DESIGN AND SYNTHESIS OF CONJUGATED POLYMERS FOR ORGANIC PHOTOVOLTAICS: TUNING THE CONJUGATED BACKBONE AND THE SUBSTITUENTS

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ABSTRACT

Qianqian Zhang: Design and Synthesis of Conjugated Polymers for Organic Photovoltaics: Tuning the Conjugated Backbone and the Substituents (Under the direction of Wei You)

Developing new conjugated polymer materials has been one of the most important driving forces for improving the performance of organic photovoltaics. This dissertation has been focused on structural design of polymers, including fine-tuning the backbone and the substituents of the polymers in order to adjust specific properties and improve the efficiency of organic photovoltaics. This dissertation details new methodologies to prepare the designed polymers and explores the structure-property relationship. We first developed regio-regular and regio-random terpolymers based on two parent copolymers with complementary absorption range. We found that adequate aggregation of these terpolymers is necessary for high performance photovoltaics. We then incorporated fluorine substituents into π linker thiophene units between the donor and the acceptor units and succeeded in controlling the positions and amount of fluorine substituents on the polymer backbone. The efficiency of the photovoltaics was remarkably improved by the fluorinated thiophene units. More importantly, we demonstrated the beneficial effects of fluorinated thiophene on improving the hole mobility and the importance of high hole mobility in improving fill factors of photovoltaics using eight structurally related polymers. Finally, in order to lower the bandgap of the polymers, we introduced strong electron withdrawing cyano group to the acceptor units. We systematically study the effect of cyano substitution on the properties of the polymers and the polymer solar cells by controlling the amount of cyano substituents. With single cyano substitution, a high device efficiency of ~ 8.6% was achieved for the monoCNTAZ polymer. All
the works highlight the importance of optimizing the polymer structure to reach high solar cell performance.
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LIST OF ABBREVIATIONS AND SYMBOLS

M(toe)  million tonnes of oil equivalent

OPV  organic photovoltaics

PSC  polymer solar cell

BHJ  bulk heterojunction

PCE  power conversion efficiency

$V_{oc}$  open Circuit voltage

$J_{sc}$  short Circuit current

$FF$  fill factor

EQE  external quantum efficiency

IQE  internal quantum efficiency

PC$_{61}$BM  phenyl-C61-butyric acid methyl ester

ITO  indium doped tin oxide

P3HT  poly(3-hexylthiophene)

BnDT  benzo[1,2-b:4,5-b']dithiophene

BT  benzo[c][1,2,5]thiadiazole

TAZ  2-methyl-2H-benzo[d][1,2,3]triazole
TT thieno[3,4-b]thiophene

DTBT 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole

HTAZ 2-alkyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole

RaBDH poly(benzodithiophene-dithienylbenzothiadiazole)-co(benzodithiophene-enedithenylbenzotriazole)

ReBDH poly(benzodithiophene-dithienylbenzothiadiazole-alt-benzodithiophene-enedithenylbenzotriazole)

T2B 1,4-di(thiophen-2-yl)benzene

PBnDT-TAZ poly(benzodithiophene-dithienyl-benzotriazole)

FTAZ 5,6-difluoro-2-alkyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole

3’-FT-HTAZ 4,7-bis(3-fluorothiophen-2-yl)-2-alkyl-2H-benzo[d][1,2,3]triazole

4’-FT-HTAZ 4,7-bis(4-fluorothiophen-2-yl)-2-alkyl-2H-benzo[d][1,2,3]triazole

3’-FT-FTAZ 5,6-difluoro-4,7-bis(3-fluorothiophen-2-yl)-2-alkyl-2H-benzo[d][1,2,3]triazole

4’-FT-FTAZ 5,6-difluoro-4,7-bis(4-fluorothiophen-2-yl)-2-alkyl-2H-benzo[d][1,2,3]triazole

monoCNTAZ 2-alkyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-5-carbonitrile

diCNTAZ 2-alkyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-5,6-dicarbonitrile

PyCNTAZ 2-alkyl-4,7-di(thiophen-2-yl)-2H-[1,2,3]triazolo[4,5-c]pyridine
<table>
<thead>
<tr>
<th><strong>PEDOT:PSS</strong></th>
<th>poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CuSCN</strong></td>
<td>copper(I) thiocyanate</td>
</tr>
<tr>
<td><strong>NBS</strong></td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td><strong>NFSI</strong></td>
<td>N-Fluorobenzenesulfonimide</td>
</tr>
<tr>
<td><strong>TBAF</strong></td>
<td>tetra-$n$-butylammonium fluoride</td>
</tr>
<tr>
<td><strong>DIAD</strong></td>
<td>diisopropyl azodicarboxylate</td>
</tr>
<tr>
<td><strong>CN</strong></td>
<td>cyano</td>
</tr>
<tr>
<td><strong>Pd$_2$dba$_3$•CHCl$_3$</strong></td>
<td>tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct</td>
</tr>
<tr>
<td><strong>Pd(PPh$_3$)$_2$Cl$_2$</strong></td>
<td>bis(triphenylphosphone)palladium(II) dichloride</td>
</tr>
<tr>
<td><strong>P(o-tol)$_3$</strong></td>
<td>tri(o-tolyl)phosphone</td>
</tr>
<tr>
<td><strong>CB</strong></td>
<td>chlorobenzene</td>
</tr>
<tr>
<td><strong>o-DCB</strong></td>
<td>ortho-dichlorobenzene</td>
</tr>
<tr>
<td><strong>TCB</strong></td>
<td>1,2,4-trichlorobenzene</td>
</tr>
<tr>
<td><strong>THF</strong></td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td><strong>$n$-BuLi</strong></td>
<td>$n$-butyllithium</td>
</tr>
<tr>
<td><strong>LDA</strong></td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td><strong>$M_n$</strong></td>
<td>number average molecular weight</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear overhauser effect spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>GIWAXS</td>
<td>grazing incidence wide angle X-ray scattering</td>
</tr>
<tr>
<td>RSoXS</td>
<td>resonant soft X-ray scattering</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION TO ORGANIC PHOTOVOLTAICS

1.1 Background of Organic Photovoltaics

Massive amount of energy is consumed every day, and the global annual energy consumption is 13,700 million tonnes of oil equivalent (Mtoe) in 2014. Among all the energy sources, oil, gas, and coal are still the leading energy sources, accounting for ~ 80% of the total energy consumption. However, the sustainability of these fossil fuels based energy is a critical concern, and burning these fossil fuels has caused heavy pollution and global warming. Thus, development of renewable energy is imperative. As a renewable and clean energy resource, solar energy has immense potential and offers an excellent solution to the problems caused by burning fossil fuels.

Currently, the major commercial solar panels are based on the crystalline silicon nowadays. Silicon-based solar cells has many drawbacks, for example, the harsh conditions and the high cost required to produce crystalline silicon, and the brittleness of the silicon materials. Compared to inorganic photovoltaics, organic photovoltaics benefit from the ability to easily tune specific properties of materials and low-cost solution based processing. Among the organic photovoltaics, polymer solar cells (PSCs) utilize soft and flexible polymer materials as one of the major components. Due to the unique properties of polymer materials, large area of flexible PSC devices can be printed by roll to roll fabrication.
We have seen incredible growth in the field of PSCs in the past fifteen years; the efficiency of a single junction PSC has recently reached ~ 13%. Enormous efforts have been devoted to developing PSCs, including optimizing the structure of PSC devices, investigating the morphology of the bulk heterojunction blends and exploring the physics of working PSCs. Along with these efforts, the design of polymer structures has always been one of the most important driving forces in enhancing the efficiency of PSCs. This chapter will provide a brief introduction to the device structure of PSCs, the working mechanism of PSCs and the general rules of polymer design.

1.2 Structure and Working Mechanism of PSCs

![Figure 1.1. The structure of a conventional configuration PSC. (Reprinted from Reference 8 with permission. Copyright Nature Publishing Group)](image)

A typical PSC device in conventional configuration is composed of the active layer sandwiched between two electrodes (Figure 1.1). The active layer is primarily responsible for absorbing and transferring solar energy into electricity. It is a bulk heterojunction blend of a donor material, e.g. polymers in PSCs, and an acceptor material, mostly fullerene derivatives. Recently, various non-fullerene acceptor materials have been developed to address the issue of low absorption of
fullerene derivatives and improve the efficiency of polymer solar cells. However, such devices are beyond the scope of this dissertation; we will focus on PSCs with fullerene derivatives (PC61BM as an example) as acceptor materials in this dissertation.

Figure 1.2. Illustration of the working processing of a PSC device.

As is depicted in Figure 1.2, the working process of an exemplary polymer:PC61BM based PSC can be described in several steps: exciton generation, charge generation, charge transport and charge extraction.

**Exciton Generation** For a PSC with PC61BM as the electron acceptor material, the polymer acts as the major absorber of sunlight since PC61BM has limited absorption. When a photon is
absorbed by the polymer, an electron is excited from the valence band onto the conduction band of the polymers. Due to the low dielectric constant of polymer semiconducting materials, the excited electron is still bound to the hole, and the thermal energy at room temperature is not sufficient to overcome the bonding energy of the hole-electron pair. Thus, it is an exciton - instead of free charge carriers - that forms after excitation in a PSC. The exciton must diffuse to the interface between the polymer and the PC$_{61}$BM and split into free charge carriers, ideally before it relaxes back to the ground state. The exciton diffusion length is \( \sim 10 \) nm, thus small domains of polymers (e.g., 15 – 30 nm) are desired for efficient charge generation.

**Charge Generation** When the exciton reaches the interface of the polymer and PC$_{61}$BM, the energy difference in the lowest unoccupied molecular orbital (LUMO) levels of the polymer and PC$_{61}$BM drives the splitting of the exciton: the electron can transfer to PC$_{61}$BM, leaving the hole left on the polymer. After the exciton splits, the electron and the hole are still loosely bounded, forming a charge transfer (CT) state. The electron and hole pair may recombine and relax back to the ground state, which is called the geminate recombination. Nevertheless, the majority of the CT state would dissociate into free charge carriers.

**Charge Transport** The free charge carriers then diffuse to the two electrodes with electrons being collected at the cathode and holes collected at the anode. Please note that not all the free charge carriers will reach the electrodes; some will recombine via non-geminate recombination (primarily bimolecular recombination). For bimolecular recombination, the recombination rate depends quadratically on the charge carrier density and the charge carrier density is inversely related to the charge carrier mobility; therefore, high charge carrier mobility is important to suppress the non-geminate recombination.
**Charge Collection** Upon reaching the electrodes, the charge carriers get extracted out of the devices. For a conventional PSC device (in contrast to an inverted PSC device), indium doped tin oxide (ITO) is the most widely used anode, and a low work function metal, such as aluminum (Al), is usually used as the cathode. Between the active layer and the electrodes, there are usually charge transporting layers to improve the interfacial properties and facilitate charge transport: a hole transporting layer such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) atop the anode, and an electron transporting layer such as lithium fluoride (LiF) underneath the cathode. Therefore, energy level matching between the charge transporting layers and the active layer is crucial to maximize the device efficiency.

### 1.3 Key Device Parameters of PSCs

![Figure 1.3. A typical J-V curve of a PSC.](image)

The efficiency of polymer solar cells is determined by three parameters: open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$) and fill factor ($FF$). A typical $J$-$V$ curve of PSCs is shown in Figure 1.3.
The power conversion efficiency (PCE) of polymer solar cells is the product of the three parameters over the input power (P_input), as is shown in the following equation.

\[
PCE = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}
\]

*Open Circuit Voltage (V_{oc})* \(V_{oc}\) is the voltage at which the photocurrent of the solar cells equals zero, and it is the largest voltage that can be achieved by a solar cell. It is closely related to the energy difference between the highest occupied molecular orbital (HOMO) level of the polymers and the lowest unoccupied molecular orbital (LUMO) level of PC_{61}BM. Though it is argued that the \(V_{oc}\) is most directly determined by the charge transfer state (CT), instead of the difference between the energy levels, and is noticeably affected by the non-geminate recombination within the device,\(^9\) it is still an empirically useful strategy to improve the \(V_{oc}\) by decreasing the HOMO level of the polymer.

*Short Circuit Current (J_{sc})* As indicated by its name, \(J_{sc}\) is the current at short circuit condition, or when voltage equals zero. It is the largest current density that can be achieved by a given solar cell. The most important factor that affects the \(J_{sc}\) values is the absorption ability of the polymer. Photons with energy lower than the bandgap of the polymer can’t be absorbed by the polymer, thus, polymers with smaller bandgaps can absorb the longer wavelength portion of the solar spectrum and improve the \(J_{sc}\) of the device. However, absorption of sunlight is only the first step in power generation. Efficiency also heavily depends on how effectively the device can convert the incident photons into extracted charges, quantified by external quantum efficiency (EQE). Various recombination processes, such as geminate recombination, non-geminate recombination and trap-assisted recombination, can cause loss of the charge carriers and consequently decrease \(J_{sc}\).
**Fill Factor (FF)** Fill factor (FF) is defined as the ratio of the maximum power output (the area of the green square in Figure 1.3) over the product of the $J_{sc}$ and $V_{oc}$ (the area of the square between the axis and the blue lines in Figure 1.3). It indicates how much of the highest current and voltage can be simultaneously achieved by a solar cell device. Among all the three parameters, $FF$ is the least understood, and it is difficult to predict how changes in polymer chemical structures may influence $FF$. The processes of charge generation, charge recombination, and charge extraction all impact the $FF$. Nevertheless, recent studies proposed that the competition between recombination and extraction of free charge carriers affect the $FF$ of the PSCs.\(^{10}\)

1.4 Design Rules of Polymer Structures for PSCs

![Figure 1.4](image_url)

**Figure 1.4.** Illustration of the components of a conjugated polymer. (Reprinted from Reference 6 with permission. Copyright 2012 American Chemical Society)

As depicted in Figure 1.4, a conjugated polymer is composed of backbone, side chains, and substituents. The polymer backbone primarily defines the basic properties of the polymer, such as its energy levels and bandgaps, and charge carriers are only transported either along the conjugated backbone or through the $\pi-\pi$ stacking of the backbones. The design of polymer backbones mainly follows the “donor-acceptor” (D-A) rule.\(^{11, 12}\) A D-A copolymer is composed of alternating electron-rich donor unit and electron-deficient acceptor unit. The HOMO energy level of the D-A copolymers is mainly determined by the donor unit while the LUMO energy level of the polymers is mainly determined by the acceptor unit. Thus, the energy levels and bandgaps of the polymers
can be readily adjusted through tuning the electron donating ability of the donor units and the electron withdrawing ability of the acceptor units. Developing novel donor and acceptor structural units was the initial focus of material design, and an overwhelming amount of D-A copolymers featuring a variety of donor and acceptor units have been synthesized and explored.\textsuperscript{6} As was discussed before, $V_{oc}$ is closely related to the energy difference between the HOMO energy level of the polymer and the LUMO energy level of PC\textsubscript{61}BM, and $J_{sc}$ is related to the absorption properties of the polymers. Given both of these stipulations, an “ideal” polymer to achieve the highest $PCE$ would have a bandgap of 1.5 eV and LUMO level of -3.9 eV.\textsuperscript{13}

Even though they do not usually contribute directly to the absorption of photons or charge transport, the side chains have noticeable effects on the photovoltaic performance. The side chains of the conjugated polymers strongly enhance the solubility and the processability of the polymers, noticeably influence the interactions and aggregation of polymer chains and the interactions of polymers with PC\textsubscript{61}BM.\textsuperscript{14-16} The elemental composition, chain length, chain shape (straight or branched), the positions on the conjugated backbones and even the branching point of the side chains must be carefully engineered in order to optimize the device efficiency of a given conjugated backbone.

Incorporating substituents into the polymer backbone is also an effective approach to tune the physical properties of the polymer and its performance in photovoltaics. For example, adding the strong electron withdrawing cyano unit can decrease the HOMO energy level and the bandgap of the polymer.\textsuperscript{17} Among all the substituents, the addition of fluorine substituent can dramatically improve the photovoltaic performance of various polymers.\textsuperscript{18-20} Currently, almost all the high performing polymers today contain fluorine substituents on the polymers. Since \textbf{Chapter 3}, \textbf{Chapter 4} and \textbf{Chapter 5} of this dissertation will focus on this interesting “fluorine” effect, we
will give a brief introduction to the effect of fluorine substituents on the properties of the conjugated polymers for solar cells.

1.5 Effect of Fluorine Substituents on the Properties of Conjugated Polymers

Fluorine substitution on polymer backbones or side chains is widely utilized to tune the properties of polymers and PSC devices, such as energy levels, backbone conformation, polymer aggregation and interactions of polymers with PC$_{61}$BM, as will be illustrated below.$^{6,7,19}$

Fluorine has the largest electronegativity (4.0 on Pauling scale), so fluorine substitution on the conjugated polymer backbones can effectively lower the HOMO level of the polymers, which usually leads to improved $V_{oc}$. In most cases, the LUMO levels are simultaneously deepened with fluorine substituents, and the bandgap and the absorption properties of the polymers are not dramatically changed.

Fluorine substituents can improve the planarity of polymer backbones and the aggregation of polymers. Fluorine substitution on the polymer backbones can introduce various types non-bonding interactions, such as C-F•••H, C-F•••S, and C-F•••π. The intramolecular interactions may lead to a more stable planar conformation of polymer backbone by increasing the energy barrier for rotation. The intermolecular interactions in addition to the enhanced planarity also often strengthen the polymer aggregation, which is important for the formation of charge transport path and improves the $J_{sc}$ and $FF$.

Fluorine substituents may also affect the morphology of the active layers. The performance of polymer solar cells is strongly dependent on the morphology of the active layers. Incorporating fluorine substituents may influence the crystallinity of the polymer, the domain size, domain purity and the relative stacking orientation of polymers at the polymers:acceptor interface. The
optimization of morphology with fluorine substituents has been shown to contribute to the improvement of efficiency of photovoltaic devices in many studies. The effect of fluorine substitution on morphology varies from case to case, depending on the systems studied, making it difficult to predict the effect of the fluorine substitution on the morphology of the active layer.

For D-A copolymers, the position of the fluorine substituent is important to the properties of the polymers; changing the fluorination position may dramatically change the solar cell performance. Several widely adopted fluorinated units with various fluorination positions are shown in Chart 1.1.

Chart 1.1. Examples of fluorinated unit highlighting the position of fluorine substituent.
Given the electron withdrawing nature of fluorine, fluorine substituents are mostly placed on the electron deficient acceptor units. The most popular include benzothiadiazole (BT), benzotriazole (TAZ), quinoxaline, thienothophene (TT) and isoindigo. There have been numerous studies about the effect of the fluorine substitution on these acceptor units, and many polymers based on these fluorinated acceptors have been published with high efficiency. The PCE of the PSCs devices is usually noticeably improved with fluorine substituent on the acceptor units.
for a variety of system-dependent reasons. For example, for polymers based on benzo[1,2-b:4,5-b’]-dithiophene (BnDT) and BT unit, it was found that with fluorine substituents, the HOMO level of the polymers was deepened, which improved the $V_{oc}$ of the PSC. Additionally, the change in dipole moment from ground state to excited state was increased, the “face-on” orientation of polymers was enhanced, and the domain purity was also improved, which suppressed the recombination and improved the $J_{sc}$ and $FF$, thus the $PCE$ was improved from 4% to 7%.\textsuperscript{21} However, for polymers based on BnDT and TAZ unit, with fluorine substituents incorporated on TAZ unit, in addition to the slight increase of $V_{oc}$, the enhanced hole mobility helped to suppress the non-geminate recombination and enhance the charge extraction efficiency, thus, the other two device parameters ($J_{sc}$ and $FF$), especially the $FF$, are significantly improved.\textsuperscript{22,26}

In contrast to the popularity of fluorine substitution on the acceptor units, fluorine substitution on the donor units hasn’t received as much attention. Benzodithiophene (BnDT) is one of the most used donor unit, but fluorine substitution on BnDT was found to significantly reduce the photochemical stability of the polymers with fluorinated BnDT and TT units, making them vulnerable to the attack of singlet oxygen.\textsuperscript{27} Besides, fluorine substitution on the electron rich BnDT unit caused a decrease of the change in dipole moment from ground state to excited state, which decreased the partial charge separation character of the excitons.\textsuperscript{28} Even though fluorine substitution on BnDT unit is detrimental to the polymers and the photovoltaic device performance, this adverse effect of fluorine substitution on BnDT unit can be circumvented by placing the fluorine substituents on the conjugated side chains of BnDT unit. There have been numerous studies showing that the fluorination on the conjugated side chains (such as thienyl and phenyl side chains) connected to the BnDT improves the $V_{oc}$ and $FF$.\textsuperscript{29,30} For example, Zhang \textit{et al.} relocated the fluorine substituents to the thienyl side chains connected to the BDT unit and
significantly improved the $V_{oc}$ values of the OPV devices without affecting the $J_{sc}$ and $FF$ values.\textsuperscript{31} The donor unit 3,3'-difluoro-2,2'-bithiophene\textsuperscript{32} has also been used to synthesize a lot of high-performance polymers.\textsuperscript{33, 34} With fluorination of the 3,3’ positions of 2,2’-bithiophene, the dihedral angle between the two thienyl rings is noticeably reduced, and the energy barrier for the rotation of the thienyl rings is also increased, leading to a more planar and stabilized backbone conformation.\textsuperscript{35} The enhanced planarity together with various nonbonding interactions introduced by the fluorine atoms significantly increases the aggregation of polymers, which improves the absorption properties of the polymers in some cases.\textsuperscript{36} The enhanced planarity of polymer backbones also improves the $\pi-\pi$ interactions and forms good charge transport pathways in PSC devices, which can improve the hole mobilities, $J_{sc}$ and $FF$ of PSCs as well.

Besides fluorine position, the amount of fluorine substituent on the polymer backbone is also of critical importance and can be controlled through two methods. The first method is to control the number of fluorine substituents on the monomers by selecting starting chemicals with different amount of fluorine substituent. For example, for BT,\textsuperscript{37} TAZ,\textsuperscript{38} quinoxaline,\textsuperscript{39} isoindigo units,\textsuperscript{25} the number of fluorine substituent was adjusted from 0 to 1 and then to 2 on the monomers to optimize the fluorine substituent amount on the polymers. The second method is preparing polymers composed of both the fluorinated and the non-fluorinated monomers while controlling the feed ratio of the two monomers.\textsuperscript{26, 40} However, the sequence of the two monomers or the regioregularity of the polymers is difficult to control given that there is usually no significant difference in the reactivity of the two monomers. The optimized amount of fluorine substituent is highly dependent on the polymer structure as a slight change in chemical structure and device fabrication conditions can remarkably affect the performance of PSC devices.\textsuperscript{41, 42} “Over fluorination” needs to be taken into consideration when fluorinated polymer structure is designed: too many fluorine substituents
on the polymer backbones can dramatically reduce the solubility and the processability of the polymer, which can adversely affect the morphology of bulk heterojunction solar cells by forming large polymer domains in the active layers.\textsuperscript{33}
CHAPTER 2

COMPARATIVE STUDY OF THE PHOTOVOLTAIC PROPERTIES OF THE PHYSICAL BLENDING OF TWO DONOR-ACCEPTOR POLYMERS WITH THE CHEMICAL BLENDING OF THE RESPECTIVE MOIETIES

2.1 Introduction

In a typical bulk heterojunction (BHJ) polymer solar cell (PSC) with fullerene derivatives as electron acceptors, the conjugated polymer functions as the major light absorber while fullerene derivatives absorb very little sunlight. Unfortunately, the inherently narrow absorption range of typical conjugated polymers, usually with a full width at half maximum on the order of 200 nm, only covers a relatively small fraction of the solar spectrum. This significantly limits the light absorption and thus the short circuit current ($J_{sc}$) of these PSCs. The “engineering” approach to addressing this issue of light absorption is to stack several solar cells with each of them capturing a different region of the solar spectrum; these cells are then connected in a series or parallel circuit (i.e., tandem cells). Though such tandem cells can maximize the light absorption and utilize it well (e.g., overcoming the thermalization loss) with much higher projected efficiency, the complex device configuration of these tandem cells has posed serious challenges in terms of fabrication and optimization. On the other hand, within the realm of single junction BHJ solar cells, various strategies have been explored to improve the light absorption and to (hopefully) further improve the efficiency of PSCs. Explored strategies include, (a) adopting more light-absorbing
C\textsubscript{70} derivatives\textsuperscript{47} (b) using multiple polymers covering different absorption ranges in the same active layer as a physical blend (e.g., ternary blend systems)\textsuperscript{8,48-50} (c) covalently integrating these conjugated polymers together (e.g., chemically blending these constituting monomers into a random copolymer)\textsuperscript{51} replacing the fullerenes with strongly absorbing acceptors\textsuperscript{52} and compensating weak absorption by using thick layers\textsuperscript{22,34} Besides replacing C\textsubscript{60} derivatives with the C\textsubscript{70} derivatives, using non-fullerene acceptors, which usually has significantly enhanced absorption compared to fullerene acceptors, has been shown successful in extending the overall absorption range and pushing up the efficiency of the PSC devices.

