75	30	0.17	
1:2	240	1.09	28	0.07	
1:3	314	1.01	34	0.11	
1:4	187	1.04	27	0.05	
[64]:PC ₆₀ BM					
1:1	603	4.27	43	1.10	
1:2	518	4.24	41	0.90	
1:3	550	3.97	37	0.81	
1:4	552	3.42	34	0.65	
[65]:PC ₆₀ BM					
1:1	456	2.89	30	0.40	
1:2	584	2.51	36	0.53	
1:3	452	2.20	38	0.38	
1:4	473	2.13	39	0.39	

Table 10: Purity Control of co	opolymers [62] – [65].		
	Radical impurity concentration		
Copolymers	(mole/mg)		
[62]	1.35×10^{-4}		
[63]	2.13×10^{-3}		
[64]	2.51×10^{-5}		
[65]	1.06×10^{-4}		



Figure 4.18: Current-Voltage (I-V) Characteristics of BHJ devices for best polymer: PC₆₀BM ratio of [62], [63], [64] and [65] copolymers.

4.4: Characterisation of Acceptor Moieties:

The acceptor moieties used for the synthesis of the copolymers were characterised to determine how they might influence the properties of the copolymers and the results are presented below.

4.4.1: Optical Properties of [54] and [56]:

The UV-Vis spectrum of EDOT [54] (Fig. 4.19) in chloroform solution gave a sharp absorption band with a peak at 323 nm and a broad absorption band with a peak at 482 nm with an onset absorbance at 580 nm Fig. 4.20. These values may suggest the

occurrence of a strong $\pi - \pi^*$ transition in the conjugated trimer and ICT interaction between the electron rich EDOT and the electron deficient BT respectively.^{184, 185}

The co-monomer DES [56] (Fig. 4.21), on the other hand, showed a broad absorption band with two peaks at 361 and 392 nm and onset of absorption around 436 nm (Fig.5.20). This may suggest that the electronic transition and ICT between the dibenzo[b,d] thiophene 5,5-dioxide and EDOT in this compound is weak in comparison to compound [54].







Figure 4.20: Normalised UV-Vis Spectra of compounds [54] and [56] in CHCl₃.



Figure 4.21: Structure of DES [56].

4.4.2: Electrochemical Properties of [54] and [56]:

The trimer [54] showed an oxidation process at 0.67 eV and further cycling between – 0.8 and 0.7 eV resulted in its polymerisation. This was evident by the growth of current in the region of – 0.5 and 0.5 eV forming a peak around – 0.3 eV and the subsequent formation of an insoluble polymer film on the surface of the Pt. electrode. The low value of the oxidation potential could be due to the presence of EDOT.¹⁹² The first fifteen cycles of the electro-polymerization at a scan rate of 100 mV s⁻¹ and the peak of the current growth are shown in Fig. 4.22; while the electro-polymerisation process is shown in Scheme 11.



Scheme 11: Electro-polymerisation of trimer [54]: i) DCM/ Bu₄NPF₆, ii) Current



Figure 4.22: Cyclic voltammogram of electro-polymerisation of [54] in DCM solution of Bu_4NPF_6 (0.1 M) at 100 mV s⁻¹ scan rate.

After rinsing the polymer film with the electrolyte solution, its redox switching in a monomer-free electrolyte solution showed a reversible process (Fig. 4.23). Such a property has also been shown by compounds having similar structure, for instance, 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole.¹⁹³



Figure 4.23: Cyclic voltammogram of the polymer of [54] in MeCN solution of Bu_4NPF_6 (0.1 M) at 100 mV s⁻¹ scan rate.

Conversely, when compound [56] was subjected to electro-polymerization under similar conditions as compound [54], it did not show any oxidation peak; but was stable (Fig. 4.24). The application of repetitive potential-sweep to the monomer solution did not seem to form a polymer on the working electrode. Therefore, despite the presence of a yellow film on the electrode after the potential sweep, its response to redox switching in a monomer-free electrolyte solution was similar to that of the intermediate (Fig. 4.25). Hence, unlike compound [54], this intermediate does not seem to undergo electropolymerization.



Figure 4.24: Cyclic Voltammogram of electro-polymerisation of [56] in DCM solution of Bu_4NPF_6 (0.1 M) at 100 mV s⁻¹ scan rate.



Figure 4.25: Cyclic voltammogram of polymerised [56] in CH_2Cl_2 solution of Bu_4NPF_6 (0.1 M) at 100 mV s⁻¹ scan rate.

The difference in the optical and electrochemical properties of these acceptor units may therefore account for the anomalies observed in the optical and electrochemical properties of their respective copolymers discussed earlier.

Chapter Five:

5.1: Conclusion:

In this study we report the synthesis and characterisation of side chain functionalised polymer based on P3HT [poly(3-hexylthioacetate)] [42] via GRIM and four novel fully aromatic LBG copolymers; namely, PFDEBT [62], PCDEBT [63], PFDES[64] and PCDES [65] via the Suzuki coupling method. All the polymers have shown good solubility in common organic solvents together with stable optical properties and good thermal stability. The PL Φ of [42] is in agreement with those of its analogues, the homothiophene polymers and its emission λ_{max} indicates that it is a good green light emitter. When used to fabricate DSSC solar cells in combination with nc-TiO₂ it showed some photovoltaic properties, though with very low PCE.

The LBG copolymers that have the same electron acceptor unit have shown similarities in their optical and electrical properties. For instance, two peaks were observed in the UV-Vis absorption spectra of both copolymers [62] and [63]; one at a shorter wavelength which could be due to electronic transition of their conjugated main chains, while the other is at a longer wavelength which could be attributed to a strong ICT interaction between the donor and acceptor groups in the polymer chains. In addition, both emit in the deep red region with emission λ_{max} of 709 and 713 nm and PL Φ values of 28 % and 27 % respectively. Similarly, copolymers [64] and [65] have shown single peak in their UV-Vis absorption spectra and both emit in the green region with emission λ_{max} of 517 and 518 nm, also both have similar PL Φ values of 55 % and 51 % respectively.