While the strategy of replacing C\textsubscript{60} derivatives (e.g., [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PC\textsubscript{61}BM)) with light absorbing C\textsubscript{70} counterparts (e.g., [6,6]-phenyl-C\textsubscript{71}-butyric acid methyl ester (PC\textsubscript{71}BM)) has been quite successful (in fact, almost all reported record-high efficiencies were obtained with PC\textsubscript{71}BM or non-fullerene acceptors), other strategies have only seen success in some cases. For example, ternary (or multiple) blend systems, where two (or more) polymers or fullerene derivatives are physically mixed in a single layer, have gained significant momentum, achieving efficiencies over 8\%\textsuperscript{8,53-55} However, “non-working” ternary blends were also reported together with working ternary blends\textsuperscript{53,56,57} highlighting the complex nature of these systems. It appears that matching the morphology or texture (e.g., both polymers being “face-on” with the same processing solvent) is an important factor\textsuperscript{53} On the other hand, terpolymers, where three different units from two parent donor:acceptor polymers are strategically combined to provide chemical blending and thus integrate the electronic and absorption features of both parent polymers, can potentially circumvent the morphology compatibility requirements of a ternary physical blend. This is because the active layer only contains two components (i.e., a terpolymer and a fullerene derivative) as in a typical binary BHJ solar cell.
Indeed, a number of terpolymers have been developed in the past few years, typically through a random copolymerization of several different electron-donating units (“donor”, D) and electron-deficient units (“acceptor”, A). However, the nature of such random copolymerization implies that the structure and composition of these random terpolymers are not well defined compared to the prevailing one donor-one acceptor copolymers. One approach to address this “randomness” is to construct a macro-monomer that places the constituent donors/acceptors in the desired pattern, before it is subjected to the final polymerization (with another donor or acceptor). Though synthetically more demanding, such a regular terpolymer has the potential to reach higher efficiency than the corresponding random terpolymer. The well-defined conjugated structure of the regular terpolymer would more likely lead to favorable device morphology compared to the unregulated structure of the random copolymer. For example, the likely existence of oligomeric segments with a different chemical and electronic/optical nature in a random copolymer could lead to poor mixing with the fullerene derivatives as well as poor molecular packing and orientation in the BHJ active layer. In principle, any two p-type conjugated polymers can form a ternary blend (i.e., physical blend) with an n-type fullerene derivative. Alternatively, the constituent units (i.e., structural moieties) of two such polymers – if they have a common structural moiety – can also be organized into a random terpolymer or a regular terpolymer, both of which can be considered chemical blends. As briefly discussed above, all three approaches have been successfully implemented with different systems; however, for any two given conjugated polymers, it is essentially impossible to predict which approach would offer the highest device efficiency unless one investigates all three approaches in a comparative manner. Unfortunately, such studies are very rare, and the results are mixed. In one study, Sun et al. reported that an alternating D–A1–D–A2 copolymer containing two acceptors (A1 and A2) in the
repeat unit (i.e., a regular terpolymer) showed a broad absorption and much higher device efficiency (5.03%) than that of the corresponding physical blend (2.40%). In another study, Khlyabich et al. obtained similar efficiencies for both the ternary blend and the random terpolymer for another pair of parent polymers. More such comparative studies are therefore needed to further explore the application and limitations of all three approaches (i.e., ternary blend, random copolymer and regular terpolymer).

We designed this comparative study by starting with a successful ternary blend we reported earlier, poly(benzodithiophene-dithienylbenzotriazole) (PBN-DT-HTAZ) and poly(benzodithiophene-dithienylbenzothiadiazole) (PBN-DT-DTBT). These two polymers share a common donor (i.e., “D” being benzodithiophene), but differ in the acceptors (i.e., “A1” being HTAZ, and “A2” being DTBT). For this comparative study, two new terpolymers were synthesized: a random copolymer poly(BnDT-HTAZ/DTBT) and a regular, alternating terpolymer poly(BnDT-HTAZ-alt-BnDT-DTBT) (Chart 2.1). The three different approaches to organizing these constituent units (ternary physical blend, random terpolymer, and regular terpolymer) give different absorption behavior, though all show a broadened absorption. However, while the ternary blend (i.e., PBN-DT-DTBT:PBN-DT-HTAZ:PC_{61}BM) shows a higher energy conversion efficiency (4.1%) than either parent binary blend (PBN-DT-DTBT:PC_{61}BM, or PBN-DT-HTAZ:PC_{61}BM), as previously reported, the two terpolymer based solar cells exhibit lower efficiency at similar active layer thicknesses (~ 110 nm). This is due to noticeably lower short circuit currents ($J_{sc}$) than that of the ternary blend device. In fact, the $J_{sc}$ of the regular alternating terpolymer device is the lowest among all devices tested; we ascribe this to a decrease in absorbance efficiency of the active layer due to reduced aggregation of the terpolymer, less than optimal morphology of the active layer, and likely electronic differences of the terpolymer compared to the parent polymers. Our
results indicate that while the ternary blend is an effective approach to extend the absorption with improved device efficiency in our series of blends, the regular terpolymer is, rather surprisingly, not. Together with previous reports, our comparative study highlights the complexity inherent in the design of novel polymers for higher efficiency solar cells.

Chart 2.1. Illustration of a physical blend, random terpolymer and regular terpolymer from two parent D-A copolymers (top) and the chemical structure of the polymers.

2.2 Design and Synthesis

The chemical structures and synthesis of all four polymers used in this study are presented in Chart 2.1. For clarity and simplicity, we will use BD, BH, Ra-BDH, and Re-BDH to represent PBnDT-DTBT, PBnDT-HTAZ, the random terpolymer (i.e., poly(BnDT-HTAZ/DTBT)), and the
regular terpolymer (i.e., poly(BnDT-HTAZ-alt-BnDT-DTBT)). Thus, the ternary blend will be referred to as BD:BH. Monomers D,\textsuperscript{60} A\textsubscript{1}\textsuperscript{22} and A\textsubscript{2}\textsuperscript{21} were readily prepared according to previous reports and were then employed to create three polymers (BH, BD, and Ra-BDH in Scheme 2.1).

We used 1:1 feed ratio of A1:A2 in the synthesis of Ra-BDH for this comparative study. The actual ratio of A1:A2 in Ra-BDH was well controlled to 1:1, as was confirmed by the high temperature NMR and elemental analysis (Table 2.1).

![Scheme 2.1. Synthesis of four polymers used in this study.](image)

However, the synthesis of the regular, alternating polymer (i.e., Re-BDH in Scheme 2.1) was only made possible after extensive exploration and optimization of reaction conditions. The key to synthesizing the Re-BDH was the preparation of the D-A2-D structure in Scheme 2.1. First, monostannylated BnDT (Compound 2.2) was prepared by treating BnDT (Compound 2.1) with 1 eq \textit{n}-BuLi (Scheme 2.2), and the crude product (without further purification) was directly subjected to the Stille coupling with dibrominated monomer A2 to afford the pre-monomer (Compound 2.3). The final step in synthesizing the polymerizable monomer, D-A2-D, was the stannylation of pre-monomer (Compound 2.3) assisted by a strong base. Interestingly, when \textit{n}-
BuLi was employed, none of the desired product was obtained. Furthermore, treating pre-monomer (Compound 2.3) with a stoichiometric amount of LDA (or slight excess) did not lead to the desired monomer, either. In fact, we discovered that 20 eq. LDA (vs. Compound 2.3) at low temperature was required to successfully convert the pre-monomer (Compound 2.3) to the polymerizable monomer D-A2-D. Less than 20 eq. LDA gave a significant amount of monostannylaed monomer, which was difficult to separate from the di-stannylated product. Finally, the monomer D-A2-D was combined with monomer A1 via the standard microwave Stille polymerization to create the regular terpolymer (i.e., Re-BDH in Scheme 2.1).

<table>
<thead>
<tr>
<th>polymers</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Cal</td>
<td>Exp</td>
<td>Cal</td>
<td>Exp</td>
</tr>
<tr>
<td>BD</td>
<td>73.55</td>
<td>74.02</td>
<td>8.98</td>
<td>8.90</td>
</tr>
<tr>
<td>BH</td>
<td>74.12</td>
<td>74.51</td>
<td>8.93</td>
<td>8.84</td>
</tr>
<tr>
<td>Ra-BDH</td>
<td>73.90</td>
<td>74.55</td>
<td>8.87</td>
<td>9.01</td>
</tr>
<tr>
<td>Re-BDH</td>
<td>73.90</td>
<td>74.28</td>
<td>8.87</td>
<td>8.90</td>
</tr>
</tbody>
</table>

Scheme 2.2. Synthesis of monomer D-A2-D.
The number averaged molecular weights ($M_n$) of BD, BH, Ra-BDH, and Re-BDH were determined to be 54, 80, 66 and 39 kg/mol, with corresponding dispersity ($D$) of 2.1, 1.9, 2.5, and 3.5, respectively (Table 2.2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kg/mol)</th>
<th>Dispersity ($D$)</th>
<th>$\lambda_{\text{max}}^\text{film}$ (nm)</th>
<th>$\lambda_{\text{max}}^\text{sol}$ (nm)</th>
<th>$E_{\text{g, opt}}$ (eV)$^a$</th>
<th>$E_{\text{HOMO}}$ (eV)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>54</td>
<td>2.1</td>
<td>702</td>
<td>563</td>
<td>1.65</td>
<td>−5.28</td>
</tr>
<tr>
<td>BH</td>
<td>80</td>
<td>1.9</td>
<td>582</td>
<td>573</td>
<td>1.96</td>
<td>−5.30</td>
</tr>
<tr>
<td>Ra-BDH</td>
<td>66</td>
<td>2.5</td>
<td>579</td>
<td>561</td>
<td>1.70</td>
<td>−5.39</td>
</tr>
<tr>
<td>Re-BDH</td>
<td>39</td>
<td>3.5</td>
<td>581</td>
<td>536</td>
<td>1.76</td>
<td>−5.29</td>
</tr>
</tbody>
</table>

$^a$ calculated from onset of UV-Vis absorption spectra of polymer films; $^b$ measured by cyclic voltammetry.

2.3 Optical and Electrochemical Properties

![Figure 2.1. UV-Vis absorption spectra of (a) four polymers in o-DCB solution and (b) films (including the ternary blend) spun cast from o-DCB solution.](image)

The UV-Vis absorption spectra of the four polymers in solution (ortho-dichlorobenzene, oDCB, was used as the solvent), and as thin films are shown in Figure 2.2a and 2.2b, respectively. Figure 2.2b also includes the absorption of the 1:1 (weight ratio) blend of BD:BH. In solution, both terpolymers (Ra-BDH and Re-BDH) show very similar absorption features, with increased
absorption width compared to either of the parent polymers (BD or BH). However, the thin film absorption of these two terpolymers is distinctively different, particularly at longer wavelengths. The characteristic absorption peaks from these two parent polymers, 430 nm for BD, 535 nm and 575 nm for BH, are clearly visible in the random terpolymer (Ra-BDH). In contrast, the absorption spectrum of the regular terpolymer (Re-BDH) is almost featureless from 350 nm to 700 nm. This difference in the thin film absorption between Ra-BDH and Re-BDH suggests that there exist oligomeric segments of (BnDT-DTBT)$_x$ and (BnDT-HTAZ)$_y$ that can aggregate in the random terpolymer, due to the random nature of the synthesis of Ra-BDH; while the regular, alternating nature of Re-BDH implies that there are no such oligomeric segments present in its structure. The aggregation of BD units (700 – 750 nm) is particularly suppressed and disrupted in both terpolymers, whereas the aggregation of the BH is partially present in the random terpolymer, but completely lacking the characteristic vibrational features in the regular terpolymer. On the other hand, the ternary blend (BD:BH at 1:1 weight ratio) covers the whole absorption range of the two parent polymers and captures corresponding absorption features including the signature for aggregation from both the two parent polymers. Finally, from the onset absorption of the thin film (Figure 2.2b), the band gaps of all studied polymers were calculated and the data were summarized in Table 2.2.

The electrochemical properties of the four polymers were evaluated via cyclic voltammetry (CV) (Figure 2.3). From the oxidation onset potentials of these polymers (vs. ferrocene/ferrocenium, Fc/Fc+), we estimated the highest occupied molecular orbital (HOMO) energy levels according to the equation $E_{\text{HOMO}} = -e(E_{\text{OX}} + 4.80 \text{V})$, with data included in Table 2.2. It is interesting to note that the calculated HOMO level of Ra-BDH appears to be ~ 0.1 eV.
lower than those of other three polymers (though we believe this slight difference is within the experimental error, given the estimative nature of CV).

![Figure 2.2. Cyclic voltammetry oxidation curves of the four polymers.](image)

2.4 Photovoltaic Properties

![Figure 2.3. Representative J-V curves (a) and related EQE (b) for all devices.](image)

The photovoltaic properties of all four polymers were measured by fabricating solar cells with a configuration of ITO/PEDOT:PSS/polymer:PC\textsubscript{61}BM/Ca/Al. In order to establish a meaningful comparison of the photovoltaic properties of all five polymers (including the ternary blend), we applied identical fabrication conditions for all five active layers as published previously, including
the processing solvent (oDCB), ratio of polymer:PC\textsubscript{61}BM (1:1 wt), and the solvent annealing time (12 hours).\textsuperscript{71} Furthermore, the thicknesses of all five active layers were maintained at \(\sim\) 110 nm, in order to eliminate any thickness induced effect on the device performance (e.g., \(J_{sc}\)), which could complicate the data interpretation and comparison.

All characteristic photovoltaic properties are summarized in Table 2.3, with representative \(J-V\) curves shown in Figure 2.4a. First of note, the open circuit voltage (\(V_{oc}\)) of the ternary blend (BD:BH) based solar cell is between those of the two parent polymer (BD or BH) based devices, which agrees well with our previous study.\textsuperscript{71} Interestingly, the \(V_{oc}\) values of the two terpolymer (Re-BDH and Ra-BDH) based solar devices are slightly higher than the higher \(V_{oc}\) of the two parent polymer based devices. This enhanced \(V_{oc}\), observed for both terpolymers, is worth noting, because most other terpolymers reported showed \(V_{oc}\) values in between the \(V_{oc}\) values of the two parent polymers.\textsuperscript{58, 65} The much higher \(V_{oc}\) values of these ternary polymers in this study, in particular compared to the low \(V_{oc}\) of the ternary blend, demonstrate that it is possible to maintain a high \(V_{oc}\) with the terpolymer approach, a clear advantage over the ternary blend approach. But as will be shown, this increased \(V_{oc}\) is not significant enough to affect the overall efficiency.

### Table 2.3. Photovoltaic properties and hole mobilities of the four polymers and physical blend of PBnDT-DTBT and PBnDT-HTAZ in their BHJ devices with PC61BM

<table>
<thead>
<tr>
<th>Polymer: PC\textsubscript{61}BM BHJ</th>
<th>Hole mobility ([\times 10^{-4}\text{cm}^2/\text{(V.S)}])</th>
<th>Thickness (nm)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(V_{oc}) (V)</th>
<th>(FF) (%)</th>
<th>PCE (%)</th>
<th>(J_{abs}) (mA/cm(^2))</th>
<th>(J_{sc}/J_{abs})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>2.25 ±0.77</td>
<td>138 ±2</td>
<td>9.22 ±0.28</td>
<td>0.813 ±0.003</td>
<td>52.4 ±0.5</td>
<td>3.93 ±0.12</td>
<td>10.84</td>
<td>0.85</td>
</tr>
<tr>
<td>BH</td>
<td>0.93 ±0.4</td>
<td>115 ±7</td>
<td>7.63 ±0.37</td>
<td>0.690 ±0.002</td>
<td>58.7 ±9</td>
<td>3.09 ±0.17</td>
<td>8.98</td>
<td>0.85</td>
</tr>
<tr>
<td>BD:BH</td>
<td>1.97 ±0.55</td>
<td>112 ±14</td>
<td>9.36 ±0.46</td>
<td>0.770 ±0.005</td>
<td>56.9 ±1.1</td>
<td>4.10 ±0.29</td>
<td>10.47</td>
<td>0.89</td>
</tr>
<tr>
<td>Ra-BDH</td>
<td>1.36 ±0.46</td>
<td>108 ±14</td>
<td>6.55 ±0.31</td>
<td>0.853 ±0.003</td>
<td>64.9 ±1.7</td>
<td>3.63 ±0.21</td>
<td>9.02</td>
<td>0.73</td>
</tr>
<tr>
<td>Re-BDH</td>
<td>0.85 ±0.24</td>
<td>111 ±17</td>
<td>5.57 ±0.25</td>
<td>0.838 ±0.006</td>
<td>57.3 ±2.3</td>
<td>2.67 ±0.13</td>
<td>7.88</td>
<td>0.71</td>
</tr>
</tbody>
</table>
The $J_{sc}$ values of the two terpolymer based devices, in particular that of the regular terpolymer (Re-BDH), are much smaller than either of the parent polymer based cells. The ternary blend, on the other hand, shows the highest $J_{sc}$ in this series of devices. It appears that chemical blending (i.e., Re-BDH and Ra-BDH) in the studied series of polymers is not a viable approach to improving the $J_{sc}$, compared to the physical blend (i.e., BD:BH). However, all three blends (Re-BDH, Ra-BDH, and BD:BH) show improved absorption width with respect to either of the parent polymers (BD or BH) (Figure 2.2b). Measurement of the external quantum efficiency (EQE) confirms the observed difference on the $J_{sc}$ of all devices (Figure 2.4b). In order to ascertain whether the lower current generation stemmed from a difference in absorption coefficients for the two terpolymers, the optical spectra of the devices were integrated to yield a theoretical expected current assuming 100% IQE. This procedure yields the values listed in Table 2.3 ($J_{abs}$). Dividing the measured $J_{sc}$ by the absorbance corrected current, $J_{abs}$, leads to a normalized ratio ($J_{sc}/J_{abs}$) which can be compared across all blends. The normalized currents cluster into two categories: the parent polymers and the physical blend (0.85, 0.85, and 0.89) and the terpolymers or chemical blend approach (0.73 and 0.71). Thus the improved $J_{sc}$ for the physical blend, is in large part due to improved absorption (since normalized currents are similar for both parent polymers and the physical blend). However, the differences in absorption cannot completely account for the different in $J_{sc}$ between the physical and chemical blends. Rather, although Ra-BDH has higher absorption coefficient than the physical blend, the physical blend does a better job of generating and collecting charges (as evidenced by the higher normalized $J_{sc}$). We also measured the long distance device hole mobility of all five blends, which are all on the order of $10^{-4}$ cm$^2$/V·s (Table 2.3); apparently, the long range device hole mobility cannot completely account for the observed
difference in $J_{sc}$ between the two terpolymers and the ternary blend, especially given such thin films (≈ 100 nm). The observed difference between the chemical blends and the other devices may also be related to the morphology or intrinsic charge generation efficiencies and geminate recombination.

**2.5 Morphology study**

To further understand the differences between Ra-BDH, Re-BDH, and the physical blend compared to the parent binary cells, we utilized a set of X-ray techniques to study the morphology and molecular packing of these polymer:fullerene blends.

Resonant Soft X-ray scattering (R-SoXS), measured at beamline 11.0.1.1 at the Advanced Light Source, provided information on the domain spacing and domain purity of the system. R-SoXS images were measured at 282.4 eV to provide good material contrast, while avoiding fluorescence. The images were processed using a modified form of the Nika software package implemented within Igor; details on the measurement and analysis methodology can be found in the experiment part. For all displayed R-SoXS sector averages (Figure 2.5), the recorded intensity was Lorentz-corrected by multiplying each curve by $q^2$, as is appropriate for the assumed 3-dimensional structures dominated by structure factor, rather than form factor. Most R-SoXS profiles and their anisotropy differences (Figure 2.5) clearly show signatures of multiple peaks, and as such, the vertical and horizontal sectors for each sample were fit with the minimum number of peaks needed. Two log-normal distributions were required to reproduce the sector averages of all samples. These distributions sometimes had similar modes, but different widths and thus different medians and were necessary for good fits even in cases where the profiles did not show any obvious sign of two features (see Appendix for Chapter 2 for details). Table 2.4 summarizes
the pertinent results of the peak fitting analysis, namely median domain spacing and relative integrated scattering intensity.

<table>
<thead>
<tr>
<th>Polymer: PC_{61}BM BHJ</th>
<th>Median domain Spacing (High-q Peak) [nm]</th>
<th>Relative Scattering Intensity (High-q Peak)</th>
<th>Median domain Spacing (Low-q Peak) [nm]</th>
<th>Relative Scattering Intensity (Low-q Peak)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>20.2 ± 2.0</td>
<td>0.68 ± 0.12</td>
<td>243 ± 36</td>
<td>0.84 ± 0.14</td>
</tr>
<tr>
<td>BH</td>
<td>24.0 ± 2.4</td>
<td>0.83 ± 0.08</td>
<td>47.0 ± 2.4</td>
<td>1.15 ± 0.10</td>
</tr>
<tr>
<td>BD:BH</td>
<td>25.1 ± 2.5</td>
<td>0.74 ± 0.12</td>
<td>328 ± 49</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>Ra-BDH</td>
<td>44.7 ± 4.5</td>
<td>1.00 ± 0.12</td>
<td>116.3 ± 5.8</td>
<td>1.00 ± 0.11</td>
</tr>
<tr>
<td>Re-BDH</td>
<td>38.0 ± 3.8</td>
<td>0.81 ± 0.07</td>
<td>65.6 ± 3.3</td>
<td>1.01 ± 0.09</td>
</tr>
</tbody>
</table>

**Figure 2.4.** R-SoXS measurements and analysis. For each sample, the calculated vertical (blue), horizontal (green), and full circular sector averages from the RSoXS images are shown. Note that the ordinate axis is logarithmic, so the curves have been given an offset via a multiplicative constant.

In the studied systems, it appears that two domain spacing distributions (in a given blend) were formed during the device fabrication: a low-q peak that corresponds to larger domains, and a high-
q peak that corresponds to the smaller domains (Table 2.4). Each peak type, as well as the sum of the peaks, was tested for possible correlation with the various photovoltaic performance metrics. Consider, first, the relative integrated scattering intensities of the small domains (i.e., high-q peaks), which were normalized for thickness and material contrast effects. The material contrast between the polymers and PCBM was calculated using near-edge X-ray absorption fine structure (NEXAFS) spectra measured on beamline 5.3.2.2 at the Advanced Light Source. As shown in Figure 2.6a, this correlates strongly with the fill factor of the studied set of polymer BHJ devices. Such correlation has been previously observed and reflects that the scattering intensity measures the combined impact of the domain purity and their volume fraction in a device, i.e., the average composition variations. More small domains or purer small domains can, up to a point, reduce the bimolecular recombination rate, thus improving the fill factor.

Furthermore, the hole mobility correlates with the median domain spacing for those domains described by the low-q peak (Figure 2.6b). We note that some domains described by this low-q peak have larger spacings than the film thickness, thus likely spanning the full width of the film and providing a direct path between electrodes, which could improve the mobility. Regarding the correlation of the normalized $J_{sc}$, i.e., those aspects of $J_{sc}$ that are not related to difference in photon absorption, we note that the normalized $J_{sc}$ groups into two tightly scattered clusters, i.e., the two chemical blends ($0.71 < J_{sc}/J_{ab} < 0.73$) and the other three devices ($0.85 < J_{sc}/J_{ab} < 0.89$). Thus, no matter what physical parameter we extract from the morphology characterization, we will not observe any correlations to the normalized $J_{sc}$, as shown in Figure 2.6c and 2.6d where the normalized $J_{sc}$ was plotted against the median domain spacing of the low-q and high-q peak, respectively.
Figure 2.5. R-SoXS parameters, extracted from peak fitting analysis of R-SoXS sector averages, as correlated with device parameters.

So the question remains: what would cause the reduced \( J_{sc} \) in these two terpolymer based solar cells? We assume that there is efficient and comparable exciton quenching, i.e., efficient charge transfer (CT) state formation, an assumption supported by the PCBM miscibility with BH \(^{80}\) and low crystallinity of the polymers, which suggest they would be unlikely to form the large, pure domains necessary to prevent exciton quenching. The low polymer crystallinity, particularly \( \pi-\pi \) stacking, has been observed in grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments performed at beamline 7.3.3 at the Advanced Light Source;\(^{81}\) further details may be found in the SI. The lack of correlation of \( J_{sc}/J_{abs} \) to any morphological parameters thus strongly implies that the differences in \( J_{sc} \) would arise from differences in charge generation and geminate
recombination. For instance, Burke and McGehee \(^8^2\) recently argued that the short range (i.e., terahertz) mobility controls charge generation, which offers one mechanism for improved \(J_{sc}\) in our series of polymers. In the terpolymer blends, the reduced aggregation, particularly of the BD units, evidenced in the UV-Vis spectra, leads to a degradation of local short range mobility, which in turn reduces the charge generation and increases geminate recombination in the un-aggregated segments of these two chemical blends.

2.6 Conclusion

In summary, we synthesized regularly alternating and random terpolymers from one donor unit and two different acceptor units. These two terpolymers were then compared to the parent D-A polymers as well as to a physical blend of the parent polymers. Both terpolymers showed extended absorption compared to the parent polymers, but had different absorption coefficients than the physical blend. Most significantly, the terpolymers exhibited a significantly reduced aggregation signature. When normalized for optical effects, the random terpolymer had comparable photovoltaic performance with the regular terpolymer, but both fell short of the physical blend, largely due to a lower \(J_{sc}\) from these terpolymers based solar cells. This was surprising since in most previously literature reports, the regular terpolymer outperformed the random polymer in each comparative study. A study of the morphologies of the samples showed that the two binary blends, the physical ternary blend, and the two terpolymer blends all have fill factors correlating with the domain purity of the smaller domain, and hole mobility correlating with the median domain spacing of the larger domains. We hypothesize that the lack of aggregation leads to low local mobilities with a negative impact on charge generation and increases geminate recombination. Overall, this study demonstrates that certain design rules for terpolymers need to be achieved in order to harness their full potential to control morphology by synthetic means. For chemical
blending to work, the material needs to have a molecular structure and overall architecture that will allow it to aggregate. Our work thus provides a useful guide for future synthesis and articulates a metric that can be easily checked by UV-Vis spectroscopy.

2.7 Experiment Section

Chemicals and Methods

All chemicals were purchased from commercial resources (Aldrich, Acros, Fisher Scientific, and Matrix) and used as received. Anhydrous THF was obtained via distillation from sodium/benzophenone prior to use. Diisopropylamine was distilled over potassium hydroxide prior to use. Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument, using 1,2,4-trichlorobenzene as the eluent (stabilized with 125 ppm BHT) at 135 °C. The obtained molecular weight is relative to the polystyrene standard. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) measurements were recorded with Bruker 400 MHz and 500 MHz DRX spectrometers. Mass Spectrometry (SI) was run on Q Exactive Orbitrap (ThermoFisher, Bremen, Germany) mass spectrometer and analyzed via Xcalibur (ThermoFisher, Breman, Germany). UV-visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). Cyclic voltammetry measurements were carried out using a Bioanalytical Systems (BAS) Epsilon potentiostat. Elemental analysis was done by Atlantic Microlab, Inc.

Cyclic Voltammetry measurements were carried out on solid films using a Bioanalytical Systems (BAS) Epsilon potentiostate with a standard three-electrode configuration. A three-electrode cell of a glassy carbon working electrode, Ag/AgNO3 (0.01M in anhydrous acetonitrile)
reference electrode, and Pt counter electrode were used. Films were dropcast onto the glassy carbon electrode from chlorobenzene and dried using a heat gun. A 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were carried out under argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential \( (E_{ox}) \) according to the following equation:

\[
HOMO = -[4.8eV + e(E_{ox} - E_{Fc/Fc^+})] \\
E_{LUMO} = E_{gap\ (optical)} + E_{HOMO}
\]

**Polymer Solar Cell Fabrication and Testing**

Photovoltaic devices were fabricated on ITO substrates that had been sonicated in deionized water, acetone, and isopropyl alcohol, for fifteen minutes each, followed by the UV-ozone treatment for another fifteen minutes. PEDOT:PSS (PH500 formulation purchased from Heraeus-Clevios) was then spuncast onto the substrates at 4000 rpm for 60 seconds and baked at 130 °C for fifteen minutes. Polymers and PCBM were dissolved in orthodichlorobenzene (\( o\text{-DCB} \)) at 10 mg/mL polymer concentration and a 1:1 polymer:PCBM ratio and heated at 130 °C for 6 hrs. The hot solution was spuncast onto the PEDOT:PSS films at 400, 500, 600, or 700 rpm for 60 seconds. The devices were then solvent annealed in sealed petri dishes for 12 hours. The devices were finished for measurement by evaporating 50 nm of calcium and 100 nm of aluminum as the cathode at a pressure of \( 3 \times 10^{-6} \) mbar. Finished devices were then measured by a solar simulator calibrated with an NREL certified standard silicon cell. Current voltage curves were measured via a Keithley 2400 digital source meter. The performance values reported are averaged from 8 cells. All steps
after the PEDOT:PSS deposition were carried out under N2 atmosphere (i.e., in N2-filled
gloveboxes).

Hole mobility was measured via the space-charge limited current (SCLC) method. Devices
were fabricated using the same procedure as described for photovoltaic devices. However, instead
of a calcium/aluminum electrode, 50 nm of palladium was evaporated at 3 × 10^{-6} mbar. Thus the
final device configuration was ITO/PEDOT:PSS/polymer:PC_{61}BM/Pd. Dark current densities
were measured in the dark using a Keithley 2400 digital source meter. Mobility values were
extracted by analyzing according to the Mott-Gurneys law using a Poole-Frenkel field-dependent
mobility.

\[
J = \frac{9}{8} \varepsilon_r \varepsilon_0 \frac{V^2}{d^2} \mu_0 \exp \left( g \sqrt{\frac{V}{d}} \right)
\]

In this case, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the dielectric constant of a polymer
(assumed to be approximately 3), \( \mu_0 \) is the zero field mobility, \( V \) is the voltage drop and \( d \) is the
thickness of the active layer. The applied voltage was not corrected for the built-in field or series
resistance. A weak Poole-Frenkel factor of \( g = 1 \times 10^{-4} \) (cm/V)^{1/2} was used. The values reported are
the average of at least four devices.

The absorption normalized \( J_{\text{sc}} \) (i.e., \( J_{\text{abs}} \)) was calculated by multiplying the incident photons
(as given by the ASTM G173-03 Reference Spectra Derived from SMARTS v. 2.9.2) by the
transmittance of the appropriate polymer:PCBM blend, measured by UV-Vis spectrophotometry.
100% internal quantum efficiency was assumed and \( J_{\text{abs}} \) was obtained by integrating over the
absorption range.
**R-SoXS Measurements**

The resonant soft X-ray scattering (R-SoXS) measurements were performed at beamline 11.0.1 at the Advanced Light Source in Berkeley, CA. The X-ray beam is produced by an undulator for high incident flux. At the sample, the beamline focuses the X-rays into an area of about 100 μm x 100 μm with an energy resolution of 0.1 eV. The detector is an in-vacuum CCD. Normalization of the incident X-ray intensity is done by measuring the flux of the direct beam simultaneously on an in-chamber photodiode and an upstream highly transparent and conductive mesh. The upstream mesh current is, by itself, an inaccurate measure of the incident flux due to carbon contamination, but unlike the photodiode current, the mesh current can be taken while an R-SoXS image is recorded. One may then use the mesh current as a bridge to normalize the intensity of all images to the true incident flux rate measured asynchronously by the photodiode.

Although several different sample-detector configurations are possible, for this experiment, all measurements were performed in transmission. To facilitate this, the samples were cast onto Si substrates that had a layer of PEDOT:PSS. Pieces of the samples were then removed from the substrate by first etching a piece of the sample of an appropriate size, then submersing the substrate into a bath of deionized water so as to dissolve the PEDOT:PSS layer and allow the sample to float free. The samples were then remounted onto Si₃N₄ windows purchased from Norcada (P/N NX5150C). The Si₃N₄ windows are 100 nm thick yet they are virtually transparent to X-rays with wavelengths in the range of interest around the C K absorption edge (250 to 350 eV).

Once the R-SoXS images were measured and the intensities normalized for incident X-ray flux, they were processed using a variant of the Nika software package that was customized for R-SoXS analysis. Vertical, horizontal, and full image sector averages were extracted from the image using the Nika code. The sector averages were Lorentz-corrected by scaling them by $q^2$, where $q$
is the magnitude of the reciprocal space lattice vector associated with the sector in question (\( q_x \) for horizontal, \( q_y \) for vertical, and \( q_r \) for circular).\(^7\) The R-SoXS sector averages shown in Figure 2.5 in the manuscript are composites taken from two images: one measured with the sample close to the detector to measure high-\( q \) scattering, and one measured with the sample far from the detector to measure low-\( q \) scattering, with sufficient overlap to allow the sector averages to be stitched together. Peaks were fit to the stitched sector averages using the least-squares algorithm implemented within Igor, a commercially-available software package. The high-\( q \) raw images are shown in Figure A1, and the results of the peak fitting process are shown in Figure A2. The vertical and horizontal sector averages for each sample are the same as those shown in Figure 2.4 in the manuscript, although the vertical and horizontal scales are linear rather than logarithmic. Note that the \( q \)-range available for fitting was not equal between the vertical and the horizontal sectors. As such, the same \( q \)-range was used when fitting both sectors, so as to keep constant the amount of information available to the fitting algorithm.

Relative composition variation is determined by computing the ratio of the integrated scattering intensity (ISI) of a feature in a sector average from a sample to the ISI of that same feature in the sector average of some standard.\(^7\) Simply stated, higher composition variation between donor-dominated and acceptor-dominated domains increases the differences between the domains with respect to how they interact with the incoming X-rays. This sharper contrast leads to stronger scattering, however, the strength of the scattering signal can be modulated by effects unrelated to the morphology of the sample. To extract relevant morphological differences among the five blends, (i.e., which sample has the highest composition variation), the ISI of each sample was normalized for thickness and for material contrast.
Thicker samples scatter more effectively, given that scattering can only occur if the radiation interacts with the sample. The effect of thickness was taken into account by normalizing the ISI by the Beer-Lambert law, where the thickness was determined using a KLA Tencor P-15 profilometer. The effect of material contrast must also be corrected, because it is fundamental to the nature of the molecules and has nothing to do with morphology: Two blends with identical morphology will nevertheless show differences in ISI if the constituents of one of the blends contrast more strongly than the other. Material contrast effects were accounted for by normalizing the ISI by the absolute value of the difference between the indices of refraction of the materials in question. The material contrast functions were computed using near-edge X-ray absorption fine structure (NEXAFS) spectra measured on beamline 5.3.2 at the Advanced Light Source.

GIWAXS Measurements

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were taken from all five blends with PCBM. The experiment was done at beamline 7.3.3 at the Advanced Light Source. The measurements were done with the sample at the critical angle (about 0.13°) so as to maximize the sample scattering signal; the angle of incidence was scanned to ensure that the true critical angle was found. The samples were mounted within a helium-filled box, so as to remove signal contamination from air scatter.

The images were analyzed using the Nika software package within Igor. The sector averages for the in-plane (IP) and out-of-plane (OoP) sectors were extracted from the images. The results of this analysis are shown in Figure A3. The GIWAXS experiment was not discussed in the main text because, upon analyzing the results, we determined that the information contained in the GIWAXS images had no bearing on the performance of the devices. Notably, the $\pi-\pi$ stacking
peak, typically in the vicinity of 1.6 Å⁻¹, is almost non-existent in all sector averages. As such, morphology does not strongly impact mobility.

**Synthesis of Monomers**

While \( D_{60} A_{122} A_{221} \) and compound 2.1 \(^{60} \) were synthesized according to literature procedure, D-A2-D was prepared following the scheme below.

**Compound 2.2: (4,8-bis(3-butylnonyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)trimethylstannane.**

To a solution of 4,8-bis(3-butylnonyl)benzo[1,2-b:4,5-b']dithiophene (**Compound 2.1**) (1.10 g, 1.98 mmol) in anhydrous THF, 2.5M n-BuLi solution in hexane (0.83 mL, 2.08 mmol) was added slowly at −78 °C. The solution soon turned green. After stirred at −78 °C for 1 h, the reaction mixture was raised to room temperature and kept stirring at room temperature for 70 minutes and then cooled down to −78 °C and kept stirring at −78 °C for 10 minutes. 1.0 M trimethyltin chloride solution in hexane (2.18 mL, 2.18 mmol) was then added at −78 °C. The reaction mixture turned yellow at the addition of trimethyltin chloride solution. Then the reaction mixture was warmed up to room temperature and was kept stirring at room temperature for another hour before the reaction mixture was poured into water and extracted with ethyl acetate (×3). The combined organic phase was washed with water (×5) and brine (×1), then dried over MgSO₄. The solvent was removed via rotavap. Yellow oil was obtained. Yield: 1.32g, 1.84mmol, 92.9%. \(^1\)H NMR (400 MHz, CDCl₃): δ 7.51 (t, 1H, \( J=14.4 \) Hz), 7.44 (s, 2H), 3.15 (m, 4H), 1.73 (m, 4H), 1.51 (m, 2H), 1.31-1.40 (m, 32H), 0.88-0.95 (m, 12H),0.50 (t, 9H, \( J=28.8 \)Hz); \(^{13}\)C NMR (400 MHz, CDCl₃): δ 141.57, 140.26, 137.16, 137.00, 135.22, 129.54, 128.64, 128.39, 125.78, 121.73, 33.88, 33.83, 33.65, 33.57, 33.35, 33.30, 33.01, 32.0, 30.76, 30.55, 29.83, 29.04, 26.78, 26.71, 23.18, 22.74, 22.72, 14.22, 14.15, 8.40.
Compound 2.3: 4-(5-(4,8-bis(3-butylnonyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)-7-(5-(4,8-bis(3-butylnonyl)benzo[1,2-b:5,4-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole. Compound 2.2 (0.578 g, 0.805 mmol) and 4,7-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (A2) (0.239 g, 0.35 mmol) was transferred into a 50 mL 2-neck flask. After three cycles of evacuation and refill with argon, 15 mL anhydrous toluene was transferred into the flask. After purging the reaction flask with argon for 15 min, bis(triphenylphosphine)palladium(II) dichloride (0.005 g, 0.007 mmol) was added under an argon stream. The reaction mixture was refluxed for 90 h. After cooling to room temperature, the reaction mixture was poured into water, extracted with ethyl acetate (×3) and dried over MgSO4. The solvent was removed via rotavap. Purple sticky oil was obtained after column chromatography on silica (hexanes: chloroform=10:1 as eluent). Yield: 0.483 g, 0.29 mmol, 84.6%. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (s, 2H), 7.89 (s, 2H), 7.58 (s, 2H) 7.46 (dd, 4H, J₁=8.4Hz, J₂=5.6Hz), 3.12-3.18 (dd, 8H, J₁=16.8Hz, J₂=8.8Hz), 2.95 (d, 4H, J=7.2Hz), 1.72-1.88 (m, 10H), 1.47-1.56 (m, 4H), 1.23-1.47 (m, 80H), 0.83-0.97 (m, 36H); ¹³C NMR (400 MHz, CDCl₃): δ 152.46, 140.63, 137.66, 137.53, 137.12, 136.02, 135.87, 135.63, 133.53, 131.67, 129.19, 128.73, 125.86, 125.33, 125.06, 121.73, 120.20, 40.28, 37.94, 34.02, 33.64, 33.62, 33.40, 33.27, 32.59, 32.02, 31.59, 30.70, 30.63, 29.88, 29.85, 29.03, 28.71, 26.78, 25.90, 23.24, 23.21, 23.18, 22.77, 22.66, 22.60, 14.28, 14.26, 14.15, 10.86. MS: calculated, 1630.76897; found, 1630.00316; Δ = - 2.6 ppm.

D-A2-D: 4-(5-(4,8-bis(3-butylnonyl)-6-(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)-7-(5-(4,8-bis(3-butylnonyl)-6-(trimethylstannyl)benzo[1,2-b:5,4-b']dithiophen-2-yl)-4-(2-ethylhexyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole. Lithium diisopropylamide (LDA) was freshly prepared before use via following procedure: to the solution
of diisopropylamine (0.147 g, 1.45 mmol) in anhydrous THF, 2.5M n-BuLi solution in hexane (0.46 mL, 1.16 mmol) was added slowly at room temperature, and the mixture was stirred at room temperature for 30 minutes. The freshly prepared LDA solution was transferred to a solution of **Compound 2.3** (0.0947 g, 0.058 mmol) in anhydrous THF at –78 °C slowly. The dark green solution was stirred at –78 °C for 2.5 h and at room temperature for 40 min. Then the reaction mixture was cooled back to –78 °C and kept stirring at –78 °C for 10 minutes before 1.0 M trimethyltin chloride solution in hexane (1.3mL, 1.3mmol) was added at –78 °C. The purple mixture was then warmed up to room temperature and was kept stirring at room temperature for 2 h. The mixture was then poured into water, and extracted with ethyl acetate (×3). The combined organic phase was washed with water (×5) and Brine (×1), then dried over MgSO₄. The solvent was removed via rotavap. Purple sticky oil was obtained. Yield: 0.0955g, 0.0488 mmol, 84.1%.

**1H NMR** (400 MHz, CDCl₃): δ 8.08 (s, 2H), 7.87 (s, 2H), 7.62 (s, 2H), 7.58 (s, 2H), 3.21 (m, 8H), 3.00 (d, 4H, J=6.8Hz), 1.75-1.95 (m, 10H), 1.57-1.62 (m, 4H), 1.25-1.57 (m, 80H), 0.85-1.05 (m, 36H), 0.48-0.62 (t, 18H, J=28Hz); **13C NMR** (400 MHz, CDCl₃): δ 152.49, 141.95, 140.59, 140.33, 137.60, 137.31, 136.99, 135.53, 135.50, 133.69, 131.67, 129.61, 128.65, 127.91, 125.38, 125.12, 120.37, 40.29, 37.89, 37.84, 33.98, 33.65, 33.61, 33.43, 33.30, 32.96, 32.57, 32.06, 30.75, 30.45, 29.90, 29.88, 29.06, 28.69, 26.83, 26.76, 25.88, 23.56, 23.28, 23.16, 22.78, 22.77, 14.30, 14.28, 10.85, 8.39. MS: calculated, 1956.38066; found, 1956.94051; Δ = + 5.6 ppm.

**Synthesis of Polymers**

All polymers were synthesized via the following procedure. A dry microwave vial containing monomers, Pd₂(dba)₃·CHCl₃ (0.002 mmol) and tri(o-tolyl)phosphine (0.016 mmol) was evacuated and refilled with argon for three times. Dry o-xylene (0.65 mL) was transferred into the tube under argon. The reaction mixture was put into microwave reactor for 10 min at 200 °C (at 300 watts)
and then cooled to room temperature. The polymer solution in hot chlorobenzene was precipitated in methanol. The resulting solid was filtered into a Soxhlet thimble and extracted with ethyl acetate, hexanes, THF, and chloroform. The solution in chloroform was concentrated under vacuum. The resulting solid was re-dissolved into hot chlorobenzene, and the solution was precipitated into methanol and filtered. The solid obtained was dried under vacuum.

The feed ratio of monomers, catalyst and ligand is:

**PBnDT-DTBT (i.e., BD):**

\[ \frac{D}{A_2}/ \frac{Pd_2(dba)_3}{CHCl_3}/ \frac{P(o-tol)_3}{=1.025/1.0/0.02/0.16} \]

**PBnDT-HTAZ (i.e., BH):**

\[ \frac{D}{A_1}/ \frac{Pd_2(dba)_3}{CHCl_3}/ \frac{P(o-tol)_3}{=1.025/1.0/0.02/0.16} \]

**Poly(BnDT-HTAZ-DTBT) (i.e., Ra-BDH):**

\[ \frac{D}{A_1}/ \frac{A_2}{Pd_2(dba)_3}/ \frac{P(o-tol)_3}{=1.025/0.5/0.5/0.02/0.16} \]

**Poly(BnDT-HTAZ-alt-BnDT-DTBT) (i.e., Re-BDH):**

\[ \frac{D-A_2-D}{A_1}/ \frac{Pd_2(dba)_3}{P(o-tol)_3}=1.025/1.0/0.02/0.16 \]

PBnDT-DTBT didn’t dissolve in CHCl during Soxhlet extraction, so after extraction with chloroform, the residual solid in the thimble was carefully removed out of the thimble and dried under vacuum. Poly(BnDT-HTAZ-alt-BnDT-DTBT) mainly dissolved in THF during the Soxhlet extraction, thus no CHCl extraction was obtained. Instead, the solution in THF was concentrated, re-dissolved into hot chlorobenzene, precipitated in methanol, filtered, and the solid obtained was dried under vacuum.
CHAPTER 3

FLUORINATED BENZENE AND THIOPHENE UNITS BASED WIDE BANDGAP POLYMERS FOR ORGANIC PHOTOVOLTAICS WITH HIGH $V_{oc}$

3.1 Introduction

Low bandgap polymers are desirable for absorption of photons at long wavelength. However, even for low bandgap polymers, the absorption range is still inherently narrow due to the lack of absorption at the short wavelength (high energy) part. Chapter 2 provided a method to address the inherently narrow absorption spectra of conjugated polymers via terpolymers composed of the monomer units of two polymers with complementary absorption spectra. In addition to the design of terpolymers and the ternary blends discussed in Chapter 2, tandem solar cells can address this issue as well by incorporating polymers with complementary absorption ranges into multiple layers. For tandem solar cells, in addition to low bandgap polymers, high performing large bandgap polymers are required for efficient tandem solar cells. One of the most popular wide bandgap polymers is poly(3-hexylthiophene) (P3HT), which has a bandgap of ~ 1.9 eV. The drawback of P3HT and fullerene derivatives based PSCs is the low $V_{oc}$ (~ 0.6 V) due to the high-lying HOMO level of P3HT. For tandem solar cells stacked in series, the $V_{oc}$ of the cells is the sum of all heterojunction layers, so it is still of great interest to design wide bandgap polymers that can afford high $V_{oc}$ values.

Based on the design rule of “D-A” polymers, the energy of HOMO and LUMO levels of the polymers are mainly affected by the donor and acceptor units respectively. Acceptor units with weak electron-withdrawing ability will enable the formation of high lying LUMO levels and an
increased the bandgaps of the polymers. In this study, six polymers based on benzo[1,2-b:4,5-b’]dithiophene (BnDT) and 1,4-di(thiophen-2-yl)benzene (T2B) were designed. Both of BnDT and T2B units are electron rich units, which is a useful approach to large bandgap polymers. For example, Wolf et al. prepared a large bandgap (optical bandgap ~ 2.1 eV) high-performance polymer ($PCE \sim 7.0\%$ with PC$_{71}$BM as acceptor material) based on two electron rich units: BnDT and fluorinated thiophene units.$^{88}$ In this study, we also incorporated fluorine substituents into the benzene and the thiophene units to improve the $V_{oc}$ of PSC devices by decreasing the HOMO levels of the polymers. In addition, fluorination of benzene and thiophene units was found to enhance the planarity of polymer backbones and $\pi-\pi$ interactions of polymer backbones$^{89}$ which can help the formation of charge transport pathways and improve the $J_{sc}$ and $FF$ of PSCs.