In addition, a bathochromic shift > 10 nm was observed in the absorption bands of the films of copolymers [62] and [63] with respect to those in solution; while the films of [64] and [65] showed a shift < 10 nm compared to those in solution. This disparity could be attributed to the structural difference existing between these two sets of polymer; while, copolymers [64] and [65] have two biphenyl nuclei alternating along the polymer backbone which may give them a more planar and better ordered molecular orientation in both solid and liquid states, copolymers [62] and [63] on the other hand have only one biphenyl nucleus alternating with a phenyl group which may make them to have different molecular configuration in the solid and liquid states.

Likewise, the copolymers have shown some discrepancies in their behaviour towards electrical effects. Both copolymers [62] and [63] have the same value of the

LUMO energy level (-3.32 eV); copolymers [64] and [65] also have the same values but it is low-lying (-3.57 eV) compared to the former suggesting that the LUMO energy level is largely dominated by the acceptor units. The HOMO of the polymers; which is supposed to be mainly determined by the donor moiety has values different from what was expected. The copolymers were expected to have a low-lying HOMO since they are based on electron donors that are known to afford copolymers with low-lying HOMO. Nevertheless, the HOMO is not only high-lying, but has shown significant difference between polymers having the same donor but different acceptor component. For instance, the values for copolymers [62] and [64] which have the same donor unit (fluorene) are -4.86 and -5.07eV respectively; while those for copolymers [63] and [65] which contain carbazole as a common donor component are -4.96 and -5.04 eV respectively. There is therefore, the possibility that the HOMO of copolymers is also influenced to a certain extent by the acceptor moiety.

The result of the preliminary test of the photovoltaic properties of polymer [42] in DSSC solar cells has shown good photovoltaic response with the cell having 20 mg polymer afforded 0.035 % PCE, 34 % FF, 1.7 mA/cm² J_{sc} and 610 mV V_{oc}. The low PCE could be attributed to low values of the FF and J_{sc}. The copolymers [62], [63], [64] and [65], on the other hand, have shown better PCE when used in BHJ solar cells. Device based on [62] with a polymer: PC₆₀BM blend ratio of 1:2 has recorded the best performance with 1.45 % PCE, 40 % FF, 5.57 mA/cm² J_{sc} and 647 mV V_{oc} while the device based on [63] with a blend ratio of 1:1 has shown the best performance for this polymer with 0.17 % PCE, 30 % FF, 1.75 mA/cm² J_{sc} and 315 mV $V_{oc}.$ Likewise, a better performance was observed in the device based on copolymer [64] with a blend ratio of 1:1 showing 1.1 % PCE, 43 % FF, 4.27 mA/cm² J_{sc} and 603 mV V_{oc} , than the device based on copolymer [65] with a blend ratio of 1:2 which has shown the best performance among the devices based on this polymer with 0.53% PCE, 36 % FF, 2.51 mA/cm² J_{sc} and 584 mV V_{oc} . The seemingly high values of FF and J_{sc} observed in the device based on copolymer [62] compared to the values for the other polymers may suggest that there was low serial resistance from the materials in the active layer which resulted in a balanced charge flow with little recombination loss.¹⁰¹ The results of the preliminary tests of the unmodified devices indicate that these polymers are potential photovoltaic materials; hence, the PCE could be optimised via modification of the active layer and/or the device.

5.2: Recommendations and suggestions for further work:

The band gap of polymer [42] is comparably similar to that of P3HT; which might have contributed to the low PCE of the DSSC solar cells based on this polymer. Based on the results of its CV, the band gap has not been effectively reduced by the functional group attached to the hexyl side chain. Therefore, it is necessary to design another side chain functionalised thiophene based polymer using functional groups that may effectively lower the band gap of the resultant polymer *via* electron push-pull effect. Triphenylamine [92] (Fig. 5.1) could be a good material for this purpose, because its derivatives have shown useful properties in electrical conductivity and they have been used in OLEDs as holetransporters.¹⁹⁴Furthermore, an organic dye based on triphenylamine derivative with a typical electron push-pull structure has been used in DSSC nc-TiO₂ using P3HT which has shown a record PCE of 2.7 %.¹⁹⁵ In addition, the planar structure of triphenylamine may give the resultant polymer a planar structure which promote intermolecular $\pi - \pi$ stacking, a condition necessary for high charge mobility.



[92]

Figure 5.1: Structure of triphenylamine [92]:

The poor solubility of compounds [55] and [57] might have affected the polymerisation of the copolymers [62], [63], [64] and [65], therefore, it is important to synthesise an acceptor moiety that has good solubility in the polymerisation solvent at r.t. The incorporation of alkyl groups in these compounds may improve their solubility and increase the chances of synthesising high molecular weight copolymers. Zhou H. et al.¹⁵⁶ in their study of the effect of alkyl groups in alkylated dithienylbenzothiadiazole (DTBT) based copolymers for BHJ solar cells, observed that the polymers containing DTBT with alkyl groups on the 4-positions of the thienyl groups [93] (Fig. 5.2) showed an improved hole mobility of 9.2 x 10^{-6} cm²/(V•s) compared to 3.9 x 10^{-6} cm²/(V•s) for the unmodified copolymer. In addition, the efficiency of related BHJ solar cells was improved. Liang and

 Yu^{16} have also observed an improved hole mobility due to presence of alkyl group; which led to large J_{sc}, thus increased PCE. The incorporation of alkyl groups in the EDOT that flanks the BT and Dibenzothiophene-S,S-dioxide in compounds [54] and [56] may therefore improve the physical and chemical properties of the copolymers based on them and subsequently the efficiency of BHJ solar cells based on the copolymers.



[93]

Figure 5.2: Structure of alkylated DTBT.

Alternatively, diketopyrrolopyrrole (DPP) [94] (Fig. 5.3) which usually must have an alkyl group attached to the 2,5-positions to make it soluble in most organic solvents; could be flanked with EDOT and copolymerised with either carbazole or fluorene donor moieties. Carbazole and fluorene have been copolymerised with thienyl containing DPP affording 2.26% and 0.88% PCE with relatively low lying HOMO energy level (-5.35and -5.42 eV) and low band-gap (1.69 and 1.78 eV) respectively.¹¹¹



Figure 5.3: Structure of alkylated [95].

The results of the electrochemical analysis of the copolymers appear to suggest that the position of the HOMO of the copolymers may also depend on the type of acceptor unit used. We therefore recommend that this phenomenon be investigated in details.

Since the BHJ devices based on the four copolymers were not modified, the morphology is yet to be optimized which probably have contributed to the relatively low PCE. The performance of these polymers in solar cells could be improved through optimizing the interpenetrating network morphology of their devices using modification techniques such as, thermal annealing, use of different solvents, varying film forming speed and the use of better acceptor than $PC_{60}BM$. The thin film UV-Vis absorption spectra of both copolymers [62] and [63] exhibited two main absorption bands in the visible range, one in the wavelength range of 370-420 nm and the other in 500-600 nm, leaving an absorption minimum around 450 nm. Badrou, R.A. and co-workers¹⁹⁶ have illustrated that $PC_{70}BM$ has higher absorption in the spectral range than $PC_{60}BM$. It absorbs in the wavelength range of 400-600; which is complementary to the absorption minimum of copolymers [62] and [63]. We therefore recommend the use of $PC_{70}BM$ as an acceptor in devices based on these polymers.

The PL Φ results of all the copolymers in solution have shown that they could be potential materials for light emitting devices. Hence, we recommend a comprehensive investigation of their photoluminescence and applications in OLEDs and OFETs. The investigation of copolymers [62] and [63] in particular is highly recommended since their emission spectra is approaching the NIR region; which makes them potential materials for use in photodynamic therapy for the treatment of cancer.

Finally, since yield and solubility issues have limited our efforts to investigate the potentials of compound [60b] (see structure above) in LBG copolymers; we recommend an investigation of the application of this trimer in the synthesis of copolymers for use in OLEDs and OPVs.

References:

- 1. Goh, M., Matsushita, S. and Akagi, K., Chem. Soc. Rev., 2010, 39, 2466-2476.
- 2. Shirakawa, H. and Ikeda, S., J. Polym., 1971, 2, 231–244.
- Ito, T., Shirakawa, H. and Ikeda, S., J. Polym., Science, Polym. Chem., 1974, 12, 11-20.
- 4. Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang C. K. and Heeger, A. J., J. Chem. Soc., Chem. Comm., 1977, 578–580.
- 5. Heeger, A. J. Angew. Chem, Int. Ed., 2001, 40, 2591-2611.
- 6. Heeger A. J., Chem. Soc. Rev., 2010, 39, 2354-2371.
- 7. Shaheen, S. E., Brabec, C. J., Sariciftci, N. S., Padinger, F., Fromherz, T., Hummelen, J. C., Appl. Phys. Lett., 2001, 78, 841-843.
- 8. Shaheen, S. E., Radspinner, R., Peyghambarian, N. and Jabbour, G. E., *Appl. Phys. Lett.*, 2001, **79**, 2996-2998.
- Irwin, M. D., Buchholz, D. B., Hains, A. W., Chang, R. P. H. and Marks, T. J., Prog. Nat. Acad. Science, 2008, 105, 2783-2787.
- 10. Chen, J. and Cao, Y. Acc. Chem. Res., 2009, 42, 1709-1718.
- 11. Havinga, E. E.; Hoeve, W.; Wynberg, H. Synth. Metals. 1993, 55, 299-306.
- Xu, S. Liu, Y., Li, J., Wang, Y. and Cao, S., Polymer Adv. Technology, 2010, 21, 663-668.
- Zhou, E., Cong, J., Tajima, K. and Hashimoto, K., Chem. Mater., 2010, 22, 4890-4896.
- Blouin, N., Michaud, A., Gendron, D., Wakim, S., Blair, E., Neagu-Plesu, R., Belletete, M., Durocher, G., Tao, Y. and Leclerc, M., J. Am. Chem. Soc., 2008, 130, 732-742.
- Yu, C-Y, Chen, C-P., Chan, S-H., Hwang, G-W. and Ting, C., Chem. Mater., 2009, 21, 3261-3269.
- 16. Liang, Y. and Yu, L., Acc. Chem. Res., 2010, 43, 1227-1236.
- Wallace, G. G., Dastoor, P. C., Officer, D. L., Too, C. O., Chem. Innovation., 2000, 30, 14-22.
- 18. Bundgaard, E. and Krebs, F. C., Sol. Energ. Mater. & Sol. Cells, 2007, 19 954-985.
- 19. Brazovskii, S. and Natasha Kirova, Chem. Soc. Rev., 2010, 39, 2453-2465.
- Blom, P. W. M., Mihailetchi, V. D., Koster, L. J. A. and Markov, D. E., Adv. Mater. 2007, 19, 1551–1566.
- 21. Pomerantz, M., Gu, X. and Zhang, S. X., Macromolecules, 2001, 34, 1817-1822.
- 22. Coakley, K. M. and McGehee, M. D., Chem. Mater., 2004, 16, 4533-4542.
- 23. Andersson, M. R., Thomas, O., Mammo, W., Svensson, M., Theander, M. and Inganas, O., *J. Mater. Chem.* 1999, **9**, 1933-1940.
- 24. Grimsdale, A. C., Cacialli, F., Gruener, J., Li, X.-C., Holmes, A. B. Moratti, S. C. and Friend, R. H., Synth. Metals, 1996, 76, 165-167.
- 25. Gierschner, J., Cornil, J. and Egelhaaf, H-J., Adv. Mater., 2007, 19, 173-191.
- 26. van Mullekom, H.A.M., Vekemans, J.A.J.M., Havinga E.E. and Meijer, E.W., Mater. Sci. & Eng. R-Reports 2001, 32, 1-40.
- 27. Roncali, J., Chem. Rev. 1997, 97, 173-205.