![Chemical structure of the six polymers](chart3.1.png)

**Chart 3.1.** Chemical structure of the six polymers.

The chemical structures of the six polymers PF0, PF1, PF2-ortho, PF2-para, PF2-T and PF4 were shown in **Chart 3.1.** In contrast to the other polymers with fluorine substituents on the benzene unit, for PF2-T, the two fluorine substituents were relocated on thiophene units. All the six polymers have wide optical bandgap (~ 2.15 eV) as intended. High $V_{oc}$ values (0.94 – 1.00 eV) were achieved for all six polymers, however, only moderate $J_{sc}$ values (3.5 – 5.5 mA/cm$^2$) were
achieved. PCE values of 1.5% - 3.2% were thus obtained. Though the PCE values are relatively low, this study provides a useful approach to designing wide bandgap polymers with large $V_{oc}$.

### 3.2 Design and Synthesis

![Scheme 3.1. Synthesis of monomers](image)

**Scheme 3.1. Synthesis of monomers**

As shown in Scheme 3.1, the synthesis of the monomers diBrT2B0, diBrT2B1, diBrT2B2-ortho, diBrT2B2-para and diBrT2B4 started from Stille coupling reactions of the commercially available dibromobenzene (with/without fluorine substituents) and (4-(2-ethylhexyl)thiophen-2-yl)trimethylstannane. Then the 1,4-di(thiophen-2-yl)benzene (T2B) compounds were brominated with NBS to obtain the monomers. The 2-ethylhexyl side chains were incorporated into the thienyl unit for adequate solubility of the polymers.

In contrast, the fT2B monomer with fluorinated thienyl unit required more steps as shown in **Scheme 3.2**. The 3-(2-ethylhexyl) thiophene (Compound 3.1) were firstly brominated with
bromine at the 2’, 4’ and 5’ positions to get Compound 3.2. Then the 2’ and 5’ positions of Compound 3.2 were protected with trimethylsilyl (TMS) groups to get Compound 3.3. The fluorination of the Compound 3.3 was realized through electrophilic fluorination with N-fluorobenzenesulfonylimide (NFSI), leading to Compound 3.4. Then the TMS protecting groups were removed with tetrabutylammonium fluoride (TBAF) solution to get Compound 3.5. Trimethylstannanyl group was then introduced to the position close to F atom to obtain Compound 3.6. Compound 3.6 was then subjected to Stille coupling reaction, followed by a bromination reaction to get the monomer dibrT2B. The synthetic details are provided in the Experiment Section. All newly prepared compounds were characterized with $^1$H NMR to confirm the chemical structure. The monomers were also further characterized with $^{19}$F NMR.

Scheme 3.3. Stille coupling reaction based polymerization.

The synthesis of the polymers was performed based on Stille coupling polymerization with microwave heating as shown in Scheme 3.3. The ratio of the BnDT monomer/the TB monomers was set as 1.025/1.000 to control the molecular weight. All polymers were subjected to Soxhlet extraction with ethyl acetate, hexanes, and chloroform. The residue polymers in the thimbles were collected for further characterization. The number average molecular weights of the polymers
measured by high-temperature GPC were between 42 to 78 kg/mol with PDI of ~ 1.8. Detailed information of the polymer properties is summarized in Table 3.1.

![Figure 3.1. High-temperature GPC curves of the six polymers.](image)

**Figure 3.1.** High-temperature GPC curves of the six polymers.

### 3.3 Optical and Electrochemical Properties

![Figure 3.2. Normalized UV-Vis of polymer (a) in TCB solution and (b) as films](image)

**Figure 3.2.** Normalized UV-Vis of polymer (a) in TCB solution and (b) as films

The UV-Vis absorption spectra of the polymers in 1,2,4-trichlorobenzene and in films were measured (**Figure 3.1(a)** and **Figure 3.1(b)**). From **Figure 3.1 (b)**, all polymers have similar absorption in solution and as thin films, indicating the fluorine substitution does not strongly affect the absorption properties of the polymers. Some minor difference still exists though: the solution absorption of PF2-T has a small absorption shoulder peak at long wavelength, which might be
caused by the slight aggregation of the polymer chains even in solution, while there is no such aggregation peak for the other polymers. Moreover, the absorption spectrum of PF2-para as a thin film is slightly red-shifted (Figure 3.1(b)), which might be caused by stronger aggregation induced by the fluorine substituents and the more symmetrical structure of the PF2-para polymers.\textsuperscript{36} The optical bandgaps of the polymers were calculated based on the onset of the film absorption and range from 2.10 eV to 2.18 eV, which are rather large bandgaps as intended.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$M_n$ (kg/mol)</th>
<th>$D$ ($M_w/M_n$)</th>
<th>HOMO (eV, eV)</th>
<th>Optical Bandgap (eV)</th>
<th>HOMO (cal, eV)</th>
<th>Bandgap (cal, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF0</td>
<td>52.0</td>
<td>1.9</td>
<td>-5.45</td>
<td>2.17</td>
<td>-5.24</td>
<td>3.53</td>
</tr>
<tr>
<td>PF1</td>
<td>42.6</td>
<td>1.8</td>
<td>-5.55</td>
<td>2.16</td>
<td>-5.23</td>
<td>3.38</td>
</tr>
<tr>
<td>PF2-ortho</td>
<td>60.3</td>
<td>1.8</td>
<td>-5.53</td>
<td>2.15</td>
<td>-5.27</td>
<td>3.34</td>
</tr>
<tr>
<td>PF2-para</td>
<td>67.9</td>
<td>1.9</td>
<td>-5.52</td>
<td>2.10</td>
<td>-5.28</td>
<td>3.29</td>
</tr>
<tr>
<td>PF2-T</td>
<td>66.7</td>
<td>1.9</td>
<td>-5.66</td>
<td>2.18</td>
<td>-5.29</td>
<td>3.44</td>
</tr>
<tr>
<td>PF4</td>
<td>77.7</td>
<td>1.8</td>
<td>-5.65</td>
<td>2.14</td>
<td>-5.34</td>
<td>3.23</td>
</tr>
</tbody>
</table>

**Figure 3.3.** CV curves of the six polymers.

The energy levels of the polymers were estimated with cyclic voltammetry and are summarized in Table 3.1. The energy levels of the polymers were also calculated using density function theory (DFT). The calculated results match the measured trend of the HOMO energy levels of the polymers, increasing the fluorine amount decreases the HOMO level energy. It is interesting that
besides the fluorine amounts, the position of the fluorine substituents also affects the HOMO level. PF2-T has a much deeper HOMO level than the other two 2F polymers, PF2-ortho and PF2-para, and the HOMO level of PF2-T is as deep as that of PF4. This might be due to the more electron rich nature of the thiophene unit than the benzene unit. Thus, adding fluorine to the thiophene unit has a stronger impact on the HOMO level in this series of polymers.

3.4 Photovoltaic Properties

![Figure 3.4](image)

**Figure 3.4.** (a) *J*-V curves and (b) EQE spectra of BHJ solar cells.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Thickness (nm)</th>
<th>J_SC (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF0</td>
<td>110</td>
<td>5.51±0.16</td>
<td>0.945±0.004</td>
<td>60.9±0.8</td>
<td>3.17±0.08</td>
</tr>
<tr>
<td>PF1</td>
<td>108</td>
<td>5.25±0.05</td>
<td>0.956±0.011</td>
<td>56.2±0.9</td>
<td>2.82±0.07</td>
</tr>
<tr>
<td>PF2-ortho</td>
<td>115</td>
<td>5.33±0.39</td>
<td>0.952±0.021</td>
<td>49.4±4.5</td>
<td>2.50±0.09</td>
</tr>
<tr>
<td>PF2-para</td>
<td>126</td>
<td>5.11±0.25</td>
<td>0.971±0.029</td>
<td>52.2±1.3</td>
<td>2.59±0.18</td>
</tr>
<tr>
<td>PF2-T</td>
<td>112</td>
<td>4.19±0.53</td>
<td>0.964±0.048</td>
<td>55.2±0.6</td>
<td>2.24±0.48</td>
</tr>
<tr>
<td>PF4</td>
<td>111</td>
<td>3.46±0.21</td>
<td>1.000±0.007</td>
<td>42.9±0.9</td>
<td>1.49±0.11</td>
</tr>
</tbody>
</table>

The photovoltaic properties of these six polymers were investigated in the bulk heterojunction (BHJ) solar cells with a standard device configuration: indium doped tin oxide
(ITO)/PEDOT:PSS/polymer:phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM)/Ca/Al with 1:1 weight ratio of polymers:PC$_{61}$BM. The $J$-$V$ curves and external quantum efficiency (EQE) curves of optimized devices are presented in **Figure 3.2 (a)** and **Figure 3.2 (b)**, respectively. And the detailed results of the photovoltaic properties are summarized in **Table 3.2**. The $V_{oc}$ values of the devices gradually increase with more fluorine substituted on the benzene ring, which is consistent with the deeper HOMO energy levels of the polymers with more fluorine atoms. The change in fluorine substituent positions on PF2-ortho, PF2-para and PF2-T does not significantly affect the $V_{oc}$ values; they are similar for all three 2F polymers. The deeper HOMO level of PFT-2 (similar to that of PF4) does not directly translate into a higher $V_{oc}$, which might be related to larger non-geminate recombination in the devices. The $J_{sc}$ values of PF0, PF1, PF2-ortho and PF2-para based devices are similar, which is consistent with the similar absorption ranges of the polymers and the similar EQE values of the solar cells. The $FF$ value decreases with more fluorine atoms, which is possibly due to the reduced solubility of the polymers with more fluorine. With decreased solubility, the polymers may precipitate out of the solution quickly and form large less-crystalline polymer domains, which is not ideal for exciton diffusion to the polymer:PC$_{61}$BM interface and the hole transport through the polymer domains. This also explains the lowest $J_{sc}$ and lowest $FF$ values obtained by devices based on PF4, which has the lowest solubility among all the polymers. Interestingly, PF2-T, which has fluorine substituents on thiophene units, showed reduced $J_{sc}$ values in its devices but improved $FF$ values compared to the other F2 polymers (PF2-ortho and PF2-para). The relocation of fluorine atoms from benzene unit to the thiophene unit might cause a change in crystallinity and aggregation of polymer backbones, which could strongly affect the morphology of the active layer and further affect the charge generation and charge recombination.

### 3.5 Conclusion
Six wide bandgap polymers based on BnDT and T2B units were prepared. The energy levels of the polymers were adjusted with fluorine substituents on the benzene and thiophene rings. $V_{oc}$ values as high as 1.0 V were achieved, which makes the polymers a good candidate for tandem solar cells. Beyond providing a useful approach to wide bandgap polymers from two electron-rich units, this study also investigated the effect of fluorinated benzene and thiophene units on the properties of the polymers. Given strong aggregation behavior of the polymers observed, further study of the morphology of the bulk heterojunction blends of the polymers with PC$_{61}$BM can offer insights into how the aggregation of the polymers affects the morphological features of the blends and the solar cell performance, which may potentially provide a guideline for material design for PSCs.

3.6 Experiment Section

**Chemicals and Methods** All chemicals were purchased from commercial sources such as Sigma-Aldrich, Fisher Scientific, Matrix and were used as was received except when specified. Anhydrous THF was distilled over sodium and benzophenone before use. Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument, using 1,2,4-trichlorobenzene as the eluent (stabilized with 125 ppm BHT) at 135 °C. The obtained molecular weight is relative to the polystyrene standard. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) measurements were recorded with Bruker 400 MHz DRX spectrometers. UV-visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). Cyclic voltammetry measurements were carried out using a Bioanalytical Systems (BAS) Epsilon potentiostat. Elemental analysis was done by Atlantic Microlab, Inc.
Cyclic Voltammetry measurements were carried out on solid films using a Bioanalytical Systems (BAS) Epsilon potentiostate with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, Ag/AgNO3 (0.01M in anhydrous acetonitrile) reference electrode, and Pt counter electrode were used. Films were dropcast onto the glassy carbon electrode from 1,2,4-trichlorobenzene and dried using a heat gun. A 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were carried out under argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferroacenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential ($E_{ox}$) according to the following equation:

$$HOMO = -[4.8eV + e(E_{ox} - E_{Fc/Fc^+})]$$

Polymer Solar Cell Fabrication and Testing

Glass substrates coated with patterned indium doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. The 150 nm sputtered ITO pattern had a resistivity of 20Ω/□. Prior to use, the substrates were ultrasonicated in deionized water, acetone, then 2-propanol for 15 minutes each. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV-Ozone for 15 min. A filtered dispersion of PEDOT:PSS in water (Clevios™ PH500 from Heraeus) was then spun cast onto cleaned ITO substrates at 4000 rpm for 60 s and then baked at 130 °C for 15 min in air to give a thin film with a thickness of 40 nm. Blends of polymer:PC$_{61}$BM (1:1 w/w, 10 mg/mL for polymer) were dissolved in 1,2,4-trichlorobenzene with heating at 130 °C for 6h. All the solutions were filtered through a 5.0 µm PTFE filter and spun-cast at an optimized rpm for 60 seconds onto the PEDOT:PSS layer at room temperature except for P4. For device with PF4, the solution of PF4:PCBM was spun-cast on the substrate preheated at 130 °C for 1 min. Then the
substrates with wet films were kept in sealed petri dishes for overnight. The devices were finished for measurement after thermal deposition of a 30 nm film of calcium and a 70 nm aluminum film as the cathode at a base pressure of $2 \times 10^{-6}$ mbar.

**Synthesis**

**General procedure of Stille coupling reaction** The reactants (reactant with bromo group 1.0 eq, and reactant with tin group 2.3 eq) and Pd(PPh$_3$)$_2$Cl$_2$ (0.02 eq) was dissolved into anhydrous toluene and purged with argon for 20 min. The reaction was refluxed at 120 °C for 40 hr, and toluene was removed with rot-vap. And the product was purified with silica gel column chromatography with hexanes as eluent.

**General procedure of bromination reaction with NBS** To the ~ 0.05 M solution of reactant (1.0 eq) in THF, NBS (2.1 eq) in THF was added at r.t.. The reaction was stirred for 40 hr and poured into water. The product was extracted with hexanes for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The solvent was removed with rot-vap. The monomers were purified with silica gel column chromatography with hexanes as eluent and recrystallized from ethanol for further purification.


*T2BF0*, yield: pale yellow oil, 60%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.58 (s, 4H), 7.14 (s, 2H), 6.85 (d, $J = 1.3$ Hz, 2H), 2.56 (d, $J = 6.8$ Hz, 4H), 1.59 (t, $J = 6.1$ Hz, 2H), 1.42 – 1.24 (m, 16H), 1.02 – 0.71 (m, 12H).

*T2BF1*, yield: pale yellow oil, 78%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.59 (t, $J = 8.2$ Hz, 1H), 7.37 (dd, $J = 3.6$, 1.9 Hz, 1H), 7.35 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.31 (d, $J = 1.4$ Hz, 1H), 7.15
(d, $J = 1.4$ Hz, 1H), 6.93 (d, $J = 1.3$ Hz, 1H), 6.88 (d, $J = 1.3$ Hz, 1H), 2.57 (t, $J = 7.5$ Hz, 4H), 1.60 (m, 2H), 1.32 (m, 16H), 0.90 (m, 12H).

**T2BF2-ortho**, yield: pale yellow oil, 68%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.37 – 7.34 (m, 2H), 7.34 – 7.31 (d, $J = 1.3$ Hz, 2H), 6.97 (d, $J = 1.3$ Hz, 2H), 2.63 – 2.54 (d, 4H), 1.61 (q, $J = 6.1$ Hz, 2H), 1.39 – 1.25 (m, 16H), 0.90 (td, $J = 6.5, 5.7, 2.2$ Hz, 12H).

**T2BF2-para**, yield: pale yellow oil, 36%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.37 (t, $J = 9.2$ Hz, 2H), 7.31 (s, 2H), 6.98 (s, 2H), 2.57 (d, $J = 6.9$ Hz, 4H), 1.60 (t, $J = 6.0$ Hz, 2H), 1.40 – 1.20 (m, 16H), 1.04 – 0.73 (m, 12H).

**T2BF4**, yield: white solid, pale yellow oil, 78%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.47 (d, $J = 1.3$ Hz, 2H), 7.12 (d, $J = 1.3$ Hz, 2H), 2.61 (d, $J = 6.8$ Hz, 4H), 1.59 (d, $J = 6.1$ Hz, 2H), 1.35 – 1.22 (m, 16H), 0.90 (m, 12H).

**dibrT2BF0**, yield: white solid, 43%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.50 (s, 4H), 6.99 (s, 2H), 2.51 (d, $J = 7.2$ Hz, 4H), 1.72 – 1.60 (m, 2H), 1.40 – 1.26 (m, 16H), 0.90 (m, 12H).

**dibrT2BF1**, yield: white solid, 45%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.51 (t, $J = 8.2$ Hz, 1H), 7.30 – 7.28 (m, 1H), 7.28 – 7.25 (m, 1H), 7.14 (d, $J = 0.9$ Hz, 1H), 7.00 (s, 1H), 2.51 (m, 4H), 1.68 – 1.60 (m, 2H), 1.41 – 1.19 (m, 16H), 0.94 – 0.84 (m, 12H). $^{19}$F NMR (376 MHz, chloroform-d) $\delta$ -113.28.

**dibrT2BF2-ortho**, yield: white solid, 89%; $^1$H NMR (400 mHz, chloroform-d) $\delta$ 7.26 (m, 2H), 7.17 (s, 2H), 2.53 (d, $J = 7.2$ Hz, 4H), 1.64 (q, $J = 6.3$ Hz, 2H), 1.39 – 1.20 (m, 16H), 0.94 – 0.82 (m, 12H). $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -139.02.
**dibrT2BF2-para**, yield: white solid, 46%; $^1$H NMR (400 mHz, chloroform-d) δ 7.29 (dd, $J = 9.4, 8.7$ Hz, 2H), 7.15 (s, 2H), 2.53 (d, $J = 7.2$ Hz, 4H), 1.65 (m, 2H), 1.43 – 1.24 (m, 16H), 0.96 – 0.86 (m, 12H). $^{19}$F NMR (376 MHz, Chloroform-d) δ -118.88.

**dibrT2BF4**, yield: white solid, 22%; $^1$H NMR (400 mHz, chloroform-d) δ 7.33 (s, 2H), 2.56 (d, $J = 7.2$ Hz, 4H), 1.70 – 1.62 (m, 2H), 1.40 – 1.28 (m, 16H), 1.03 – 0.81 (m, 12H). $^{19}$F NMR (376 MHz, Chloroform-d) δ -140.75.

**Synthesis of diBrfT2B**

**2,3,5-tribromo-4-(2-ethylhexyl)thiophene (Compound 3.2)** To the solution of 3-(2-ethylhexyl)thiophene (0.98 g, 5.0 mmol) in dichloromethane (dichloromethane), bromine (3.20 g, 20 mmol) was added dropwise. The reaction was slowly warmed to 0 °C in dark overnight. Then the reaction mixture was quenched with cold KOH solution. The produce was extracted with dichloromethane for 2 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The solvent was removed with rot-vap. The product was purified with with silica gel column chromatography with hexanes as eluent. Yield, colorless oil, 1.90 g, 4.4 mmol, 88%. $^1$H NMR (400 MHz, Chloroform-d) δ 2.57 (d, $J = 7.3$ Hz, 2H), 1.71 (m, 1H), 1.40 – 1.17 (m, 8H), 0.89 (m, 6H).

**3-bromo-4-(2-ethylhexyl)thiophene-2,5-diylbis(trimethylsilane) (Compound 3.3)** To the solution of Compound 3.2 (0.87 g, 2.0 mmol) in anhydrous THF, 2.5 M n-butyllithium solution in hexanes (1.6 mL, 4.0 mmol) was added at -78 °C under argon slowly and stirred for 15 min. Trimethylsilyl chloride (0.54 g, 5.0 mmol) was added and slowly warmed to r.t. overnight. The reaction was quenched with water, and the product was extracted with hexanes for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was
dried over magnesium sulfate. The solvent was removed with rot-vap. The product was purified with silica gel column chromatography with hexanes as eluent. Yield, colorless oil, 0.81 g, 1.94 mmol, 97%. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta 2.65\) (d, \(J = 7.6\) Hz, 2H), \(1.78\) (q, \(J = 6.5\) Hz, 1H), \(1.36 - 1.14\) (m, 8H), \(0.86\) (q, \(J = 7.3\) Hz, 6H), \(0.39\) (s, 9H), \(0.34\) (s, 9H).

\((3\text{-}(2\text{-ethylhexyl})\text{-}4\text{-fluorothiophene-2,5-diyl})\text{bis(trimethylsilane)}\) (Compound 3.4) To the solution of Compound 3.3 (0.84 g, 2.0 mmol) in anhydrous THF, 2.5 M \(n\)-butyllithium solution in hexanes (0.88 mL, 2.2 mmol) was added at -78 °C under argon slowly and stirred for 20 min. Solution of NFSI (0.95 g, 3.0 mmol) in anhydrous THF was added to the reaction slowly, and the reaction was kept at -78 °C and slowly warmed to r.t. overnight. The reaction was quenched with water, and the product was extracted with hexanes for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The solvent was removed with rot-vap. The product was purified with silica gel column chromatography with hexanes as eluent. Yield, colorless oil, 0.21 g, 0.58 mmol, 29%. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta 2.51\) (d, \(J = 7.5\) Hz, 2H), \(1.68 - 1.57\) (m, 1H), \(1.36 - 1.14\) (m, 8H), \(0.87\) (m, 6H), \(0.33\) (s, 9H), \(0.31\) (s, 9H). \(^19\)F NMR (376 MHz, chloroform-d) \(\delta -119.55\).

\(3\text{-}(2\text{-ethylhexyl})\text{-}4\text{-fluorothiophene}\) (Compound 3.5) To the solution of Compound 3.4 (2.56 g, 7.1 mmol) in THF, 1.0 M TBAF solution in THF (15.7 mL, 15.7 mmol) was added at 0 °C. The reaction mixture as stirred at r.t. and tracked with TLC and \(^1\)H NMR until the reaction was finished (~ 3 hr). The reaction mixture was poured into water, and the product was extracted with hexanes for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The solvent was removed with rot-vap. The product was purified with silica gel column chromatography with hexanes as eluent. Yield, colorless oil, 0.77 g, 3.6 mmol, 50%. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta 6.81\) (t, \(J = 3.8\) Hz,
1H), 6.65 (d, J = 3.5 Hz, 1H), 2.46 (d, J = 7.0 Hz, 2H), 1.60 (m, 1H), 1.34 – 1.20 (m, 8H), 0.95 – 0.78 (m, 6H). 19F NMR (376 MHz, chloroform-d) δ -131.71.