- 28. Hess, B. A. Jr. and Schaad, L. J. J. Am. Chem. Soc. 1973, 95, 3907-3912.
- 29. Hess, B. A., Schaad, L. J. and Holyoke, C. W., Tetrahedron, 1972, 28, 3657-3667.
- 30. Kroon, R., Lenes, M., Hummelen, J. C., Blom, P.W.M. and De Boer, B., *Polym. Rev.* 2008, **48**, 531-582.
- 31. Liang, Y., Xu, Z., Xia, J., Tsai, S-T., Wu, Y., Li, G., Ray, C. and Yu, L., *Adv. Mater.*, 2010, **22**, E135-E138.
- Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L. and Pettersson, H., Chem. Rev. 2010, 110, 6595-6663.
- Erwin, M. M., Kadavanich, A. V., Mcbride, J., Kippeny, T., Pennycook, S. and Rosenthal, S. J., *Eur. Phys. J.* D, 2001, 16, 275-277.
- 34. Cook, S., Unpublished PhD. Thesis in chemistry, Imperial College London, 2006.
- 35. Chapin, D. M., Fuller, C. S. and Pearson, G. L., J. Appl. Phys., 1954, 25, 676-677.
- 36. Miles, R. W., Hynes K. M. and Forbes I., Prog. Crystal Growth Charact. Mater., 2005, **51**, 1.42.
- 37. Miles, R. W., Zoppi, G. and Forbes I., Materialstoday, 2007, 10, 1-8.
- Green, M. A., Emery, K., Hishikawa, Y., Warta, W. and Dunlop, E. D., Prog. Photovolt. Res. Appl. 2012, 20, 12-20.
- Li, C., Liu, M., Pschirer, N. G., Baumgarten, M. and Mullen, K., Chem. Res. 2010, 110, 6817-6855.
- 40. Zhou, H., Yang, L., Stoneking, S. and W. You, ACS. Appl. Mater. Interf., 2010, 2, 1377-1383.
- 41. Wienk, M. M., Struijk, M. P. and Janssen, R. A. J., Chem. Phys. Lett. 2006, 422, 488-491.
- 42. Scharber, M. C., Muhlbacher, D., Koppe, M., Denk, P., Waldauf, C., Heeger, A. J. and Brabec, C. J., Adv. Mater. 2006, 18, 789–794.
- Soci, C., Hwang, I. W., Moses, D., Zhu, Z., Waller, D., Gaudiana, R., Brabec, C. J. and Heeger, A. J. Adv. Funct. Mater. 2007, 17, 632–636.
- 44. Huynh, W. U., Dittmer, J. J. and Alivisatos, A. P., Science, 2002, 295, 2425-2427.
- Krebs, F. C., Jorgensen, M., Norrman, K., Hagemann, O., Alstrup, J., Nielsen, T. D., Fyenbo, J., Larsen, K. and Kristensen, J., Sol. Energ. Mater. & Sol. Cells, 2009, 93, 422-441.
- 46. Friend, R. H., Pure Appl. Chem., 2001, 73, 425-430.
- 47. Weinberger, B. R., Akhtar, M. and Gau, S. C., Synth. Metals, 1982, 4, 187-197.
- 48. Glenis S; Tourillon, G. and Gannier, F., Thin Solid Films, 1986, 139, 221-231.
- 49. Karg, S., Riess, W., Dyakonov, V., Schwoerer, M., Synth. Metals, 1993, 54, 427-433.
- Marks, R. N., Halls, J. J. M., Bradley, D. D. C., Friend R. H. and Holmes, A. B., J. Phys., Condens., Mater., 1994, 6, 1379-1394.
- Greenham, N. C., Peng X. G. and Alivisatos, A.P., *Future Generation Photovoltaic Technologies*, Book Series: AIP Conference Proceedings Issue 404, Published 1997, AIP Press, American Institute of Physics 500 Sunnyside Boulevard, Woodbury, NY 11797-2999, pp. 295-301.
- 52. Mayer, A. C. Shawn, R. S., Hardin, B. E., Rowell M. W. and McGehee, M. D. *Mater.*, *Today*, 2007,10, 28-33.
- 53. Huynh, W. U., Peng, X. and Alivisatos, A.P., Adv., Mater., 1999, 11, 923-927.

- Blom P. W. M., de Jong, M. J. M. and Vleggaar, J. J. M., Appl. Phys. Letters, 1996, 68. 3308-3310.
- 55. Tang C. W., Appl., Phys., Letters, 1986, 48, 183-185.
- 56. Onoda, M. and Tada, K. Cur. Appl. Phys., 2003, 3, 141-147.
- 57. Sun, S. S. and Sariciftci, N. S. Organic Photovoltaic Mechanism, Material and Devices, Taylor and Francis, (2005).
- Sariciftci, N. S., Smilowitz, L., Heeger, A. J., Wudl, F., Science, 1992, 258, 1474-1476.
- Sariciftci, N. S., Braun, D., Zhang, C., Srdanov, V. I., Heeger, A. J., Stucky, G., Wudl, F., Appl. Phys. Lett. 1993, 62, 585-587.
- 60. Halls, J. M., Pichler, K., Friend, R. H., Moratti, S. C., Holmes, A. B., *Appl. Phys. Letters*, 1996, **68**, 3120-3122.
- 61. Savenije, T. J., Warman, J. M. and Goossens, A., Chem. Phys. Letters, 1998, 287, 148-153.
- Arango, A. C., Johnson, L. R., Bliznyuk, V. N., Schlesinger, Z., Carter, S., Horhold, H. H., Adv. Mater. 2000, 12, 1689-1692.
- 63. Yu, G., Gao, J., Hummelen, J. C., Wudl, F. and Heeger, A. J., Science. 1995, 270, 1789-1791.
- 64. Peumans, P., Yakimov A. and Forrest, S.R., J. Phys., 2003, 93, 3693-3723.
- 65. Shaheen, S. E., Ginley D.S. and Jabbour, G.E., MRS Bulletin, 2005, 30 10-19.
- Janssen, R. A. J., Hummelen J.C. and Sariciftci, N.S., *MRS Bulletin*, 2005, 30, 33-36.
- 67. Vogel, M., Strotmann, J., Johnev, B., Lux-Stainer, M. Ch. and Fostiropoulos, K., *Thin Solid Films*, 2006, **511**, 367-370.
- Waldauf, C., Scharber, M. C., Schilinsky, P., Hauch J. A. and Brabec, C. J., J. Appl. Phys., 2006, 99, 104503-1-104503-6.
- Chirvase, D., Chiguvare, Z., Knipper, M., Parisi, J., Dyakonov, V., Hummelen, J. C., J. Appl. Phys. 2003, 93, 3376-3383.
- Koster, L. J. A., Smits, E. C. P., Michailetchi, V. D. and Blom, P. W. M., *Phys. Rev.* B, 2005, 72, 085205.
- 71. Dittmer, J. J., Marseglia, E. A. and Friend, R. H., Adv. Mater., 2000, 12, 1270-1274.
- Greenham, N. C., Peng, X. and Alivisatos, A. P., Phys. Rev. B., 1996, 54, 17628-17637.
- Zotti, G., Vercelli, B., Berlin, A., Pasini, M., Nelson, T. L., McCullough, M. D. and Virgili, T., *Chem. Mater.* 2010, 22, 1521-1532.
- 74. Arango, A. C., Carter, S. A. and Brock, P. J., *Appl. Phys. Letters*, 1999, 74, 1698-1700.
- 75. Coakley, K. M., and McGeHee, M. D., Appl. Phys. Letters, 2003, 83, 3380-3382.
- Kwong, C. Y., Choy, W. C. H., Djurisic, A. B., Chui, P. C. and Chan, W. K., Nanotechnology, 2004, 15, 1156-1161.
- 77. Gunes, S., Marjanovic, N., Nedeljkovic, J. M. and Sariciftci, N. S., *Nanotech*nology, 2008, **19**, 1-5.

- Sharma, G. D., Suresh, P. Sharma, S. K and Roy, M. S., Sol. Energ. Mater. & Sol. Cells, 2008, 92, 61-70.
- 79. Yu, G. and Heeger, A. J. J. Appl. Phys. 1995, 78, 4510-4515.
- Halls, J. J. M., Walsh, C. A., Greenham, N. C., Marseglia, E. A., Friend, R. H., Moratti, S. C., Holmes, A. B., *Nature* 1995, 376, 498-500.
- Granstrom, M., Petritsch, K., Arias, A. C., Lux, A., Andersson, M. R., Friend, R. H., Nature 1998, 395, 257-260.
- Martens, T., D'Haen, J., Munters, T., Beelen, Z., Goris, L., Manca, J., D'Olieslaeger, M., Vanderzande, D., De Schepper, L. and Andriessen, R., *Synth. Metelas*, 2003, 138, 243-247.
- Hoppe, H., Niggemann, M., Winder, C., Kraut, J., Hiesgen, R., Hinsch, A., Meisner, D. and Sariciftci, N. S., Adv. Funct. Mater., 2004, 14, 1005-1011.
- Mihailetchi, V. D., Koster, L. J. A., Blom, P. W. M., Melzer, C., de Boer, B., van Duren, J. K. J. and Janssen, R. A. J., *Adv. Funct. Mater.*, 2005, 15, 795-801.
- 85. Mihailetchi, V. D., Wildeman, J. and Blom, P. W. M. Phys. Rev. Letters, 2005, 94, 126602-1-126602-4.
- Padinger, F., Rittberger, R. S. and Sariciftci, N. S., Adv. Funct. Mater. 2003, 13, 85-88.
- 87. Liang, Y. and Yu, L., Polym. Rev., 2010, 50, 454-473.
- 88. Dennler, G., Scharber, M. C. and Brabec, C. J. Adv. Mater. 2009, 21, 1323-1338.
- Gadisa, A., Mammo, W., Andersson, L. M., Admassie, S., Zhang, F., Andersson, M. R. and Inganas, O., Adv. Funct. Mater., 2007, 17, 3836 –3842
- Zhang, F., Jespersen, K. G., Bjorstrom, C., Svensson, M., Andersson, M. R., Sundstrom, V., Magnusson, K., Moons, E., Yartsev, A. and Inganas, O., *Adv. Funct. Mater.*, 2006, 16, 667–674.
- Andersson, L. M., Zhang, F., and Inganas, O., *Appl. Phys. Letters*, 2007, 91, 071108-1-071108-3.
- 92. Beaupre, S., Boudreault, P-L. T. and Leclerc, M., Adv. Mater. 2010, 22, E6-E27.
- 93. Gendron, D. and Leclerc M., Environ. Sci., 2011, 4, 1225-1237.
- 94. Leclerc, M. J. Polym. Sci. Part A, 2001, 39, 2867-2873.
- Svensson, M., Zhang, F., Veentra, S. C., Verhees, W. J. H., Hummelen, J. C., Kroon, J. M., Inganas O., and Andersson, M. R., *Adv. Mater.* 2003, 15, 988-991.
- 96. Kitazawa, D., Watanabe, N., Yamamoto S. and Tsukamoto, J., *Appl. Phys. Letters*, 2009, **95**, 053701-1 053701-3.
- Boudreault, P-L. T., Michaud, A. and Leclerc, M., *Macromol. Rapid Comm.* 2007, 28, 2176-2179.
- Grazulevicius, J. V., Strohriegl, P., Pielichowski, J. and Pielichowski, K., Prog. Polym. Sci., 2003, 28, 1297-1353.
- Li, J., Dierschke, F., Wu, J., Grimsdale, A. C. and Mullen, K., J. Mater. Chem., 2006, 16, 96-100.
- Leclerc, N., Michaud, A., Sirois, K., Morin, J.-F. and Leclerc, M., Adv. Funct. Mater. 2006, 16, 1694-1704.
- 101. Blouin, N., Michaud, A. and Leclerc, M. Adv. Mater. 2007, 19, 2295-2300.