(4-(2-ethylhexyl)-3-fluorothiophen-2-yl)trimethylstannane (Compound 3.6) To the solution of Compound 3.5 (0.70 g, 3.3 mmol) in anhydrous THF, 2.5 M n-butyllithium solution in hexanes (1.5 mL, 3.75 mmol) was added under argon at -78 °C slowly and stirred at r.t for 90 min. The reaction was cooled to -78 °C for 10 min before 1.0 M trimethyltin chloride solution in hexanes (4.41 mL, 4.41 mmol) was added. The reaction was stirred at r.t. overnight before it was poured into water. The product was extracted with hexanes for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The solvent was removed with rot-vap. The product was pure enough for the coupling reaction. Yield, colorless oil, 1.24 g, 3.28 mmol, 100%. 1H NMR (400 MHz, Chloroform-d) δ 7.05 (d, J = 3.0 Hz, 1H), 2.45 (d, J = 6.9 Hz, 2H), 1.56 (m, 1H), 1.38 – 1.19 (m, 8H), 0.88 (m, 6H), 0.47 – 0.29 (m, 9H). 19F NMR (376 MHz, chloroform-d) δ -123.57.

fT2B The coupling reaction followed the general procedure of Stille coupling reaction. Yield, white solid, 76%. 1H NMR (400 MHz, Chloroform-d) δ 7.66 (s, 4H), 6.77 (d, J = 4.5 Hz, 2H), 2.50 (d, J = 6.9 Hz, 4H), 1.69 – 1.56 (m, 2H), 1.44 – 1.21 (m, 16H), 0.90 (td, J = 7.4, 3.0 Hz, 12H). 19F NMR (376 MHz, chloroform-d) δ -130.12.

diBrfT2B The bromination reaction followed the general procedure of bromination reaction with NBS. Yield, white solid 57%. 1H NMR (400 MHz, Chloroform-d) δ 7.57 (s, 4H), 2.48 (d, J = 7.3 Hz, 4H), 1.69 (m, J = 6.3 Hz, 2H), 1.45 – 1.17 (m, 16H), 0.91 (q, J = 7.1 Hz, 12H). 19F NMR (376 MHz, chloroform-d) δ -124.59.
CHAPTER 4
FLUORINATED THIOPHENE UNITS IMPROVE PHOTOVOLTAIC DEVICE PERFORMANCE OF DONOR-ACCEPTOR COPOLYMERS

4.1 Introduction

Further understanding the structure-property relationship of conjugated polymers and small molecules for solar cells has been driving this research field forward with newer and better materials.\textsuperscript{6, 7} Among all the material design strategy, fluorine substitution is unique.\textsuperscript{18, 19} Provided that fluorine substituents were mostly placed on the acceptor units with only several examples of successful fluorinated donor units as was discussed in Chapter 1, fluorine substitution on the \( \pi \) linker units, which play important roles in affecting properties of conjugated polymers and the device characteristics of the related solar cells\textsuperscript{93, 94}, is scarcely studied. One such example has been documented by the Heeney group.\textsuperscript{95, 96} In their studies, Fei et al. added a difluorinated thiophene unit in between the dithienogermole (D) and the benzothiadiazole (A), and the fluorinated polymer showed much higher device efficiency than the non-fluorinated counterpart, mainly due to a much increased \( J_{sc} \).\textsuperscript{95} With fluorine substituents on the thiophene unit, dipole moment change from ground state and excite state was increased, and the \( \pi-\pi \) stacking of the polymers was increased as well, which favored the formation and stabilization of charge transfer excitons and reduced the non-geminate recombination respectively, thus, the \( J_{sc} \) was significantly improved.\textsuperscript{96} Furthermore, when Liu et al. used this difluorinated thiophene to copolymerize with
thieno[3,4-\text{c}]pyrrole-4,6-dione (i.e., TPD, an acceptor unit), as-synthesized polymer can be used as a polymer acceptor to pair with a low band gap polymer to reach decent device efficiency.\(^{97}\)

As one of the first groups in discovering the peculiar “F effect” (i.e., fluorinated polymer leading to enhanced device performance),\(^{21,22,26,38}\) we have a keen interest to further explore this interesting behavior. For example, in our earlier work, we revealed that adding fluorine substituents to the benzotriazole unit in the D-A polymer (i.e., from PBnDT-HTAZ to PBnDT-FTAZ) can increase the hole mobility in the related bulk heterojunction (BHJ) device by one order of magnitude, which directly accounts for the much improved \(FF\) of the PBnDT-FTAZ based BHJ device.\(^{26}\) In our current study, inspired by the recent success on employing the fluorinated bithiophene and the difluorinated thiophene, we decided to explore the effect of fluorination of these two flanking thiophene units between the BnDT (D) and benzotriazole (A) units. Since each flanking thiophene has two hydrogen atoms (3’ and 4’) that can be substituted with fluorine atoms, together with the \(m\)-H/FTAZ units, we chose to synthesize four new fluorinated BnDT-TAZ based polymers (\textbf{Chart 4.1}). These four additional fluorinated polymers constitute a series of structurally closely related polymers to further our understanding on the impact of fluorination. For conciseness yet clarity, we will use HTAZ, FTAZ, 3’-FT-HTAZ, 4’-FT-HTAZ, 3’-FT-FTAZ and 4’-FT-FTAZ to represent the polymers in the following discussion, while \(m\)-HTAZ, \(m\)-FTAZ, \(m\)-3’-FT-HTAZ, \(m\)-4’-FT-HTAZ, \(m\)-3’-FT-FTAZ and \(m\)-4’-FT-FTAZ are used to indicate the corresponding monomers. Specifically, 3’-FT-HTAZ and 4’-FT-HTAZ are isomeric to the original FTAZ polymer. More importantly, having these fluorinated thiophenes allow us to have access to the tetrafluorinated polymer, 3’-FT-FTAZ and 4’-FT-FTAZ, which are also isomeric to each other. Together with previously studied PBnDT-HTAZ and PBnDT-FTAZ polymers, this set of six
polymers offer a comprehensive system to allow us to probe the “F effect”, with a focus on both the number (0, 2, 4) and the position of the fluorination.

![Chart 4.1](image)

**Chart 4.1.** A series of fluorinated PBnDT-TAZ polymers, highlighting the position and the number of fluorinations.

Interestingly, our results show that relocating the two fluorine substituents from the fluorinated benzotriazole unit to the two flanking thienyls does not negatively impact the device performance. While 4'-FT-HTAZ based BHJ device offers similar device characteristics (e.g., $J_{sc}$, $V_{oc}$ and $FF$) to those of FTAZ based one, the 3'-FT-HTAZ presents even higher device efficiency than that of FTAZ based one (7.4% vs. 6.6%), mainly due to the much improved $V_{oc}$. However, with additional two fluorine substituents on the central benzotriazole unit, i.e., converting 3'-FT-HTAZ to 3'-FT-FTAZ, this tetra-fluorinated polymer only shows an increased band gap and a reduced $J_{sc}$ value in its device, largely due to the steric hindrance from adjacent fluorine substituents. When such steric hindrance is removed in the case of 4'-FT-FTAZ, we are delighted to discover that this tetra-fluorinated polymer (4'-FT-FTAZ) based BHJ cells can not only maintain the high $J_{sc}$ and high $FF$ as FTAZ based devices do, but also achieve noticeably increased $V_{oc}$. Thus, an overall efficiency of 7.7% is obtained for 4'-FT-FTAZ based device, which is the highest in the studied set of six polymers. Our results clearly demonstrate that adding fluorine substituents to these
bridging thiophene units, if judiciously designed, can be a very effective design strategy to further enhance the efficiency of related BHJ solar cells.

4.2 Design and Synthesis

Scheme 4.1. Synthesis of the monomers containing fluorinated thiophene units.

Scheme 4.2. Synthesis of the common precursor (4.3) and the byproduct (4.14).

The key to the synthesis of these four new fluorinated PBnDT-TAZ polymers is to control the fluorination position in these two flanking thienyl units in regard to the central benzotriazole, i.e., achieving the synthesis of monomers m-3’FT-(H/F)TAZ and m-4’FT-(H/F)TAZ in Scheme 4.1. We chose Stille coupling to construct these symmetrical monomers from mono-fluorinated thiophene (FT) and (fluorinated) benzotriazole, which would require the synthesis of two isomeric mono-fluorinated thiophene units with the properly positioned trimethyl tin group (i.e.,
Compound 4.5 and Compound 4.8 in Scheme 4.1). To maximize the synthetic efficiency, a divergent route was designed, with the common precursor Compound 4.3 as the point of divergence towards Compound 4.5 and Compound 4.8. Specifically, the 2’ and 5’ positions of 3-bromothiophene (Compound 4.1) were first protected with trimethylsilyl (TMS) groups to render Compound 4.2, which was then treated with n-butyllithium and underwent electrophilic fluorination with N-fluorobenzenesulfonimide (NFSI) to offer Compound 4.3.\(^9^8\) We noticed that a significant amount of disulfide byproduct (Compound 4.14) was formed as a result of ring opening reactions of thiophene units (Scheme 4.2). We utilized \(^1\)H NMR, \(^{13}\)C NMR and mass spectrometry to characterize the chemical structure of Compound 4.14, and the chemical structure of Compound 4.14 was finally confirmed by single crystal X-ray (Figure A4). More detailed information about the formation of the byproduct can be found in Experiment Section. This issue was alleviated by adding the required amount of n-butyllithium and NFSI in several portions, which significantly improved the yield of Compound 4.3 from 10% (if added in one portion) to 50% (if added in several portions). Since the position close to the fluorine atom on the substituted thiophene 3 is more reactive, a selective bromination of the 2’ position of Compound 4.3, followed by lithium-halogen exchange and stannylation, offered the desired precursor Compound 4.5, ready for the next Stille coupling and bromination to prepare the monomer, m-3’FT-(H/F)TAZ. On the other hand, the synthesis of precursor Compound 4.8, the isomer to Compound 4.5, started with the iodination of Compound 4.3 to reach an intermediate Compound 4.6. Again, taking advantage of the more reactive 2’ position of Compound 4.6, we selectively anchored a TMS protecting group at the 2’ position, leaving 5’ position for lithium-halogen exchange and stannylation to successfully synthesize Compound 4.8. This key precursor (Compound 4.8) then underwent standard Stille coupling with (fluorinated) benzotriazole,
followed by bromination, to offer the other monomers, *m*-4′FT-(H/F)TAZ. The positions of fluorine in *m*-3′-FT-HTAZ and *m*-4′-FT-HTAZ were well explained by comparing the *H* NMR spectra of these two monomers with that of *m*-HTAZ monomer (with/without bromine groups) (Figure 4.1) and further confirmed by proton NOESY spectra (Figure 4.3). In addition, the strong 19F-19F coupling of the *m*-3′-FT-FTAZ indicated that the fluorine substituents on two flanking thienyls are close to the fluorine on the central FTAZ unit (Figure 4.2). These NMR characterizations clearly indicate the successful control of fluorination position on these flanking thienyls through our synthetic approach (Scheme 4.1). More reaction details were included in Supporting Information (Experiment Section).

**Figure 4.1.** Comparison of *H* NMR of *m*-HTAZ (before and after bromination), *m*-3′-FT-HTAZ and *m*-4′-FT-HTAZ.
Figure 4.2. Comparison of $^{19}$F NMR of monomer 3'-FT-FTAZ and 4'-FT-FTAZ.

Figure 4.3. NOESY spectrum of monomer 3'-FT-HTAZ and 4'-FT-HTAZ.

All monomers were subjected to the Stille coupling based polymerization according to Scheme 4.3, following the polymerization condition previously optimized to reach desirable molecular weight. However, given the vicinity of fluorine to the bromine on the flanking thienyl units in the case of 4'-FT monomers, the reactivity of these two monomers is affected. We noticed that, for monomer $m$-4'-FT-HTAZ, extended polymerization time and reduced ligand:catalyst ratio (3:1
of P(o-tol)$_3$ to Pd, instead of 4:1) were required to reach sufficiently high molecular weight of 32 kg/mol. As for 4’-FT-FTAZ, extended polymerization time and increased catalyst loading vs. monomers (from 2% to 4%) were required to get sufficiently high molecular weight of 21 kg/mol. Nevertheless, the molecular weight values of those two 4’-FT polymers are still relatively low when compared with other polymers in this study (Table 4.1), likely due to the low solubility of these two 4’-FT polymers. Lastly, we were able to further increase the molecular weights of these two 4’-FT polymers by adding DMF as a co-solvent for polymerization, however, the increased molecular weight further decreased the solubility of the polymer, without any noted improvement on efficiencies of related BHJ devices (Table A6 and Table A7 in Appendix). The molecular weights of the polymers were measured by high temperature gel permeation chromatography (GPC), and results were summarized in Table 4.1. More polymerization details were included in Experiment Section.

Scheme 4.3. Stille-coupling based polymerizations to create the set of six polymers.
4.3 Computation and Modeling

**Figure 4.4.** Computed twisting angles of the most stable conformation of one repeating unit.

We performed density functional theory (DFT) calculations at the DFT B3LYP/6-311+G(d) level of theory\textsuperscript{100-102} on one repeating unit of all six polymers in this study, focusing on the twisting angles between adjacent units and the energy levels of these polymers. To reduce the computation time yet still maintaining the branched nature of the side chains, isopropyl chains were used to replace the long and branched side chains in the repeating unit. **Figure 4.4** presents the most stable conformations for these six different yet structurally tightly related repeating units (i.e., the only difference being the number and positions of fluorine substituents), from which we calculated the energy levels and band gaps. The related results are summarized in **Table 4.1**. Furthermore, the computed electron distribution at ground and excited states of one repeating unit of all six polymers is provided in **Figure A4 in appendix**.

Overall, the fluorination positions of these two flanking thienyl units has a strong impact on the most stable conformation and the twisting angles between adjacent aromatic units (**Figure 4.4**); in contrast, adding two fluorine substituents to the central benzotriazole only introduce little perturbation to the conformation and the twisting angle (e.g., comparing HTAZ and FTAZ in **Figure 4.4**). Notably, adding a fluorine atom to the 3’ position of the thienyl units not only switches
the relative orientation of the central benzotriazole (TAZ) unit (in regard to the flanking thienyls) in the most stable conformation, but also slightly increases the twisting angles between the BnDT unit and the adjacent thienyl units (i.e., comparing 3’-FT-HTAZ and HTAZ). We ascribe such changes to the relative strength of different hydrogen-bonding interactions (e.g., N⋯H vs. F⋯H), the S⋯F interaction, electrostatic interactions and steric interactions.\textsuperscript{96,103} For example, the newly emerged F (on 3’-FT)⋯H (on TAZ) hydrogen bonding eliminates the N (on TAZ)⋯H (on thiophenyl) hydrogen bonding and results in flipping the central TAZ unit in 3’-FT-HTAZ. However, with two additional fluorine substituents on benzotriazole in the case of 3’-FT-FTAZ, the repulsive electrostatic interactions of F (on 3’-FT)⋯F (on fluorinated TAZ) for the conformer as shown in Figure 4.4, and F (on 3’-FT)⋯N (on fluorinated TAZ) for the other conformer where the fluorinated TAZ is flipped, significantly increase the dihedral angle between 3’-FT and the fluorinated TAZ. On the other hand, switching the fluorination from the 3’ position to the 4’ position not only allows to maintain the original conformation of the thienyl-TAZ-thienyl, also further decreases the dihedral angle between the BnDT unit and the thienyl unit likely due to the newly added S (on BnDT)⋯F (on 4’-FT) interaction. All these features lead to almost perfectly planar backbones for 4’-FT-HTAZ and 4’-FT-FTAZ, which explains the smaller band gaps of these two 4’-FT polymers calculated by DFT (Table 4.1).

4.4 Optical and Electrochemical Properties

After obtaining all six polymers in this study, we next investigated how the position and number of fluorine substituents would affect the optical properties of these polymers. As shown in Figure 4.5b, the absorption edge of 3’-FT-HTAZ is essentially identical to those of FTAZ and HTAZ, indicating a similar band gap of ~2.0 eV for these three polymers (Table 4.1). This experimental result matches very well with the similar most stable conformations for these three
polymers (Figure 4.4). In contrast, the severe steric hindrance observed in the 3’-FT-FTAZ (Figure 4.4) results in a large hypsochromic shift of its absorption edge by ~70 nm, leading to an enlarged optical band gap of 2.23 eV estimated from the onset of film absorption (Figure 4.5b). On the other hand, the almost perfect planar conjugated backbones of these two 4’-FT polymers (4’-FT-HTAZ and 4’-FT-FTAZ), as shown in Figure 4.4, shift their absorption edges to longer wavelength by ~40 nm, narrowing their band gaps to ~1.9 eV (Figure 4.5b). Interestingly, while 3’-FT-FTAZ demonstrates a further red-shift of its absorption in the solid state due to aggregation of conjugated polymers (Figure 4.5b), the individual UV-Vis absorption spectrum of the other five polymers as thin films (Figure 4.5b) is almost identical to their individual UV-Vis spectrum in solution (Figure 4.5a). This implies that the other five polymers would have a strong tendency to aggregate even in the solution state. To verify this, we measured the temperature dependent of UV-Vis absorption of each polymer solution (Figure 4.6). Indeed, the shoulder near the absorption edge of the solution UV-Vis, indicative of the aggregated state of conjugated polymers, gradually disappears at elevated temperatures. However, the threshold temperature for the complete suppression of aggregation varies: at 30 °C for 3’-FT-HTAZ, 50 °C for HTAZ, ~ 100 °C for FTAZ and ~ 100 °C for 4’-FT-HTAZ. Strikingly, for 4’-FT-FTAZ, this absorption shoulder is still visible even at 110 °C (Figures 4.6). Since this threshold temperature is believed to indicate the strength of aggregation of conjugated polymers in solution,34,88 we can estimate the strength of aggregation for these six polymers as follows: 3’-FT-FTAZ < 3’-FT-HTAZ < HTAZ < FTAZ ~ 4’-FT-HTAZ < 4’-FT-FTAZ. Apparently, the strong aggregation behavior of 4’-FT polymers and weak aggregation behavior of 3’-FT polymers in solutions can be correlated with the large difference in the planarity of conjugated backbones between 3’-FT polymers and 4’-FT polymers (Figure 4.4).
Figure 4.5. Normalized UV-Vis spectra of all six polymers (a) in their solutions in trichlorobenzene (TCB) and (b) as thin films cast from their TCB based solutions.

We estimated the highest occupied molecular orbital (HOMO) energy levels for all six polymers with cyclic voltammetry (CV). While the actual voltammograms are presented in Figure 4.7, these experimentally determined HOMO energy levels are summarized in Table 4.1, together with the HOMO levels and the LUMO (i.e., lowest occupied molecular orbital) levels calculated via DFT. While there is a noticeable difference between the experimental result and the calculated one for the HOMO energy level for each polymer – commonly observed for these conjugated polymers, the impact of fluorination on the HOMO level in this series of polymers has shown the similar trend for either calculated results or experimental ones. Specifically, adding two fluorine substituents to either the central TAZ unit (i.e., FTAZ) or to the 4’ positions of the two flanking thienyl units (i.e., 4’-FT-HTAZ) helps lower the HOMO level of fluorinated polymers by roughly the same amount (~ 0.1 eV). Furthermore, adding two more fluorine substituents to the 4’ positions of these two flanking thienyl units of FTAZ (i.e., 4’-FT-FTAZ) further deepens the HOMO level, whereas the lowest HOMO level of 3’-FT-FTAZ (isomer to 4’-FT-FTAZ) can be explained by the twisted conjugated backbone together with the four fluorine substituents.
Figure 4.6. Temperature dependent UV-Vis of polymer solutions in TCB.
Figure 4.7. Cyclic voltammetry curves of the six polymers.

Table 4.1. Molecular weights, calculated and measured energy levels and band gaps of all six polymers

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<tr>
<th>Polymers</th>
<th>$M_n$ (kg/mol)</th>
<th>$D$ (Mw/Mn)</th>
<th>HOMO$^a$ (cal, eV)</th>
<th>LUMO$^a$ (cal, eV)</th>
<th>Band Gap$^a$ (cal, eV)</th>
<th>HOMO$^b$ (CV, eV)</th>
<th>Band Gap$^c$ (opt, eV)</th>
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<td>1.90</td>
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</tbody>
</table>

$^a$ calculated by DFT; $^b$ measured by cyclic voltammetry; $^c$ band gap estimated from the onset of UV-Vis absorption of polymer films

4.5 Photovoltaic Properties

The photovoltaic properties of all six polymers were investigated in the bulk heterojunction (BHJ) solar cells with a normal device configuration: indium doped tin oxide (ITO)/copper(I) thiocyanate (CuSCN)/polymer:phenyl-C61-butyric acid methyl ester (PC$_{61}$BM)/Ca/Al. The $J$-$V$ curves and external quantum efficiency (EQE) curves of optimized devices are presented in Figure
4.8a and 4.8b, respectively, with the related device characteristics summarized in Table 4.2. Given the low HOMO levels of these polymers, we selected CuSCN, which has high ionization potential (5.5 eV),\textsuperscript{104} as the hole transporting layer (HTL) to form Ohmic contact with the BHJ blend. We also attempted to optimize the processing condition for different polymers, in particular, the solvent and additives, and the active layer thickness, in order to obtain the maximum device efficiency for each polymer based BHJ blend. It appears that chlorobenzene (CB) with 3% additive 1,8-diiodooctane (DIO) offers the best device performance for 3’-FT-HTAZ and 3’-FT-FTAZ, while TCB seems to be the best choice of solvent for the other four polymers. For comparison, we also evaluated devices employing poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) as the HTL, with the data summarized in Table A3 in Appendix. In fact, comparable device characteristics were achieved for HTAZ, FTAZ and 3’-FT-HTAZ when switching from CuSCN to PEDOT:PSS, whereas lower device performance was observed for 3’-FT-FTAZ, 4’-FT-HTAZ and 4’-FT-FTAZ with PEDOT:PSS as the HTL, mainly due to decreased $V_{oc}$ and $FF$ values.

![Figure 4.8](image.png)

**Figure 4.8.** (a) $J-V$ curves and (b) EQE spectra of BHJ solar cells based on all six polymers.
Table 4.2. Photovoltaic parameters of polymer solar cells with CuSCN as HTL

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
<th>Mobility ($\times 10^{-3}$ cm$^2$/V·s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>TCB</td>
<td>249</td>
<td>11.10±0.25</td>
<td>0.741±0.001</td>
<td>53.3±1.3</td>
<td>4.39±0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>FTAZ</td>
<td>TCB</td>
<td>308</td>
<td>12.02±0.25</td>
<td>0.805±0.001</td>
<td>68.0±1.0</td>
<td>6.58±0.21</td>
<td>1.20</td>
</tr>
<tr>
<td>3’-FT-HTAZ</td>
<td>CB+3%DIO</td>
<td>272</td>
<td>11.72±0.15</td>
<td>0.909±0.002</td>
<td>69.6±1.0</td>
<td>7.42±0.14</td>
<td>4.62</td>
</tr>
<tr>
<td>4’-FT-HTAZ</td>
<td>TCB</td>
<td>205</td>
<td>12.02±0.58</td>
<td>0.820±0.001</td>
<td>69.3±0.9</td>
<td>6.82±0.32</td>
<td>1.26</td>
</tr>
<tr>
<td>3’-FT-FTAZ</td>
<td>CB+3%DIO</td>
<td>154</td>
<td>6.01±0.27</td>
<td>0.991±0.006</td>
<td>51.2±0.8</td>
<td>3.05±0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>4’-FT-FTAZ</td>
<td>TCB</td>
<td>223</td>
<td>12.39±0.41</td>
<td>0.922±0.003</td>
<td>67.8±2.9</td>
<td>7.74±0.36</td>
<td>2.78</td>
</tr>
</tbody>
</table>

*Hole mobility of HTAZ, 3’-FT-HTAZ and 3’-FT-FTAZ based devices was measured with PEDOT:PSS as hole transporting layer.

**Short Circuit Current ($J_{sc}$)**. The first observation is that $J_{sc}$ values of BHJ devices for these three difluorinated polymers (FTAZ, 3’-FT-HTAZ and 4’-FT-HTAZ) are similar and noticeably higher than that of the non-fluorinated polymer (HTAZ) based BHJ device (Table 4.2). This clearly indicates that the fluorine can exert a similar beneficial impact on improving the $J_{sc}$ even being on these more electron-rich thienyl units. Combining fluorinated thienyls with fluorinated TAZ, i.e., 4’-FT-FTAZ, offers a negligible enhancement on the $J_{sc}$ of its BHJ device. This implies that excessive fluorination of the HTAZ polymer does not offer an additional boost to the $J_{sc}$ of its device, but it does not introduce negative influence to the $J_{sc}$, either. However, 3’-FT-FTAZ, the structural isomer to 4’-FT-FTAZ, only shows significantly reduced $J_{sc}$ with its device. This can be largely ascribed to the much-increased band gap of 3’-FT-FTAZ, due to its distorted conjugated backbone. Additionally, 3’-FT-FTAZ based BHJ device also shows significantly lower EQE values in its spectrum (Figure 4.8b) than other polymers. This is not due to an insufficient exciton quenching, since the photoluminescence (PL) quenching efficiencies of the BHJ blends based on
the four new polymers are all over 90% (Figure A85 and Table A3 in Appendix). Thus, the low EQE values in the case of 3'-FT-FTAZ is likely caused by other factors, e.g., significant loss of charge carriers to various recombinational losses due to a low hole mobility.

**Open Circuit Voltage (V_{oc})**. Though the position of two fluorine substituents on the HTAZ polymer (i.e., FTAZ, 3'-FT-HTAZ and 4'-FT-HTAZ) does not seem to affect the $J_{sc}$ values of BHJ devices, it has a strong impact on the $V_{oc}$ values. For example, relocating the two fluorine substituents from the fluorinated TAZ unit to the 4' position of the two flanking thienyl units (i.e., from FTAZ to 4'-FT-HTAZ) only offers marginal improvement of the $V_{oc}$ value (from 0.805 V to 0.820 V). However, the relocation of fluorine substituents to the 3’ position of the two flanking thienyl units (i.e., from FTAZ to 3'-FT-HTAZ) results in a significant boost of the $V_{oc}$ value to 0.909 V. Adding two more fluorine substituents onto the difluorinated polymers can further increase the $V_{oc}$ values, reaching 0.922 V for 4'-FT-FTAZ and ~1 V for 3'-FT-FTAZ. In fact, the trend of $V_{oc}$ values matches well with that of HOMO levels of these six polymers (Table 4.1): for example, the lowest HOMO level of 3'-FT-FTAZ is translated into the highest $V_{oc}$ of the corresponding BHJ device. Nevertheless, given that the value of $V_{oc}$ is affected by other factors than just the HOMO level, we will discuss the $V_{oc}$ further in the following section.

**Fill Factor (FF)**. One of the most unique features for FTAZ is the high $FF$ (~ 70%) of its BHJ device even with an active layer as thick as 300 nm.\textsuperscript{22} We are pleased to find that this desirable feature is maintained with the other two di-fluorinated polymers (3'-FT-HTAZ and 4'-FT-HTAZ) and the tetra-fluorinated 4'-FT-FTAZ, all of which show high values of $FF$ (~ 70%) in their BHJ devices (Table 4.2; complete data sets at different thickness in Table A4 and Table A5 in Appendix). In our previous study, Li et al. discovered that the high $FF$ of FTAZ was determined by its high hole mobility (on the order of $10^{-3}$ cm$^2$/V·s)).\textsuperscript{26} This high mobility enables a fast charge
extraction to the electrodes, resulting in a low steady state charge carrier density and much reduced recombination. Given the structural similarity of 3’-FT-HTAZ, 4’-FT-HTAZ and 4’-FT-FTAZ to that of FTAZ, we speculated that a high hole mobility would also be the reason of the observed high FF for these BHJ devices. This was confirmed by the measured hole mobilities for these polymers in their BHJ blends, which are all on the order of $10^{-3} \text{ cm}^2/(\text{V} \cdot \text{s})$ at different thicknesses of the active layer (Figure 4.9). On the other hand, the low hole mobility of 3’-FT-FTAZ, which is on the order of $10^{-4} \text{ cm}^2/(\text{V} \cdot \text{s})$, explains the noticeably lower FF of its BHJ device, similar to the case of HTAZ.

**Figure 4.9.** Hole mobilities at different thicknesses for the four novel polymer:PC61BM blends.

These results indicate that adding two fluorine substituents to the 4’ position on the two flanking thienyl units in the HTAZ polymer (i.e., 4’-FT-HTAZ) has almost identical impact on all device characteristics as adding two fluorine substituents to the central TAZ unit (i.e., FTAZ). Notably, substituting fluorine to the 3’ position on the two flanking thienyl units (i.e., 3’-FT-HTAZ) offers even higher device efficiency than that of FTAZ based device (7.4% vs. 6.6%), primarily due to a much increased $V_{oc}$ (0.909 V vs. 0.805 V). With a slightly higher $V_{oc}$ and $J_{sc}$ of its BHJ device than those of 3’-FT-HTAZ based device, the tetra-fluorinated 4’-FT-FTAZ further
improves the device efficiency to 7.7%. In contrast, its isomer, 3'-FT-FTAZ, suffers from a low $J_{sc}$ value and $FF$ and leads to the lowest device efficiency in those series of polymers.

4.6 CT States and Energy Loss Mechanisms

First proposed by Vandewal et al., it is generally accepted that $V_{oc}$ is primarily determined by the interfacial charge-transfer (CT) states between the donor and the acceptor materials rather than by the energy level difference between the HOMO of the donor material and LUMO level of the acceptor material. This relationship is quantitatively shown as equation (1). To further understand the trend in $V_{oc}$ values in this series of polymers, we carried out high sensitivity EQE measurements and fitted the obtained spectra (Figure A6) using equation (2) to obtain the energy of the CT state ($E_{CT}$). Furthermore, we can estimate the loss due to non-geminate recombination ($\Delta E_{NG}$) via $\Delta E_{NG} = E_{CT} - eV_{oc}$, and the charge separation energy/exciton splitting energy ($\Delta E_{CS}$) via $\Delta E_{CS} = E_{opt} - E_{CT}$, which is another significant loss mechanism. Table 4.3 summarizes all results from these calculations.

Indeed, the energy of the CT state ($E_{CT}$) linearly matches the $V_{oc}$ value, with the energy losses from $E_{CT}$ to $eV_{oc}$ are similar (~0.62 eV) for all BHJ blends and fall into the range of 0.5 to 0.7 eV, typically observed for organic solar cells. This indicates that the energy losses due to non-geminate recombination are similar for all studied BHJ systems. Thus, the observed difference in the $V_{oc}$ values is from the difference in the required energy for exciton splitting in different BHJ systems ($\Delta E_{CS} = E_{opt} - E_{CT}$). While the driving force for the exciton splitting ($\Delta E_{CS}$) is around 0.25 eV for HTAZ, FTAZ and 4'-FT-FTAZ, we obtained very low driving forces to split excitons for
3’-FT-HTAZ and 4’-FT-FTAZ (~ 0.1 eV), and an even lower driving force for 3’-FT-FTAZ (0.06 eV). Similar results (i.e., extremely low $\Delta E_{CS}$ yet highly efficient exciton splitting) have been recently reported in other systems\textsuperscript{107, 108} as well; thus, it becomes increasingly clear that a high $\Delta E_{CS}$ is not a prerequisite for efficient exciton splitting and charge generation.

Table 4.3. The energy of CT state of polymer solar cells and $V_{oc}$ loss

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{oc}$ (V)</th>
<th>$E_{opt}^*$ (eV)</th>
<th>$E_{CT}$ (eV)</th>
<th>$E_{CT} - eV_{oc}$ (eV)</th>
<th>$E_{opt} - E_{CT}$ (eV)</th>
<th>Total Loss: $E_{opt} - eV_{oc}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>0.74</td>
<td>1.66</td>
<td>1.36</td>
<td>0.62</td>
<td>0.30</td>
<td>0.92</td>
</tr>
<tr>
<td>FTAZ</td>
<td>0.80</td>
<td>1.66</td>
<td>1.42</td>
<td>0.62</td>
<td>0.24</td>
<td>0.86</td>
</tr>
<tr>
<td>3’-FT-HTAZ</td>
<td>0.91</td>
<td>1.66</td>
<td>1.54</td>
<td>0.63</td>
<td>0.12</td>
<td>0.75</td>
</tr>
<tr>
<td>4’-FT-HTAZ</td>
<td>0.82</td>
<td>1.66</td>
<td>1.44</td>
<td>0.62</td>
<td>0.22</td>
<td>0.84</td>
</tr>
<tr>
<td>3’-FT-FTAZ</td>
<td>0.99</td>
<td>1.66</td>
<td>1.60</td>
<td>0.61</td>
<td>0.06</td>
<td>0.67</td>
</tr>
<tr>
<td>4’-FT-FTAZ</td>
<td>0.92</td>
<td>1.66</td>
<td>1.56</td>
<td>0.64</td>
<td>0.10</td>
<td>0.74</td>
</tr>
</tbody>
</table>

*$E_{opt}$ of PC$_{61}$BM was used because it is the minimal $E_{opt}$ value in the BHJ blends.

4.7 Morphology

While some device characteristics of polymer solar cells can be largely correlated with the optical and electrochemical properties of the conjugated polymer employed in such a solar cell (e.g., $V_{oc}$ with the HOMO level), further understanding other characteristics – including mobility, $FF$ and $J_{sc}$ – would require insights into the morphological features of such a bulk heterojunction blend. For example, in our previous studies, Li et al. showed that increasing the molecular weight ($M_n$) of FTAZ polymer from 10 kg/mol to 40 kg/mol could induce more “face-on” orientation of the conjugated backbone, leading to a higher hole mobility.\textsuperscript{80} Furthermore, FTAZ having a higher $M_n$ (40 kg/mol) also showed a smaller domain size (~22 nm) for the polymer-enriched domains, benefiting the exciton dissociation and charge extraction.\textsuperscript{80} In this study, we continued to apply 2D grazing incidence wide angle X-ray scattering (GIWAXS) and resonant soft X-ray scattering (R-SoXS) to investigate the morphology in BHJ blends and in the neat polymer film.
Figure 4.10. 2D GIWAXS patterns of (a-d) neat polymer films, (e-h) blends of polymer.

Figure 4.11. 1D profiles of neat polymer films and polymer: PC$_{61}$BM blends.
Overall, these four new fluorinated polymers demonstrate low crystallinity in their neat polymer films, indicated by the broad (h00) diffraction peaks in their 2D GIWAX patterns (Figure 4.10 and Figure 4.11), a feature that has been also observed for analogous HTAZ and FTAZ.26 From the 2D GIWAXS patterns of neat polymer films shown in Figure 4.11 a-d, the simultaneous appearance of out-of-plane (010) and in-plane (100) observed in pure 4’-FT polymers indicates that both 4’-FT-FTAZ and 4’-FT-HTAZ preferentially form crystallites adopting face-on orientation relative to the substrates. However, distinctive trends are found for 2D GIWAXS patterns of 3’-FT polymers, where both (100) and (010) peaks display out-of-plane preference. This suggests the formation of rolling-log crystallites, which adopt statistically random orientations with the backbone direction locked within the plane parallel to the substrate.109 Furthermore, the 1D GIWAXS profiles of polymer: PC_{61}BM blends (Figure 4.11) show that the position of the PC_{61}BM diffraction peaks (q = 1.35 Å^{-1}) are similar for all blends, indicating that the fluorination on these flanking thienyl units does not change the aggregate size of PC_{61}BM in BHJ blends. In addition, the orientation preference of polymers is maintained when blended with PC_{61}BM (Figure 4.10). In fact, these features and results from 2D GIWAXS and the associated pole figures correlate strongly with the results presented earlier. For example, the orientation preference is closely related with the planarity of the polymer backbones. A planar conjugated backbone would promote the “face-on” orientation of the crystallites, as we have observed for these two 4’-FT polymers. A twisted backbone, on the other hand, would induce randomness in the orientation of the crystallites, as observed in the case of these two 3’-FT polymers as well as FTAZ. Though orientation of crystallites of those polymers are different, compared to HTAZ (0F) which showed very weak π-π stacking in blend with PC_{61}BM,26 the four fluorine-substituted polymers, 3’-FT-HTAZ, 3’-FT-FTAZ, 4’-FT-HTAZ and 4’-FT-FTAZ, show much enhanced π-π
stacking, indicated by the strong (010) peak in Figure 4.11d. This enhanced π-π stacking helps form continuous intermolecular hole transport channel traversing the thick film. However, we speculate that the severe steric hindrance between the conjugated units of 3’-FT-FTAZ would lead to much reduced intramolecular hole transport and result in the observed low hole mobility of 3’-FT-FTAZ based BHJ blends.

We further estimated the crystallinity of the polymers. The coherence length of the π-π stacking in the “face-on” crystallites of 4’-FT-FTAZ, estimated from the Scherrer’s equation110 (Figure A7 in Appendix), is 30 Å, which is noticeably larger than that of 4’-FT-HTAZ (20 Å, which probably contributes to the higher hole mobility.

As we and others have demonstrated,111-113 R-SoXS can provide overall compositional morphology including domain spacing, domain purity and orientation of polymer chains relative to D/A interface. The morphological features of the respective BHJ blends of polymer:PC61BM – probed by R-SoXS – are very similar for 3’-FT-HTAZ, 4’-FT-HTAZ and 4’-FT-FTAZ based blends (Figure A8 and Table A8 in Appendix), and are not strongly related to the device performance (Table 2). This finding is not particularly surprising, given that these four fluorinated polymers are structurally highly similar to the original FTAZ and HTAZ and no appreciable difference in morphological features for FTAZ and HTAZ was identified via R-SoXS.26

4.8 Conclusion

The most important finding in this study is that the performance-enhancing “F effect” can be well maintained when relocating these fluorine substituents from the electron deficient acceptor unit – benzotriazole in our case – to the electron rich thiophene units. This is supported by the fact that the 4’-FT-HTAZ polymer, as an isomer to the previously well-studied FTAZ polymer, offers almost identical device characteristics (Voc, Jsc, FF and mobility) to those of FTAZ based BHJ
devices. Combining this newly discovered “F (thiophene) effect” with the previously reported “F(acceptor) effect”, the tetra-fluorinated polymer, 4’-FT-FTAZ, shows the highest device performance in this series of six structurally (closely) related polymers. The over 10% increase of device efficiency of 4’-FT-FTAZ when compared with FTAZ, is mainly due to the much improved $V_{oc}$ of 4’-FT-FTAZ (0.92 V, vs. 0.80 V for FTAZ base device). This can be largely ascribed to the very low driving force for the exciton splitting in the case of 4’-FT-FTAZ ($\sim$ 0.1 eV), which reduces the loss from the band gap to $V_{oc}$ (i.e., small $V_{oc}$ loss).

Though the morphological features for these new fluorinated thiophene based polymers (3’-FT-HTAZ, 4’-FT-HTAZ and 4’-FT-FTAZ) are largely similar (e.g., domain spacing and domain purity), the position of these fluorine substituents on these flanking thiophenes (3’ vs 4’) appears to have subtle impact on the molecular packing. For example, more “face-one” orientation of the conjugated backbone in the BHJ blend is observed for these two 4’-FT polymers, while a more “rolling log” like orientation is implied for these two 3’-FT polymers. Nevertheless, we want to emphasize that these are very minute differences, which do not seem to have a dramatic effect on key device characteristics ($V_{oc}$, $J_{sc}$, FF and mobility).

In conclusion, we have discovered another version of the “F effect”, coined as “F (thiophene) effect”, with a series of PBnDT-TAZ polymers with varying number and position of fluorine substituents. Since many conjugated polymers with exceptional photovoltaic performance have a “donor-thiophene-acceptor-thiophene” pattern in their repeating units, it is very likely that incorporating these newly discovered mono-fluorinated thiophenes into their conjugated repeating units can boost the device efficiency even further by taking advantage of the performance-enhancing “F (thiophene) effect”.

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4.9 Experiment Section

Chemicals and Methods

All chemicals were purchased from commercial source (Sigma-Aldrich, Fisher, Matrix, etc.) and were used as received except when specified. THF was distilled over sodium and benzophenone before use. Anhydrous toluene was purchased in sealed bottle from Fisher. Anhydrous o-xylene was purchased in sealed bottle from Sigma-Aldrich. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (Pd$_2$dba$_3$·CHCl$_3$) was purchased from Sigma-Aldrich and was recrystallized in chloroform/acetone. Tri(o-tolyl)phosphine (P(o-tol)$_3$) was recrystallized in hexanes. For reactions under argon, the glassware was evacuated and refilled with argon for three times and charged with reactants.

Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument, using 1,2,4-trichlorobenzene (TCB) as the eluent (stabilized with 125 ppm BHT) at150 °C, or performed on Agilent PL220 instrument with TCB as the eluent (stabilized with 250 ppm BHT) at160 °C. The obtained molecular weight is relative to the polystyrene standard. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometers (400 MHz, 500 MHz or 600 MHz). Mass Spectrometry was run on a Q Exactive Orbitrap (ThermoFisher, Bremen, Germany) mass spectrometer and analyzed via Xcalibur (ThermoFisher, Bremen, Germany). UV-visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). Elemental analysis was done by Atlantic Microlab, Inc.
Cyclic Voltammetry (CV). CV measurements were carried out on solid films using a Bioanalytical Systems (BAS) Epsilon potentiostat with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, Ag reference electrode and Pt counter electrode were used. Films were drop-cast onto the glassy carbon electrode from hot chloroform solution (2 mg/mL, with tetrabutylammonium hexafluorophosphate added at 100% wt% relative to polymers) and dried using a heat gun. 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were carried out under argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential \(E_{\text{ox}}\) according to the following equation:

\[
HOMO = -[4.8eV + e(E_{\text{ox}} - E_{Fc/Fc^+})]
\]

Photovoltaic Device Fabrication. Glass substrates coated with patterned indium doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. The sputtered ITO had a thickness of ~150 nm and a resistivity of 20 \(\Omega/\square\). Prior to use, the substrates were ultrasonicated in deionized water, acetone, and then 2-propanol for 15 minutes each. The substrates were dried under a stream of nitrogen gas and subjected to the treatment of UV-Ozone for 15 min. A filtered dispersion of PEDOT:PSS in water (Clevios™ PH500 from Heraeus) was then spun cast onto cleaned ITO substrates at 4000 rpm for 60 s and then baked at 130 °C for 15 min in air to give a thin film with a thickness of about 40 nm. For devices with CuSCN as the buffer layer, the CuSCN was dissolved in diethylsulfide with a concentration of 22.7 mg/mL under stirring for 1 h. Then the CuSCN solution was filtered by 0.2 \(\mu\)m poly(tetrafluoroethylene) (PTFE) filter and spun-cast onto the cleaned ITO substrates at 7000 rpm for 60 s and then baked at 100 °C for 15 min in air to give a thin film with a thickness of ~ 40 nm. For FTAZ, HTAZ, 4’-FT-FTAZ, 4’-FT-HTAZ, blends of
polymer:PC$_{61}$BM (1:2 w/w) were dissolved in 1,2,4-trichlorobenzene with heating at 130 °C for 6 h. For 3'-FT-HTAZ and 3'-FT-FTAZ, blends of polymer:PC$_{61}$BM (1:2 w/w) were dissolved in chlorobenzene with 3vol% DIO with heating at 110 °C for 6 h and cooled to 80 °C before spin coating. All solutions were filtered through a 5.0 µm PTFE filter and spun-cast at an pre-selected rpm for 60 seconds onto the PEDOT:PSS or CuSCN layer for conventional structure. For FTAZ, HTAZ, 4'-FT-FTAZ, 4'-FT-HTAZ, the substrates were transferred into vacuum chamber immediately after spin-coating and then dried at 30 mmHg below atmosphere for 30 min. For 3'-FT-HTAZ and 3'-FT-FTAZ, the films were kept in covered petri disk overnight after spin-coating. The devices were finished for measurement after the thermal deposition of a 30 nm film of calcium and a 70 nm aluminum film as the cathode for the conventional structure at a base pressure of 2 × 10$^{-6}$ mbar. There were 8 devices per substrate, with an active area of 13 mm$^2$ per device. Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW/cm$^2$ (Oriel 91160, 300 W) calibrated by an NREL certified standard silicon cell. Current density versus voltage (J-V) curves was recorded with a Keithley 2400 digital source meter. EQE was detected under monochromatic illumination (OrielCornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode (Model No.: Newport 71580). All fabrication steps after adding the PEDOT:PSS or CuSCN layer onto ITO substrate, and characterizations were performed in gloveboxes under nitrogen atmosphere.

**SCLC Hole Mobility.** SCLC hole mobility was acquired through the hole-only devices with a configuration the same as optimal photovoltaic device except changing the cathode of Ca/Al to MoO$_3$ 10 nm/Al. The experimental dark current densities $J$ of polymer:PC$_{61}$BM blends were measured when applied with voltage from 0 V to 5 V. The applied voltage $V'$ was corrected from
the voltage drop $V_{rs}$ due to the series resistance and contact resistance from ITO/PEDOT:PSS or ITO/CuSCN, which were measured from a reference device without the layer of polymer:PC$_{61}$BM. From the plots of $J^{0.5}$ vs $V$, hole mobilities of copolymers was deduced from the Mott-Gurneys law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h V^2 \frac{V}{L^3}$$

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the dielectric constant of the polymer which is assumed to be around 3, $\mu_h$ is the hole mobility, $V$ is the voltage drop across the device, and $L$ is the film thickness of the active layer.

*High sensitive EQE to Determine the CT State.* The high sensitive EQE measurement was performed at NCSU for 3’-FT-FTAZ:PC$_{61}$BM, 4’-FT-HTAZ:PC$_{61}$BM and 4’-FT-FTAZ:PC$_{61}$BM, while high sensitive EQE for HTAZ:PC$_{61}$BM, FTAZ:PC$_{61}$BM and 3’-FT-HTAZ:PC$_{61}$BM was measured at UNC. High sensitive EQE measurements at NCSU were conducted using an in-house setup consisting of a Xenon DC arc lamp, an ORIEL 74125 monochromator, a Keithley 428 current amplifier, an SR 540 chopper system and a Stanford Research Systems SR830 DSP lock-in amplifier. For the calibration of the spectrum, a Si and a Ge photodiode purchased from Newport Corporation were used as necessary. A 700 nm and 1000 nm long-pass filters were used in order to isolate the desired part of the spectrum for the monitoring of the sub-bandgap response. The high sensitive EQE measurement at UNC was conducted using a similar in-house setup except that a monochromatic illumination (OrielCornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), a monocrystalline silicon diode (Model No.: Newport 71580) for calibration, and a 665 nm long-pass filters (Thorlabs FGL665S) was used accordingly and the signal was recorded by SR830 DSP lock-in amplifier in current mode without using the Keithley 428 current amplifier.
**Density Functional Theory Calculation.** DFT calculations were performed to obtain the optimized structure, the electron density distributions, and HOMO and LUMO energy levels for one repeating unit of each of six conjugated polymers studied in this work. The calculations were carried out at the DFT B3LYP/6-311+G(d) level of theory.\textsuperscript{100-102} HOMO and LUMO surfaces were plotted with GaussView version 5.0.8. All quantum mechanical calculations have been carried out using Gaussian 09 version E.01 package\textsuperscript{114} with no symmetry constraint, tight self-consistent field (SCF) convergence criteria, and ultrafine integration grids. After a full geometry optimization, a single point frequency calculation was performed to verify that the structures obtained were indeed a minimum on the potential energy surface with no imaginary frequency.

**Grazing Incidence Wide Angle X-ray Scattering.** GIWAXS was measured at beamline 7.3.3 of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.\textsuperscript{115} The 10 keV. X-ray beam was incident at a grazing angle of 0.13 °, which maximized the scattering intensity from the samples and minimized the scattering intensity from the substrate. The scattered intensity was detected with a Dectris Pilatus 1M photon counting detector.

**Resonant Soft X-ray Scattering.** R-SoXS was measured at beamline 11.0.1.2 of the ALS\textsuperscript{72} on blend films. Data were acquired at the photon energy of 283.6 eV where the contrast between polymer and fullerene is relatively high enough for these materials, yet does not lead to beam damage or background fluorescence.

**Single crystal X-ray diffraction** data were collected using a Bruker D8 ADVANCE Series II at room temperature. The crystal structures were solved and refined by Shelx1 and Olex software.\textsuperscript{116,117}
Synthesis of monomers


Synthesis of (3-bromothiophene-2,5-diy)b(is(trimethylsilane) (Compound 4.2, under argon) LDA was prepared in following method before use: diiso-propylamine was distilled over KOH, and n-butyllithium (2.5 M in hexanes, 64.4 mL, 161 mmol) was added to the solution of diiso-propylamine (21.25 g, 210 mmol) at –78 °C in THF slowly and was stirred for 30 min. LDA solution was added to solution of 3-bromothiophene (11.41 g, 70 mmol) in THF at –78 °C. And the reaction mixture was stirred at –78 °C for 1 hour and then at r.t for 2 hours. The reaction was cooled down to –78 °C prior to the addition of trimethylsilyl chloride (19.77 g, 182 mmol). The reaction mixture was stirred at r.t. overnight. Then the reaction mixture was poured into a mixture of water and ethyl acetate (1:1). The aqueous layer was extracted with Ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The crude product was purified through silica column chromatography (hexanes as the eluent). Yield: colorless oil, 20.0 g, 93%. ¹H NMR (400 MHz, chloroform-d) δ 7.20 (s, 1H), 0.40 (s, 9H), 0.31(s, 9H). ¹³C NMR (126 MHz, chloroform-d) δ 146.68, 139.93, 138.97, 118.27, -0.07, -0.55.