- 102. Wakim, S., Beaupre, S., Blouin, N., Aich, B.-R., Rodman, S., Gaudiana, R., Tao, Y., Leclerc, M., J. Mater. Chem. 2009, 19, 5351-5358.
- 103. Chu, T-Y., Alem, S., Verly, P. G., Wakim, S., Lu, J., Tao, Y., Beaupré, S., Leclerc, M., Bélanger, F., Désilets, D., Rodman, S., Waller, D. and Gaudiana, R., *Appl. Phys. Letters*, 2009, **95**, 063304-1 – 063304-3.
- 104. Park, S. H., Roy, A., Beaupre, S., Cho, S., Coates, N., Moon, J. S., Moses, D., Leclerc, M., Lee, K., Heeger, A. J., *Nature Photonics*, 2009, **3**, 297-302.
- 105. Chu, T. Y., Alem, S., Verly, P. G., Wakim, S., Tse, S. C., Lu, J., Tao, Y., Beaupre, S., Leclerc, M., Belanger, F., Desilets, D., Rodman, S. and Gaudiana, R., 26th European Photovoltaic Solar Energy Conference and Exhibition, Hamburg, Germany, 2010.
- Gendron, D., Morin, P-O., Najari, A. and Leclerc, M. Macromol. Rapid Comm. 2010, 31, 1090-1094.
- 107. Farnum, D. G., Mehta, G., Moore, G. G. I. and Siegal, F. P., *Tetrahedron Letters.*, 1974, 29, 2549-2552.
- 108. Wienk, M. M., Turbiez, M., Gilot, J. and Janssen, R. A. J., Adv. Mater. 2008, 20, 2556-2560.
- 109. Bijleveld, J. C., Gevaerts, V. S., Nuzzo, D. D., Turbiez, M., Mathijssen, S. G. J., de Leeuw, D. M., Wienk, M. M. and Janssen, R. A. J., *Adv. Mater.* 2010, 22, E242– E246.
- 110. Zou, Y., Gendron, D., Aich, B-R., Najari, A., Tao, Y. and Leclerc, M. *Macromolecules*, 2009, **42**, 2891-2894.
- 111. Zhou, E., Yamakawa, S., Tajima, K., Yang, C. and Hashimoto, K., Chem. Mater. 2009, 21, 4055–4061.
- 112. Huo, L., Hou, J., Chen, H-Y., Zhang, S., Jiang, Y., Chen, T. L. and Yang, Y., *Macromolecules*. 2009, **42**, 6564–6571.
- 113. Chen, G.-Y., Chiang, C.-M., Kekuda, D., Lan, S.-C., Chu, C.-W. and Wei, K.-H., J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 1669-1675.
- 114. Neef, C. J., Brotherston, I. D. and Ferraris, J. P., Chem. Mater., 1999, 11, 1957-1958.
- 115. Lee, K. and Sotzing, G. A., Macromolecules, 2001, 34, 5746-5747.
- 116. Lee, B., Seshadri, V., Palko, H. and Sotzing, G. A., Adv. Mater., 2005, 17, 1792-1795.
- 117. Yao, Y., Liang, Y., Shrotriya, V., Xiao, S., Yu, L. and Yang Y., Adv. Mater. 2007, 19, 3979–3983.
- 118. Liang, Y., Wu, Y., Feng, D., Tsai, S-T., Son, H-J., Li, G. and Yu, L., J. Am. Chem. Soc. 2009, 131, 56–57.
- Green, M. A., Emery, K., Hishikawa, Y. and Warta, W., Prog. Photovolt. Res. Appl. 2011, 19, 84-92.
- 120. http://www.konarka.com.
- 121. Zou, Y., Najari, A., Berrouard, P., Beaupre, S., Aich, B-R., Tao, Y. and Leclerc, M., J. Am. Chem. Soc. 2010, 132, 5330–5331.

- 122. Chu, T.-Y., Lu, J., Beaupre, S., Zhang, Y., Pouliot, J.-R., Wakim, S., Zhou, J., Leclerc, M., Li, Z., Ding, J. and Tao, Y., J. Am. Chem. Soc., 2011, 133, 4250-4253.
- 123. Schwartz, B. J., Ann. Rev. Phys. Chem. 2003, 54, 141-172.
- 124. Inigo, A. R., Chiu, H.-C., Fann, W., Huang, Y-S., Jeng, U. S., Hsu, C. H., Peng, S.-A. Chene, K-Y., Synth. Metals, 2003, 139, 581–584.
- 125. Hoofman, R. J. O. M., de Haas, M. P., Siebbeles, L. D. A., Warman, J. M., Nature, 1998, 392, 54-56.
- Campbell, A. R., Hodgkiss, J. M., Westenhoff, S., Howard, I. A., Marsh, R. A., McNeill, C. R., Friend, R. H. and Greenham, N. C., *Nano Letters*, 2008, 8, 3942-347.
- 127. Lenes, M., Morana, M., Brabec, C. J. and Blom, P. W. M., Adv. Funct. Mater. 2009, 19, 1106–1111.
- 128. Lee, J. K., Ma, W. L., Brabec, C. J., Yuen, J., Moon, J. S., Kim, J. Y., Lee, K., Bazan, G. C., and Heeger, A. J., *J. Am. Chem. Soc.* 2008, **130**, 3619-3623.
- 129. Oregan, B; Grätzel, M., Nature, 1991, 353, 737-740.
- 130. Mishra, A., Fisher, M. K. R. and Bauerle, P., Angw. Chem. Int. Ed., 2009, 48, 2474-2499
- 131. Bach, U., Lupo, D., Conte, P., Moser, J. E., Welssortel, F., Salbeck, J., Spreitzer, H. and Gratzel, M., *Nature*, 1998, **395**, 583-585.
- 132. Dittmer, J. J., Petrisch, K., Marseglia, E. A., Friend, R. H., Rost, H., Holmes, A. B., Synth. Metals, 1999, 102, 879-880.
- Gebeyehu, D., Brabeca, C. J., Sariciftci, N. S. Vangeneugden, D., Kiebooms, R., Vanderzande, D., Kienberger, F. and Schindler, H., Synth., Metals, 2002, 125, 279-287.
- 134. Zafer, C., Karapire, C., Sariciftci, and N. S., Icli, S., Sol. Energ. Mater. & Sol. Cells, 2005, 88, 11–21.
- 135. Tsekouras, G., Too, C.O. and Wallace, G.G., Synth. Metelals, 2007, 157, 441-447.
- 136. Komiya, R., Han, L., Yamanaka, R., Islam, A., Mitate, T., J. Photochem. Photobiol. A, 2004,164, 123–127.
- Schmidt-Mende L., Bach, U., Humphery-Baker, R., Horiuchi, T., Miura, H., Ito, S., Uchida, S. and Gratzel, M., Adv. Mater. 2005, 17, 813-815.
- Reyes-Reyes, M., Kim, K., Carroll, D. L. Appl. Phys. Letters, 2005, 87, 083506-1 083506-3.
- 139. Kim, J. Y., Kim, S. H., Lee, H. H., Lee, K., Ma, W. L., Gong, X.and Heeger, A. J., Adv. Mater. 2006, 18, 572-576.
- 140. Ma, W. L., Yang, C. Y., Gong, X., Lee, K.and Heeger, A. J., Adv. Funct. Mater. 2005, 15, 1617–1622.
- Perzon, E., Wang, X., Admassie, S., Inganas, O., Andersson, M. R., *Polymer*, 2006, 47, 4261–4268.
- 142. Iraqi, A., Crayston, J. A. and Walton, J. C., J. Mater. Chem. 1998, 8, 31-36.
- 143. Beaujuge, P. M., AMB, C. M. and Reynolds, J. R., Acc. Chem. Res. 2010, 43, 1396-1407.
- 144. Blouin, N. and Leclerc, M., Acc. Chem. Res. 2008, 41, 1110-1119.

- 145. Scherf, U. and List, E. J. W., Adv. Mater. 2002, 14, 477-487.
- List, E. J. W., Guentner, R., de Freitas, P. S., Scherf, U., Adv. Mater. 2002, 14, 374-378.
- 147. Lin W. J., Chen W. C., Wu, W. C., Niu Y. H., Jen, A. K. Y., *Macromolecules*, 2004, 37, 2335-2341.
- 148. Hou, Q., Xu, Y., Yang, W., Yuan, M., Peng, J., Cao, Y., J. Mater. Chem. 2002, 12, 2887–2892.
- Zhou, Q., Hou, Q., Zheng, L., Deng, X., Yu, G., Cao, Y., *Appl. Phys. Letters*, 2004, 84, 1653–1655.
- Slooff, L. H., Veenstra, S. C., Kroon, J. M., Moet, D. J. D., Sweelssen, J., Koetse, M. M., *Appl. Phys. Letters*, 2007, 90, 143506-1 143506-3.
- 151. Chen C. P., J. Am. Chem. Soc. 2008, 130, 12828-12833
- 152. Hou, J., J. Am. Chem. Soc. 2008, 130, 16144-16145.
- 153. Baek, N. S., Chem. Mater. 2008, 20, 5734-5736.
- 154. Lu, J., Liang, F., Drolet, N., Ding, J., Tao, Y. and Movileanu, R., Chem. Commun., 2008, 5315–5317.
- 155. Mullekom, H. A. M., Vekemans, J. A. J. M., Meijer, E. W., J. Chem. Eur. 1998, 4, 1235-1243.
- Zhou, H., Yang, L., Xiao, S., Liu, S. and You, W., *Macromolecules*, 2010, 43, 811-820.
- 157. Karikomi, M., Kitamura, C., Tanaka, S. and Yamashita, Y., J. Am. Chem. Soc. 1995, 117, 6791-6792.
- 158. Perepichka, I. I., Perepichka, I. F., Bryce, M. R. and Pålsson, L-O., Chem. Commun., 2005, 3397-3399.
- 159. Munaff, G.A., Ph.D. Thesis in Chemistry, University of Wales, Bangor UK, 1995.
- 160. Bauerle, P., Wurthner, F. and Heid, S., Angew. Chem. Int. Ed. Engl. 1990, 29, 419-420.
- 161. Zhai, L., Pilston, R. L., Zaiger, K. L., Stokes, K. K. and McCullough, R. D. Macromolecules, 2003, 36, 61-64.
- 162. Fukuri, N., Masaki, N., Kitmaura, T., Wada, Y. and Yanagida, S., J. Phys. Chem. B. 2006, **110**, 25251-25258.
- 163. Al-Dmour, H., Unpublished PhD Thesis, University of Wales Bangor. 2007, 60.
- Patra, D., Duryodhan, S., Harihara, P., Dhananjay, K., Chih-Wei, C., Hong-Cheu, L., J. Polym. Sci. A: Polym. Chem., 2010, 48, 5479-5489.
- 165. Lee, K-H., Morino, K., Sudo, A. and Endo, T., Polym. Bull. 2011, 67, 227-236
- 166. Mancilha, F. S., Brenno, A. D. N., Aline, S. L., Paulo, F. M. Jr., Frank, H. Q., Reinaldo, S. G. and Jairton, D., *Eur. J. Org. Chem.*, 2006, 4924-4933.
- 167. Yang, R., Renyu, T., Jingai, Y., Yong, Z., Jian, Y., Qiong, H., Wei, Y., Chi, Z. and Yong, C., *Macromolecules*, 2005, **38**, 244-253.
- Li, J.-C., Lee, H-Y., Lee, S-H., Zong, K., Jin, S-H. and Lee, Y-S., Synth. Metals, 2009, 159, 201–208.
- Yokoyama, A., Miyakoshi, R. and Yokozawa, T., *Macromolecules*, 2004, 37, 1169-1171.