Synthesis of (3-fluorothiophene-2,5-diy)b(is(trimethylsilane) (Compound 4.3, under argon) Method 1: To a solution of Compound 4.2 (1.54 g, 5 mmol) in THF, n-butyllithium solution (2.5 M in hexanes) was added slowly at –78 °C and was stirred for 15 min at –78 °C before addition of N-Fluorobenzenesulfonylimide (NFSI) solution in THF. The reaction was stirred
at – 78 °C for 2 hours and slowly warmed to r.t. overnight. The reaction mixture was then poured into a mixture of water and ethyl acetate (1:1). The aqueous layer was extracted with Ethyl acetate (∗ 2), and the combined organic layer was washed with water (∗ 2) and brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The crude product was purified through silica column chromatography (hexanes as eluent). Yield: colorless oil, 0.13 g, 10%

**Compound 4.14** was obtained as pale brown solid and was further purified via recrystallization in methanol.

**Method 2**: To a solution of **Compound 4.2** (6.15 g, 20 mmol), n-butyllithium solution (2.5 M in hexanes, 2.4 mL, 6 mmol, 0.3 eq) was added slowly at – 78 °C and was stirred for 15 min at – 78 °C before addition of NFSI (1.9 g, 6 mmol, 0.3 eq) solution in THF. The reaction was stirred at – 78 °C for 45 min. Second portion of n-butyllithium (6 mmol, 0.3 eq) was added at – 78 °C and stirred for 15 min before the addition of the second portion of NFSI (6 mmol, 0.3 eq) solution in THF. The reaction was stirred for an additional 45 min. The rest part of n-butyllithium (0.2 eq ∗ 3) was added in three portions, and after the addition of each portion of n-butyllithium solution (stirred for 15 min), NFSI (0.2 eq ∗ 2 + 0.4 eq) solution in THF was added and stirred for 45 min before the addition of the next portion of n-butyllithium solution. When all the NFSI solution was added, the reaction was stirred for 2 hours at – 78 °C and slowly warm to r.t. overnight. The reaction was then poured into a mixture of water and ethyl acetate (1:1). The aqueous layer was extracted with Ethyl acetate (∗ 2), and the combined organic layer was washed with water (∗ 2) and brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The crude product was purified through silica column chromatography (hexanes as eluent). Yield: colorless oil, 1.47 g, 30%.
Method 3: To the solution of Compound 4.2 (4.82 g, 15.68 mmol) and NFSI (5.93 g, 18.81 mmol) in THF, n-butyllithium solution (2.5 M in hexanes, 3.13 mL, 7.84 mmol) was added slowly at – 78 °C. The reaction mixture was stirred for 45 min at – 78 °C prior to the addition of the second portion of n-butyllithium solution (2.5 M hexanes, 3.13 mL, 7.84 mmol). After 45 min, the third portion of n-butyllithium solution (2.5 M hexanes, 3.13 mL, 7.84 mmol) was added and stirred for 15 min. Then NFSI (3.95 g, 12.54 mmol) solution in THF was added to the reaction and stirred for 45 min before the addition of the fourth portion of n-butyllithium solution (2.5 M hexanes, 5.0 mL, 12.54 mmol). The reaction mixture was stirred for 2 hr at – 78 °C and slowly warm to r.t. overnight. The reaction was then poured into a mixture of water and ethyl acetate mixture (1:1). The aqueous layer was extracted with Ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The crude product was purified through silica column chromatography (hexanes as eluent). Yield: colorless oil, 2.30 g, 53%. 1H NMR (400 MHz, chloroform-d): δ 6.96 (s, 1H), 0.32 (s, 9H), 0.30 (s, 9H). 13C NMR (126 MHz, chloroform-d): δ 165.82 - 163.76 (d, J = 259.6 Hz), 145.68, 124.48 -124.25 (dd, J = 28.98 Hz, 1.26 Hz), 120.91 -120.67 (d, 3.02 Hz), 0.23, 0.31. 19F (376 MHz, chloroform-d) δ -122.54.

**1,2-bis((Z)-1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)disulfane (Compound 4.14)**

![Chemical Structure (left) and single crystal structure of Compound 4.14.](image)
Mass spectrometry for C_{20}H_{38}S_{2}Si_{4} (M/z, APPI): calc. 454.149215, found 454.14918. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) δ 5.80 (2H), 0.27 (18H), 0.21 (18H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 159.74, 115.29, 105.77, 100.99, 0.06, 0.01.

Crystal data of **Compound 4.14.** C\(_{20}\)H\(_{38}\)S\(_{2}\)Si\(_{4}\), M = 454.98, Orthorhombic, Pbca, a = 13.0804(7) Å, b = 20.2601(11) Å, c = 22.1465(11) Å, V = 5869.0(5) Å\(^3\), Z = 8, D\(_{calc}\) = 1.030 g·cm\(^{-3}\), F(000) = 1968.0, μ = 0.349 mm\(^{-1}\), T = 293 K, 34701 reflections measured, 5540 unique reflections (R\(_{int}\) = 0.0491), 3980 observed reflections [I > 2σ(I)] with R1 (wR2) = 0.0391 (0.0961), R1 (wR2) = 0.0635 (0.1085) (all data), GOF = 1.018. CCDC 1556487.

**Synthesis of (5-bromo-4-fluorothiophen-2-yl)trimethylsilane (Compound 4.4)** To a solution of **Compound 4.3** (0.39 g, 1.59 mmol) in 15 mL dichloromethane and 5 mL acetic acid, NBS (0.30 g, 1.67 mmol) was added. The reaction was stirred in dark at r.t. overnight before it was poured into a mixture of water and ethyl acetate (1:1). The aqueous layer was extracted with Ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and brine. The organic solution was dried over magnesium sulfate and concentrated with rotavap. The crude product was purified through silica column chromatography (hexanes as eluent). Yield: colorless oil, 0.33 g, 83%. \(^{1}\)H NMR (400 MHz, chloroform-d) δ 6.86 (d, J = 1.7 Hz, 1H), 0.29 (s, 9H). \(^{13}\)C NMR (126 MHz, chloroform-d) δ 157.37 (d, J = 263.0 Hz), 140.62, 123.18 (dd, J = 22.7, 1.5 Hz), 95.98 (d, J = 23.3 Hz), -0.44. \(^{19}\)F NMR (376 MHz, chloroform-d) δ -128.37.

**Synthesis of (4-fluoro-5-(trimethylstannyl)thiophen-2-yl)trimethylsilane (Compound 4.5, under argon)** To a solution of **Compound 4.4** (1.80 g, 7.11 mmol) in THF, \(n\)-butyllithium solution (2.5 M in hexanes, 3.10 mL, 7.82 mmol) was added slowly at – 78 °C and stirred for 15 min before addition of trimethyltin chloride solution (1.0 M in hexanes, 9.25 mL, 9.25 mmol). The
reaction was stirred for 25 min at – 78 °C and put into water bath and stirred for 90 min before it was poured into a mixture of water and ethyl acetate mixture (1:1). The aqueous layer was extracted with ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The product was good for use of the following coupling reaction. Yield: colorless solid, 2.30 g, 96%. $^1$H NMR (400 MHz, chloroform-d) $\delta$ 7.01 (d, $J = 2.4$ Hz, 1H), 0.39 (s, 9H), 0.30 (s, 9H). $^{13}$C NMR (126 MHz, chloroform-d) $\delta$ 165.80 (d, $J = 253.4$ Hz), 147.26, 123.59 (d, $J = 30.4$ Hz), 118.30 (d, $J = 42.4$ Hz), -0.17, -8.24. $^{19}$F NMR (376 MHz, chloroform-d) $\delta$ -123.38.

**Synthesis of 3-fluoro-2,5-diiodothiophene (Compound 4.6, under argon)**

To a solution of Compound 4.3 (3.53 g, 14.32 mmol) in dichloromethane, ICl solution (1.0 M in dichloromethane, 30.7 mL, 30.7 mmol) was added at 0 °C slowly. The reaction was stirred for 3 hr before it was poured into a mixture of water and ethylacetate (1:1). The aqueous layer was extracted with Ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and Brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The crude product was purified through a small silica column chromatography with hexanes as eluent. Yield: colorless oil, 4.0 g, 83%. $^1$H NMR (400 MHz, chloroform-d) $\delta$ 6.87 (d, $J = 1.8$ Hz, 1H). $^{13}$C NMR (151 MHz, chloroform-d) $\delta$ 160.30 (d, $J = 263.2$ Hz), 126.67 (d, $J = 26.8$ Hz), 75.09 (d, $J = 10.0$ Hz), 55.96 (d, $J = 27.2$ Hz). $^{19}$F NMR (376 MHz, chloroform-d) $\delta$ -116.97.

**Synthesis of (3-fluoro-5-iodothiophen-2-yl)trimethylsilane (Compound 4.7, under argon)**

To the solution of Compound 4.6 in THF (4.06 g, 11.47 mmol), n-butyllithium solution (2.5 M in hexanes, 4.82 mL, 12.04 mmol) was added slowly at -78 °C and stirred for 20 min before addition of trimethylsilyl chloride (1.43 g, 13.2 mmol). The reaction was stirred -78 °C for 2 hr and moved to r.t for 2 hr before it was poured into a mixture of water and ethylacetate (1:1). The aqueous layer
was extracted with ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and Brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The product was purified via silica column chromatography (hexanes as eluent). Yield: colorless oil, 3.36 g, 97%. $^1$H NMR (400 MHz, chloroform-d) δ 6.97 (1H), 0.30 (9H). $^{13}$C NMR (151 MHz, chloroform-d) δ 162.27 (d, $J=259.7$ Hz), 127.29 (d, $J=30.7$ Hz), 123.04 (d, $J=30.9$ Hz), 76.60 (d, $J=9.4$ Hz), -0.54. $^{19}$F NMR (376 MHz, chloroform-d) δ -117.32.

**Synthesis of (3-fluoro-5-(trimethylstanny1)thiophen-2-yl)trimethylsilane (Compound 4.8, under argon)**

To the solution of Compound 4.7 (3.24 g, 10.79 mmol) in THF, n-butyllithium solution (2.5 M in hexanes, 4.96 mL, 12.41 mmol) was added slowly at -78 °C under Argon and stirred for 45 min before trimethyltin chloride solution (1.0 M in hexanes, 14.0 mL, 14.0 mmol) was added. The reaction was stirred -78 °C for 10 min and moved to r.t for 2 hr before it was poured into a mixture of water and ethylacetate (1:1). The aqueous layer was extracted with Ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and Brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The product was good for use of the following coupling reaction. Yield: colorless oil, 3.47 g, 95%. $^1$H NMR (400 MHz, chloroform-d) δ 6.91 (d, $J=2.2$ Hz, 1H), 0.36 (s, 9H), 0.32 (s, 9H). $^{13}$C NMR (151 MHz, chloroform-d) δ 165.13 (d, $J=260.5$ Hz), 143.58, 125.39 (d, $J=27.9$ Hz), 121.03 (d, $J=31.1$ Hz), -0.42, -8.30. $^{19}$F NMR (376 MHz, chloroform-d) δ -124.03.

**Synthesis of 2-(2-butyloctyl)-4,7-bis(3-fluoro-5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 4.10) and 2-(2-butyloctyl)-5,6-difluoro-4,7-bis(3-fluoro-5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 4.10’)** (under argon)

To the solution of Compound 4.5 (2.5 eq) and 4,7-dibromo-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (Compound 4.9, 1.0 eq) or 4,7-dibromo-2-(2-butyloctyl)-5,6-difluoro-
2H-benzo[d][1,2,3]triazole (Compound 4.9', 1.0 eq) in anhydrous toluene, bis(triphenylphosphine)palladium(ii) dichloride (0.03 eq) was added under argon stream. The mixture was purged with argon for 15 min before refluxed for 2 days. Then toluene was removed via rotovap. And the reaction mixture was purified through silica gel column. For Compound 4.10, hexanes/dichloromethane = 12/1 to 8/1 as eluent for column, yield: yellow solid, 43%. Mass spectrometry for C₃₂H₄₇N₅F₂S₂Si₂ ([M]/z, APPI): cal 631.27180, found 631.27003. ¹H NMR (500 MHz, chloroform-d) δ 7.90 (s, 2H), 7.06 (s, 2H), 4.78 (d, J = 6.2 Hz, 2H), 2.28 (m, 1H), 1.49 – 1.22 (m, 16H), 1.01 – 0.79 (m, 6H), 0.37 (s, 18H). ¹³C NMR (126 MHz, chloroform-d) δ 156.93 (d, J = 267.1 Hz), 141.92, 139.94 (d, J = 4.6 Hz), 124.14 (d, J = 5.0 Hz), 123.99 (d, J = 8.1 Hz), 122.30 (d, J = 12.4 Hz), 120.65 (d, J = 4.0 Hz), 59.67, 39.26, 32.05, 31.64, 31.32, 29.76, 28.71, 26.52, 23.18, 22.86, 14.38, 14.29, -0.27. ¹⁹F NMR (376 MHz, chloroform-d). δ -126.06.

For Compound 4.10', hexanes/dichloromethane = 14/1 to 10/1 as eluent for column, yield: pale yellow solid, 65%. Mass spectrometry for C₃₂H₄₅N₅F₄S₂Si₂ ([M]/z, APPI): cal 667.25295, found 667.25140. ¹H NMR (500 MHz, chloroform-d) δ 7.08 (s, 2H), 4.66 (d, J = 6.6 Hz, 2H), 2.32 – 2.18 (m, 1H), 1.37 – 1.20 (m, 16H), 1. – 0.77 (m, 6H), 0.37 (s, 18H). ¹³C NMR (126 MHz, chloroform-d) δ 157.31 (d, J = 269.8 Hz), 148.71 (d, J = 19.1 Hz), 146.68 (d, J = 19.1 Hz), 142.57 (d, J = 4.0 Hz), 140.15 – 136.84 (m), 123.85 (d, J = 23.9 Hz), 114.48 (d, J = 17.8 Hz), 108.18 – 106.48 (m), 60.30, 39.24, 31.96, 31.51, 31.19, 29.71, 28.57, 26.37, 23.13, 22.81, 14.26, -0.32. ¹⁹F NMR (376 MHz, chloroform-d) δ -121.30 – -122.18 (m), -131.91 – -132.91 (m).

**Synthesis of 4,7-bis(5-bromo-3-fluorothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (Compound 4.11) and 4,7-bis(5-bromo-3-fluorothiophen-2-yl)-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (Compound 4.11’) (under argon)** To the
solution of **Compound 4.10** (1.0 eq) or **Compound 4.10’** (1.0 eq) in dichloromethane : acetic acid = 10 : 1, NBS (2.05 eq) was added under argon. The reaction mixture was stirred in dark at r.t. under argon overnight. Then the reaction mixture was poured into a mixture of water and ethylacetate (1:1). The aqueous layer was extracted with Ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and Brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. The crude product was purified through silica gel column (hexanes/dichloromethane = 10/1), and the monomers were further recrystallized in ethanol.

For **Compound 4.11**, yellow solid, 68%. Mass spectrometry for C$_{32}$H$_{30}$N$_3$F$_2$S$_2$Br$_2$ ([M+H]$^+$/z, ESI): cal 644.02103, found 644.02153. $^1$H NMR (500 MHz, chloroform-d) δ 7.84 (s, 2H), 6.95 (s, 2H), 4.73 (d, $J = 6.3$ Hz, 2H), 2.24 (p, $J = 6.3$ Hz, 1H), 1.56 – 1.00 (m, 12H), 1.06 – 0.41 (m, 6H). $^{13}$C NMR (126 MHz, chloroform-d) δ 153.98 (d, $J = 267.7$ Hz), 141.25, 123.98 (d, $J = 12.6$ Hz), 120.85 (d, $J = 27.9$ Hz), 119.79 – 119.59 (m), 119.33 (d, $J = 11.2$ Hz), 113.29 (d, $J = 13.4$ Hz), 39.36, 32.08, 31.61, 31.40, 29.82, 28.70, 26.42, 23.22, 22.89, 14.34, 14.31. $^{19}$F NMR (376 MHz, chloroform-d) δ -121.40.

For **Compound 4.11’**, pale yellow solid, 40%. Mass spectrometry for C$_{32}$H$_{28}$N$_3$F$_4$S$_2$Br$_2$ ([M+H]$^+$/z, ESI): cal 680.00218, found 680.00302. $^1$H NMR (400 MHz, chloroform-d) δ 7.01 (s, 2H), 4.64 (d, $J = 6.7$ Hz, 2H), 2.42 – 2.01 (m, 1H), 1.45 – 1.06 (m, 16H), 0.88 (M, 6H). $^{13}$C NMR (151 MHz, chloroform-d) δ 154.20 (d, $J = 270.5$ Hz), 148.57 (d, $J = 19.6$ Hz), 146.87 (d, $J = 19.4$ Hz), 138.51 – 136.69 (m), 120.81 (d, $J = 27.2$ Hz), 114.77 (d, $J = 12.0$ Hz), 111.17 (d, $J = 16.6$ Hz), 108.36 – 105.79 (m), 60.34, 39.13, 31.81, 31.27, 31.04, 29.58, 28.39, 26.10, 22.98, 22.68, 14.14, 14.09. $^{19}$F NMR (376 MHz, chloroform-d) δ -116.01 (d, $J = 36.4$ Hz), -129.52 – -132.17 (m).
Synthesis of 2-(2-butyloctyl)-4,7-bis(4-fluoro-5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 4.12) and 2-(2-butyloctyl)-5,6-difluoro-4,7-bis(4-fluoro-5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 4.12’) (under argon)

To the solution of Compound 4.8 (2.5 eq) and Compound 4.9 (1.0 eq) or Compound 4.9’ (1.0 eq) in anhydrous toluene, bis(triphenylphosphine)palladium(ii) dichloride (0.03 eq) was added under argon stream. The mixture was purged with argon for 15 min before refluxed for 2 days. Then toluene was removed via rotovap. And the reaction mixture was purified through silica gel column.

For Compound 4.12, hexanes/dichloromethane = 20/1 as eluent for column, yellow solid, 36%.

Mass spectrometry for C$_{32}$H$_{47}$N$_3$F$_4$S$_2$Si$_2$ ([M]/z, APPI): cal 631.27180, found 631.26980. 1H NMR (400 MHz, chloroform-d) δ 7.86 (s, 2H), 7.59 (s, 2H), 4.75 (d, J = 6.5 Hz, 2H), 2.30 (q, J = 6.2 Hz, 1H), 1.46 – 1.07 (m, 16H), 0.88 (dt, J = 21.2, 6.9 Hz, 6H), 0.39 (s, 18H). 13C NMR (151 MHz, chloroform-d) δ 163.29 (d, J = 255.8 Hz), 142.68 (d, J = 8.1 Hz), 141.63, 123.52, 121.84, 117.93 (d, J = 31.5 Hz), 115.57 (d, J = 30.4 Hz), 59.93, 39.12, 31.83, 31.40, 31.15, 29.59, 28.48, 26.22, 22.99, 22.67, 14.12, 14.08, -0.40. 19F NMR (376 MHz, chloroform-d) δ -117.52.

For Compound 4.12’, hexanes/dichloromethane = 30/1 as eluent for column, yellow solid, 60%.

Mass spectrometry for C$_{32}$H$_{45}$N$_3$F$_4$S$_2$Si$_2$ ([M]/z, APPI): cal 667.25295, found 667.25124. 1H NMR (400 MHz, chloroform-d) δ 8.05 (s, 2H), 4.74 (d, J = 6.4 Hz, 2H), 2.38 – 2.08 (m, 1H), 1.49 – 1.17 (m, 16H), 1.01 – 0.72 (m, 6H), 0.40 (s, 18H). 13C NMR (151 MHz, chloroform-d) δ 163.09 (d, J = 254.8 Hz), 148.28 (d, J = 19.4 Hz), 146.59 (d, J = 19.6 Hz), 137.30 – 137.08 (m), 135.43 (d, J = 8.9 Hz), 120.38 (d, J = 32.1 Hz), 118.41 (d, J = 29.5 Hz), 109.81 (d, J = 10.5 Hz), 59.93, 39.09, 31.83, 31.41, 31.14, 29.57, 28.49, 26.25, 22.97, 22.67, 14.12, 14.08, -0.45. 19F NMR (376 MHz, chloroform-d) δ -119.68, -133.86.
Synthesis of 4,7-bis(5-bromo-4-fluorothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (Compound 4.13) and 4,7-bis(5-bromo-4-fluorothiophen-2-yl)-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (Compound 4.13′) (under argon) To the solution of Compound 4.12 (1 eq) or Compound 4.12′ (1 eq) in dichloromethane : acetic acid = 10 : 1), NBS (2.05 eq) was added under argon. The reaction mixture was stirred in dark at r.t. under argon for 2 days. Then the reaction mixture was poured into a mixture of water and ethylacetate (1:1). The aqueous layer was extracted with ethyl acetate (× 2), and the combined organic layer was washed with water (× 2) and Brine. The organic solution was dried over magnesium sulfate and concentrated with rotovap. And the crude product was purified through silica gel column (hexanes/dichloromethane = 20/1 as eluent), and the monomers were further recrystallized.

For Compound 4.13, recrystallized in ethanol, yellow solid, 60%. Mass spectrometry for C$_{32}$H$_{30}$N$_3$F$_2$S$_2$Br$_2$ ([M+H]/z, ESI): cal 644.02103, found 644.02131. $^1$H NMR (400 MHz, chloroform-d) δ 7.74 (s, 2H), 7.51 (s, 2H), 4.75 (d, $J$ = 6.6 Hz, 2H), 2.51 – 2.07 (m, 1H), 1.47 – 1.19 (m, 11H), 1.08 – 0.80 (m, 5H). $^{13}$C NMR (101 MHz, chloroform-d) δ 156.20 (d, $J$ = 260.0 Hz), 141.35, 137.68 (d, $J$ = 8.6 Hz), 123.02 (d, $J$ = 2.2 Hz), 121.34, 116.46 (d, $J$ = 26.3 Hz), 92.34 (d, $J$ = 22.1 Hz), 60.04, 39.17, 31.84, 31.42, 31.19, 29.60, 28.48, 26.19, 22.99, 22.67, 14.09. $^{19}$F NMR (376 MHz, chloroform-d) δ -125.25.

For Compound 4.13′, recrystallized in iso-propanol, yellow solid, 90%. Mass spectrometry for C$_{32}$H$_{28}$N$_3$F$_4$S$_2$Br$_2$ ([M+H]/z, ESI): cal 680.00218, found 680.00300. $^1$H NMR (400 MHz, chloroform-d) δ 7.97 (s, 2H), 4.74 (d, $J$ = 6.5 Hz, 2H), 2.35 – 2.11 (m, 1H), 1.46 – 1.20 (m, 16H), 0.99 – 0.70 (m, 6H). $^{13}$C NMR (151 MHz, chloroform-d) δ 156.09 (d, $J$ = 259.2 Hz), 148.24 (d, $J$ = 20.1 Hz), 146.55 (d, $J$ = 19.7 Hz), 136.87 (t, $J$ = 4.1 Hz), 130.77 (d, $J$ = 9.7 Hz), 119.40 (dd, $J$ =
26.8, 3.2 Hz), 110.25 – 107.77 (m), 95.18 (dt, J = 22.3, 4.9 Hz), 60.09, 39.19, 31.85, 31.40, 31.16, 29.60, 28.48, 26.21, 23.00, 22.68, 14.11, 14.10. $^{19}$F NMR (376 MHz, chloroform-d) $\delta$ -126.85, -133.63.

**Synthesis of polymers**

BnDT monomer, TAZ monomers, Pd$_2$(dba)$_3$·CHCl$_3$ and P(o-tol)$_3$ were charged into a 10 mL vial designed for microwave reactor. The mixture was evacuated and refilled with argon for three cycles before addition of anhydrous o-xylene under argon stream. The reaction was heated up to 200 °C and hold for some time in a CEM microwave reactor (the polymerization time for each polymer was provided in the following part). After the polymerization, the crude polymer was dissolved in hot chlorobenzene and precipitated into stirring methanol. The collected polymer was extracted via a Soxhlet extractor with EtOAc, hexanes and chloroform. The polymer solution in chloroform was concentrated via rotavap. The collected polymer was re-dissolved into hot chlorobenzene and precipitated into methanol. The polymer was then collected via filtration and dried under vacuum.