- Iovu, M. C., Sheina, E.E., Gil, R. R. and McCullough, R. D., *Macromolecules*, 2005, 38, 8649-8656.
- 171. Xu, J. K., Wei, Z. H., Du, Y. K., Pu, S. Z., Hou, J. and Zhou, W. Q., J. Appl. Polym. Sci., 2008, 109, 1570-1576.
- 172. Amou, S., Haba, O., Shirato, K., Hayakawa, T., Ueda, M., Takeuchi, K. and Asai, M., J. Polym. Sci. Part A: polym. Chem., 1999, 37, 1943-1948.
- 173. Ishida, H., Tobita, S., Hasegawa, Y., Katoh, R., Nozaki, K., Coord. Chem. Rev. 2010, 254, 2449–2458.
- Perepichka, I. F., Perepichka, D. F., Meng, H., Wudl, F., Adv. Mater. 2005, 17, 2281-2305.
- 175. Inganas, O., Svensson, M., Zhang, F., Gadisa, A., Persson, N. K., Wang, X. and Andersson, M. R., *Appl. Phys. Letters*, 2004, **79**, 31-35.
- 176. Freeman, A.W., Marie, U. and Megan, E. C., J. Org. Chem. 2005, 70, 5014-5019
- 177. Smith, P. A. S. and Brown, B. B., J. Am. Chem. Soc., 1951, 73, 2435-2437.
- 178. Heinrich, L., Chem. Berichte. 1953, 86, 522-524.
- 179. Cadogan, J. I. G., Cameron-Wood, M., Mackie, R. K. and Searle, R. J. G., J. Chem. Soc. 1965, 4831.
- Fukuda, M. Sawada, K. and Yoshino, K., Jpn. J. Appl. Phys., 1989, 20, L1433-L1435.
- 181. Miyaura, N., Yamada, K. and Suzuki, A., Tetrah. Letters, 1979, 20, 3437-3440
- 182. Bernius, M. T., Inbasekaran, M., O'Brien, J. and Wu, W., Adv. Mater., 2000, 12, 1737-1749.
- 183. Matos K. and Soderquist, J. A., J. Org. Chem., 1998, 63, 461-470.
- 184. Duan, C., Chen, K-S., Huang, F., Yip, H-L., Liu, S., Zhang, J., Alex, K.-Y. J. and Cao, Y., Chem. Mater. 2010, 22, 6444-6452.
- 185. Biniek, L., Fall, S., Chochos, C. L., Anokhin, D. V., Ivanov, D. A., Leclerc, N., Leveque, P. and Heiser, T., *Macromolecules*, 2010, **43**, 9779-9786.
- 186. Kim, J., Park, S. H., Cho, S., Jin, Y., Kim, J. Kim, I., Lee, J. S., Kim, J. H., Woo, H. Y., Lee, K. and Suh, H., *Polymer*, 2010, **51**, 390-396.
- 187. Li, W., Qin, R., Zhou, Y., Andersson, M., Li, F., Zhang, C., Li, B., Liu, Z., Bo, Z. and Zhang, F., *Polymer*, 2010, **51**, 3031-3038.
- 188. Aïch, R. B., Blouin, N., Bouchard, A. and Leclerc, M., Chem. Mater., 2009, 21, 751-757.
- 189. Zhang, L., He, C., Chen, J., Yuan, P., Huang, L., Zhang, C., Cai, W., Liu, Z. and Cao, Y., *Macromolecules*, 2010, 43, 9771-9778.
- 190. Hou, J., Park, M-H., Zhang S., Yao, Y., Chen, L.M., Li, J-H., and Yang, Y., Macromolecules, 2008, 41, 6012-6018.
- 191. Kostyanovshy, V. A., Susarova, D. K., Peregudov, A. S. and Pavel, T. A., *Thin Solid Films*, 2011, **519**, 4119-4122.
- 192. Akoudad, S. and Roncali, J., Chem. Commun., 1998, 2081-2082.
- Atwani, O., Baristiran, C., Erden, A. and Sonmez, G., Synth. Metals, 2008, 158, 83-89.

- 194. Shi, W., Fan, S., Huang, F., Yang, W., Liu, R. and Cao, Y., J. Mater. Chem., 2006, 16, 2387-2394.
- 195. Jiang, K-J., Manseki, K., Yu, Y-H., Masaki, N., Suzuki, K., Song, Y-L. and Yanagida, S., Adv. Funct. Mater., 2009, 19, 2481-2485.
- 196. Badrou, R. A., Zou, Y., Leclerc, M. and Tao, Y., Organic Elect., 2010, 11, 1053-1058.

Appendix:



A1: Gel permeation chromatography (GPC) of compound [42].



A2: Gel permeation chromatography (GPC) of compound [62].



A3: Gel permeation chromatography (GPC) of compound [63].



A4: Gel permeation chromatography (GPC) of compound [64].



A5: Gel permeation chromatography (GPC) of compound [65].



B1: Thermogravimetric analysis spectrum of compound [62]



B2: Thermogravimetric analysis spectrum of compound [63]



B3: Thermogravimetric analysis spectrum of compound [64]



B4: Thermogravimetric analysis spectrum of compound [65]



C1: Plot of integrated fluorescence intensity vs. absorbance of compound [62].

C2: Plot of integrated fluorescence intensity vs. absorbance of compound [63].





C3: Plot of integrated fluorescence intensity vs. absorbance of compound [64].

C4: Plot of integrated fluorescence intensity vs. absorbance of compound [65].