**Optimized polymerization conditions (molecular weight shown in table 1):**

**HTAZ:** $m$-BnDT/$m$-HTAZ/ Pd$_2$(dba)$_3$·CHCl$_3$/ P(o-tol)$_3$ = 1.030/1.000/0.020/0.160. Polymerization time: 10 min. $M_n = 70.3$ kg/mol, $M_w = 239.7$ kg/mol, PDI = 3.41$^a$

**FTAZ:** $m$-BnDT/$m$-FTAZ/ Pd$_2$(dba)$_3$·CHCl$_3$/ P(o-tol)$_3$ = 1.020/1.000/0.020/0.160. Polymerization time: 10 min. $M_n = 54.8$ kg/mol, $M_w = 104.1$ kg/mol, PDI = 1.90$^a$

**3'-FT-HTAZ:** $m$-BnDT/$m$-3’-FT-HTAZ/Pd$_2$(dba)$_3$·CHCl$_3$/ P(o-tol)$_3$ = 1.000/1.000/0.020/0.160. Polymerization time: 10 min. $M_n = 82.6$ kg/mol, $M_w = 157.8$ kg/mol, PDI = 1.91$^a$
**3'-FT-FTAZ:**  \( m\text{-BnDT/m-3'-FT-FTAZ/} \quad \text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3 / \quad \text{P(o-tol)}_3 \quad = \)
1.000/1.000/0.020/0.160. Polymerization time: 10 min. \( M_n = 101.1 \text{ kg/mol}, \quad M_w = 194.5 \text{ kg/mol}, \quad \text{PDI} = 1.92^a \)

**4'-FT-HTAZ:**  \( m\text{-BnDT/m-4’-FT-HTAZ} / \quad \text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3 / \quad \text{P(o-tol)}_3 \quad = \)
1.000/1.000/0.020/0.120. Polymerization time: 40 min. \( M_n = 31.9 \text{ kg/mol}, \quad M_w = 86.5 \text{ kg/mol}, \quad \text{PDI} = 2.70^b \)

**4'-FT-FTAZ:**  \( m\text{-BnDT/m-4’-FT-FTAZ} / \quad \text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3 / \quad \text{P(o-tol)}_3 \quad = \)
1.000/1.000/0.040/0.320. Polymerization time: 40 min. \( M_n = 21.4 \text{ kg/mol}, \quad M_w = 53.8 \text{ kg/mol}, \quad \text{PDI} = 2.51^a \)

When DMF/o-xylene = 1/10 were utilized for polymerization (same condition as no DMF, molecular weight of polymers:

**4'-FT-HTAZ:** \( M_n = 37.1 \text{ kg/mol}, \quad M_w = 108.0 \text{ kg/mol}, \quad \text{PDI} = 2.91^b \)

**4'-FT-FTAZ:** \( M_n = 26.0 \text{ kg/mol}, \quad M_w = 62.6 \text{ kg/mol}, \quad \text{PDI} = 2.40^b \)

^a molecular weight was measured via GPC at 150 °C

^b molecular weight was measured via GPC at 160 °C
CHAPTER 5
ASYMMETRIC POLYMERS WITH FLUORINATED THIOPHENE: THE FLUORINE AMOUNT MATTERS

5.1 Introduction

In Chapter 4, relocation of the fluorine substitution from the acceptor (TAZ) unit to the π linker thiophene unit maintained the “efficiency-enhancing” effect of fluorine substitution on the acceptor (TAZ) unit: noticeably improved $V_{oc}$ values due to the decreased HOMO levels, and significantly improved $FF$ due to the remarkably enhanced hole mobility. Through combining the fluorinated thiophene and the fluorinated TAZ unit, the tetra-fluorine substituted polymer further improve the efficiency of the PSC devices. In addition to the change in fluorine substituent position, it is interesting to consider the effect of fluorine substituent amount: with two fluorine substituents on either the acceptor unit (FTAZ) or on the thiophene unit (3’-FT-HTAZ and 4’-FT-HTAZ), the $PCE$ was remarkably improved from 4% to 7%; however, with only one fluorine substituent, the PSC performance of monoFTAZ polymer was between those of HTAZ and FTAZ polymers and resembled that of the 50% HTAZ and FTAZ random terpolymer. It seems at least two fluorine substituents per repeating unit are necessary for high performance of PSCs (hole mobility of $\sim 10^{-3}$ cm$^2$/V•s, $FF$ of $\sim 70\%$ at 200 – 300 nm films and $PCE$ of $\sim 7\%$). In order to thoroughly investigate the effect of the number and the position of the fluorine substituents, in this study, we designed two new PBnDT-TAZ based polymers with one fluorine substituent per repeat-
-ing unit (3’-FT-T-HTAZ and 4’-FT-T-HTAZ) and another PBnDT-TAZ based polymer with three fluorine substituents (4’-FT-T-FTAZ). For 3’-FT-T-HTAZ and 4’-FT-T-HTAZ, the position of the single fluorine substituent changes from the 3’ position to the 4’ position of the thiophene unit; for 4’-FT-T-FTAZ, two fluorine substituents are placed on the TAZ unit and one fluorine substituent is placed on the 4’ position of the thiophene unit. The chemical structures of the polymers were shown in Chart 5.1. For clarity, we will use 3’-FT-T-HTAZ, 4’-FT-T-HTAZ and 4’-FT-T-FTAZ to represent the polymers while using m-3’-FT-T-HTAZ, m-4’-FT-T-HTAZ and m-4’-FT-T-FTAZ for the corresponding monomers. Together with the polymers studied in Chapter 4, ten PBnDT-TAZ based polymers were prepared with similar chemical structure yet with a variation in the position and the number of the fluorine substituents on the polymer backbones. These ten structurally related polymers allow us to thoroughly study the effect of fluorine substitution on the properties of the polymers.

Notably, with an odd number of fluorine substituents, the chemical structures of the three monomers become asymmetric, introducing local regio-irregularity in the polymers. The regio-irregularity of the polymers may influence the crystallinity, the π-π interactions and the aggregation of polymers chains, thereby impacting of the charge transport properties of the PSC devices.

In this study, the two new 1F polymers, 3’-FT-T-HTAZ and 4’-FT-T-HTAZ, provide moderate PCE values of ~ 5.0 %, very close to that of monoFTAZ and lying between those of HTAZ and FTAZ. For the PBnDT-TAZ polymers, the improvement of hole mobility with fluorine substitution is important to the FF and PCE of PSCs. Compared with the polymers with two fluorine substituents or four fluorine substituents per repeating unit (see Chapter 4 for details), 3’-FT-T-HTAZ and 4’-FT-T-HTAZ do not show a noticeable enhancement of hole mobility over
HTAZ, especially for 3’-FT-T-HTAZ. With three fluorine atoms per repeating unit, 4’-FT-T-FTAZ achieves a hole mobility of $1.6 \times 10^{-3}\text{cm}^2/(\text{V}\cdot\text{s})$ and thus high $PCE$ of ~ 6.7%, similar to that of FTAZ but lower than the efficiency achieved by the 4F polymer (4’-FT-FTAZ). Though the regioirregularity of the polymers may affect the performance of the polymers, this study emphasizes the importance of fluorine substituent amount for the PSC performance: despite the difference in the fluorine substituent position, the three 1F polymers show similar photovoltaic performance; on the other side, the 3F polymer with more fluorine substituents achieves noticeably improved efficiency.

![Chemical structure of the asymmetric polymers.](chart)

**Chart 5.1.** Chemical structure of the asymmetric polymers.

### 5.2 Design and Synthesis

The synthesis of the monomers is shown in Scheme 5.1 and Scheme 5.2. The fluorinated thiophene units were prepared according to the synthetic methodology detailed in Chapter 4. Due to the asymmetric structure of the monomers, the two thiophene rings were coupled to the TAZ units in two separated steps. For monomers $m$-3’-FT-T-HTAZ and $m$-4’-FT-T-HTAZ, the non-fluorinated thiophene unit was coupled to the TAZ unit before the fluorinated thiophene unit was coupled in the second step to reduce the consumption of the more synthetically difficult fluorinated
thiophene compounds. This methodology also works for the preparation of monomer \( m\)-4'-FT-T-FTAZ as well. However, a different approach to \( m\)-4'-FT-T-FTAZ was adopted in this study, as shown in Scheme 5.2. Compound 5.8 was the byproduct of the coupling reaction for the preparation of \( m\)-4'-FT-FTAZ (Chapter 4), with only one fluorinated thiophene coupled to the TAZ unit. Compound 5.8 was then subjected to a Stille coupling reaction with trimethyl(5-(trimethylstannyl)thiophen-2-yl)silane to get Compound 5.9, followed by bromination. All products were characterized by \(^1\)H NMR and \(^{19}\)F NMR to confirm the chemical structure. More synthetic details were included in the Experiment Section.

Scheme 5.1. Synthesis of \( m\)-3'-FT-T-HTAZ and \( m\)-4'-FT-T-HTAZ.

Scheme 5.2. Synthesis of \( m\)-4'-FT-T-FTAZ.
The synthesis of the polymers was based on the Stille coupling based polymerization with microwave heating (Scheme 5.3). In Chapter 4, we noted the lower reactivity of \( m\text{-4’-FT-HTAZ} \) and \( m\text{-4’-FT-FTAZ} \) with two fluorine substituents on the 4’ positions of the thiophene units, and extended reaction time (40 min) was needed for the polymerization of those two monomers. For the two asymmetric monomers \( m\text{-4’-FT-T-HTAZ} \) and \( m\text{'-4’-FT-T-FTAZ} \) with one fluorine substituent on the 4’ position of the thiophene unit, their reactivity appears to be only slightly affected, and their polymerization required shorter time (20 min) than \( m\text{-4’-FT-HTAZ} \) and \( m\text{-4’-FT-FTAZ} \) for a high molecular weight polymers, however, this time (20 min) was still longer than the time needed to polymerize other TAZ monomers (10 min). More reaction details can be found in Experiment Section.

Scheme 5.3. Stille coupling based polymerization for the three polymers

5.3 Optical and Electrochemical Properties

The UV-Vis absorption of the polymers in 1,2,4-trichlorobenzene (TCB) and as films are shown in Figure 5.2. The absorption spectra of the four polymers are similar in both solutions and as thin films. In Chapter 4, we found that the two polymers with two fluorine substituents on 4’ positions of the two thiophene unit, \( 4\text{-FT-HTAZ} \) and \( 4\text{-FT-FTAZ} \), have more planar polymer backbones, and the UV-Vis absorption spectra of the polymers showed red-shift by \( \sim 40 \) nm when compared with the other polymers. With only one fluorine substituent on one of the 4’ positions of the two thiophene units, the absorption spectra of \( 4\text{-FT-T-HTAZ} \) and \( 4\text{-FT-T-FTAZ} \) only
slightly red-shift compared with monoFTAZ and 3’-FT-T-HTAZ. We ascribe this to the asymmetric structure of the monomers, where only the region of fluorinated thiophene and the adjacent BnDT could be planarized, leaving the region of the non-fluorinated thiophene units unaffected. Thus, less red-shift was observed.

The HOMO levels were investigated by cyclic voltammetry (CV) (Figure 5.2). The HOMO level of the polymers is mainly affected by the amount of the fluorine substituents on the polymer backbone. The HOMO levels of the three 1F polymers are similar to each other, while the energy of the HOMO level of the 3F is deepened by ~ 0.1 eV.

**Figure 5.1.** UV-Vis absorption spectra of (a) solutions in TCB and (b) as thin films.

**Figure 5.2.** CV curves of the four asymmetric polymers.
Table 5.1. The molecular weight, optical and electrochemical properties of the polymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$M_n$ (kg/mol)</th>
<th>$D$ ($M_w/M_n$)</th>
<th>Absorption onset (nm)</th>
<th>HOMO(^a) (eV)</th>
<th>Band gap(^b) (opt, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoFTAZ</td>
<td>70.3</td>
<td>3.4</td>
<td>621</td>
<td>-5.47</td>
<td>1.99</td>
</tr>
<tr>
<td>3'-FT-T-HTAZ</td>
<td>72.0</td>
<td>2.4</td>
<td>626</td>
<td>-5.45</td>
<td>1.98</td>
</tr>
<tr>
<td>4'-FT-T-HTAZ</td>
<td>41.4</td>
<td>2.8</td>
<td>639</td>
<td>-5.50</td>
<td>1.94</td>
</tr>
<tr>
<td>4'-FT-T-FTAZ</td>
<td>44.0</td>
<td>2.6</td>
<td>631</td>
<td>-5.55</td>
<td>1.96</td>
</tr>
</tbody>
</table>

\(^a\)HOMO levels were measured by CV; \(^b\)Band gap were estimated by the absorption onset.

5.4 Photovoltaic Properties

![Figure 5.3. (a) Representative J-V curves and (b) EQE curves of the BHJ devices.](image)

The photovoltaic properties of the four polymers were investigated in the bulk heterojunction (BHJ) solar cells with a normal device configuration: indium doped tin oxide (ITO)/hole transporting layer/polymer:phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM)/Ca/Al. The J-V curves and external quantum efficiency (EQE) curves of optimized devices are presented in Figure 5.3a and 5.3b, respectively, with the related device characteristics summarized in Table 5.2. For each polymer, we attempted to optimize the processing condition, including the hole transporting layer materials, the solvent, the additives and the active layer thickness, in order to obtain the maximum device efficiency for each polymer based BHJ blend. It appears that chlorobenzene (CB) with 3%
additive 1,8-diiodooctane (DIO) and poly(3,4-ethylenedioxythiophene) polystyresulfonate (PEDOT:PSS) offer the best device performance for 4’-FT-T-HTAZ, while TCB and copper(I) thiocyanate (CuSCN) seem to be the best choice of solvent and HTL material for 3’-FT-T-HTAZ and 4’-FT-T-FTAZ. For monoFTAZ, devices were prepared with PEDOT:PSS as HTL and TCB as solvent.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Hole mobility ($\times 10^{-3}$ cm$^2$/V•s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoFTAZ</td>
<td>224</td>
<td>11.26±0.41</td>
<td>0.778±0.005</td>
<td>63.2±2.0</td>
<td>5.53±0.27</td>
<td>0.44</td>
</tr>
<tr>
<td>3’-FT-T-HTAZ</td>
<td>238</td>
<td>11.53±0.18</td>
<td>0.793±0.002</td>
<td>53.8±1.2</td>
<td>4.92±0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>4’-FT-T-HTAZ</td>
<td>203</td>
<td>10.34±0.27</td>
<td>0.791±0.004</td>
<td>61.8±1.2</td>
<td>5.06±0.11</td>
<td>0.34</td>
</tr>
<tr>
<td>4’-FT-T-FTAZ</td>
<td>275</td>
<td>11.41±0.35</td>
<td>0.869±0.003</td>
<td>67.1±1.2</td>
<td>6.65±0.18</td>
<td>1.70</td>
</tr>
</tbody>
</table>

**Open Circuit Voltage ($V_{oc}$).** The $V_{oc}$ values increase almost linearly with the number of fluorine: the $V_{oc}$ of monoFTAZ, 3’-FT-T-HTAZ and 4’-FT-T-HTAZ (1F) is the average of HTAZ (0F) and FTAZ (2F); the $V_{oc}$ of 4’-FT-T-FTAZ (3F) is the average of FTAZ (2F) and 4’-FT-FTAZ (4F) (Chapter 4). In Chapter 4, fluorine position also noticeably affects the $V_{oc}$ values, for example, $V_{oc}$ of 3’-FT-HTAZ is ~ 0.1 eV higher than those of FTAZ and 4’-FT-HTAZ though the three polymers have the same amount of fluorine substituents (2F). However, for the three 1F polymers, the fluorine position does not significantly affect the $V_{oc}$ values. This matches the similar HOMO levels of three 1F polymers.

**Short Circuit Current ($J_{sc}$).** The $J_{sc}$ values for all polymers are similar, which is consistent with the similar absorption properties of the polymers except for 4’-FT-T-HTAZ. As discussed in
Chapter 4, the enhanced hole mobility by fluorination of either TAZ or thiophene units slightly improves the $J_{sc}$, however, the increase in $J_{sc}$ is very minor, thus we wouldn’t expect significant change in $J_{sc}$ in this study by changing the amount of fluorine substituents. The reasons for the low $J_{sc}$ of 4’-FT-T-HTAZ is unclear yet; but we speculate that morphology could be a big part, thus further optimization of the device fabrication condition may help to improve the $J_{sc}$.

Fill Factor (FF). For the PBnDT-TAZ based polymers, the hole mobilities strongly affect the $FF$ values of the devices by influencing the charge extraction efficiency. With two and four fluorine substituents, we observed significantly improved hole mobility. In this study, we found that the hole mobilities of the 4’-FT-T-HTAZ and monoFTAZ were also improved compared with HTAZ, despite only having one fluorine substituent, but not as high as the 2F polymers (FTAZ, 3’-FT-HTAZ and 4’-FT-HTAZ). For 3’-FT-T-HTAZ, the hole mobility is not improved compared with HTAZ. The lower hole mobility of 3’-FT-T-HTAZ explains well why this polymer has the lowest $FF$ values among all the three 1F polymers. For the 3F polymer, 4’-FT-T-FTAZ, a hole mobility of $1.7 \times 10^{-3} \text{ cm}^2/\text{(V} \cdot \text{s})$ was achieved, which accounts for the high $FF$ values of $\sim 67\%$ at $\sim 300$ nm. For the ten PBnDT-TAZ based polymers, the $FF$ values substantially depend on the hole mobilities as shown in Figure 5.3, which is consistent with our previous study. Based on these results, it seems a threshold hole mobility of $1 \times 10^{-3} \text{ cm}^2/\text{(V} \cdot \text{s})$ is necessary for the PBnDT-TAZ based polymers to achieve high $FF$ ($\sim 65\%$) for thick devices ($\sim 300$ nm). However, further improvement of hole mobility within the order of $1 \times 10^{-3} \text{ cm}^2/\text{(V} \cdot \text{s})$ does not further improve the fill factor of the devices.
5.5 Conclusion

Three novel asymmetric polymers with fluorinated thiophene units were prepared. To complement our study (Chapter 4), an odd number of fluorine atoms (one fluorine and three fluorine atoms per repeating unit) were incorporated into the polymers with control of the position of the fluorine substituents. This study provides a synthetic methodology to prepare the asymmetric monomers and polymers. The photovoltaic properties of the asymmetric polymers strongly depend on the amount of the fluorine substituents and only marginally on the fluorine positions. Control of the regioregularity of the polymers is under progress now, and the PCE of the PSC devices might be improved with controlled regioregularity.

In summary, ten PBnDT-TAZ based polymers in total were presented in Chapter 4 and Chapter 5. The FF values of the PSC devices are significantly affected by the hole mobility. The newly developed fluorinated thiophene units as π linker units can effectively enhance the hole mobilities of the BHJ devices, therefore, high FF values were achieved with thick films. Provided that many conjugated polymers with exceptional photovoltaic performance have a “donor-
thiophene-acceptor-thiophene” pattern in their repeating units, incorporation of fluorinated thiophene units can potentially be a useful approach to further improve the efficiency of PSCs.

5.6 Experiment Section

Chemicals and Methods. **Chemicals and Methods**

All chemicals were purchased from commercial sources (Sigma-Aldrich, Fisher, Matrix, etc.) and were used as received except when specified. THF was distilled over sodium and benzophenone before use. Anhydrous toluene was purchased in sealed bottle from Fisher. Anhydrous o-xylene was purchased in sealed bottle from Sigma-Aldrich. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (Pd₂dba₃·CHCl₃) was purchased from Sigma-Aldrich and was recrystallized in chloroform/acetone. Tri(o-tolyl)phosphine (P(o-tol)₃) was recrystallized in hexanes. For reactions under argon, the glassware was evacuated and refilled with argon for three times and charged with reactants.

Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on an Agilent PL220 instrument with TCB as the eluent (stabilized with 250 ppm BHT) at 160 °C. The obtained molecular weight is relative to the polystyrene standard. ¹H and ¹³C nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometers (400 MHz, 500 MHz or 600 MHz). Mass Spectrometry was run on a Q Exactive Orbitrap (ThermoFisher, Bremen, Germany) mass spectrometer and analyzed via Xcalibur (ThermoFisher, Breman, Germany). UV-visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments).

*Cyclic voltammetry* was measured in the same method as **Chapter 4**.
SCLC hole mobility was measured in the same method as Chapter 4.

Photovoltaic Device Fabrication. Glass substrates coated with patterned indium doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. The sputtered ITO had a thickness of ~150 nm and a resistivity of 20 Ω/□. Prior to use, the substrates were ultrasonicated in deionized water, acetone, and then 2-propanol for 15 minutes each. The substrates were dried under a stream of nitrogen gas and subjected to the treatment of UV-Ozone for 15 min. A filtered dispersion of PEDOT:PSS in water (Clevios™ PH500 from Heraeus) was then spun cast onto cleaned ITO substrates at 4000 rpm for 60 s and then baked at 130 °C for 15 min in air to give a thin film with a thickness of about 40 nm. For devices with CuSCN as the buffer layer, the CuSCN was dissolved in diethylsulfide with a concentration of 22.7 mg/mL under stirring for 1 h. Then the CuSCN solution was filtered by 0.2 μm poly(tetrafluoroethylene) (PTFE) filter and spun-cast onto the cleaned ITO substrates at 7000 rpm for 60 s and then baked at 100 °C for 15 min in air to give a thin film with a thickness of ~40 nm. For monoFTAZ, 3’-FT-T-HTAZ and 4’-FT-T-FTAZ, blends of polymer:PC_{61}BM (1:2 w/w) were dissolved in 1,2,4-trichlorobenzene with heating at 130 °C for 6 h. For 4’-FT-T-HTAZ, blends of polymer:PC_{61}BM (1:2 w/w) were dissolved in chlorobenzene with 3vol% DIO with heating at 110 °C for 6 h and cooled to 80 °C before spin coating. All solutions were filtered through a 5.0 μm PTFE filter and spun-cast at an pre-selected rpm for 60 seconds onto the PEDOT:PSS or CuSCN layer for conventional structure. For monoFTAZ, 3’-FT-T-HTAZ and 4’-FT-T-FTAZ, the substrates were transferred into vacuum chamber immediately after spin-coating and then dried at 30 mmHg below atmosphere for 30 min. For 4’-FT-T-HTAZ, the films were kept in covered petri dish overnight after spin-coating. The devices were finished for measurement after the thermal deposition of a 30 nm film of calcium and a 70 nm aluminum film as the cathode for conventional structure at a base pressure of 2 × 10^{-3}.
There were 8 devices per substrate, with an active area of 13 mm² per device. Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW/cm² (Oriel 91160, 300 W) calibrated by an NREL certified standard silicon cell. Current density versus voltage (J-V) curves was recorded with a Keithley 2400 digital source meter. EQE was detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode (Model No.: Newport 71580). All fabrication steps after adding the PEDOT:PSS or CuSCN layer onto ITO substrate, and characterizations were performed in gloveboxes under nitrogen atmosphere.

**Synthesis of monomers**

*Trimethyl(5-(trimethylstannyl)thiophen-2-yl)silane (Compound 5.2)* To the solution of thiophene (0.84 g, 10 mmol) in anhydrous THF, 2.5 M n-butyllithium solution in hexanes (4.2 mL, 10.5 mmol) was added at 0 °C under argon and stirred at r.t. for 1 hr before trimethylsilyl chloride (1.20 g, 11 mmol) was added. The reaction was stirred at r.t. for another 1 hr and cooled down to 0 °C for 10 min. n-Butyllithium solution in hexanes (4.6 mL, 11.5 mmol) was added and stirred at r.t. for one hour before the addition of 1.0 M trimethylin chloride solution (13 mL, 13 mmol). The reaction was stirred at r.t. overnight and was quenched with water. The product was extracted with ethyl acetate for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The solvent was removed with rot-vap, and the product was dried over vacuum. Yield, pale yellow solid, 0.32 g, ~100%. \(^1\)H NMR (400 MHz, Chloroform-d) δ 7.40 (d, \(J = 3.0\) Hz, 1H), 7.30 (d, \(J = 3.1\) Hz, 1H), 0.37 (s, 9H), 0.33 (s, 9H).
4-bromo-2-(2-butyloctyl)-7-(5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole

(Compound 5.4) To the solution of Compound 5.3 (0.52 g, 1.17 mmol) and trimethyl(5-(trimethylstannyl)thiophen-2-yl)silane (0.45 g, 1.40 mmol) in anhydrous toluene, Pd(PPh₃)₂Cl₂ (0.049 g, 0.07 mmol) was added under argon. The reaction mixture was purged with argon for 20 min before being refluxed overnight. The solvent was removed with rot-vap. The crude product was purified by silica gel column chromatography with hexanes : dichloromethane = 30 : 1 to 10 : 1 as eluent. Yield, pale yellow oil, 0.20 g, 33%. ¹H NMR (400 MHz, Chloroform-d) δ 8.10 (d, J = 3.5 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 3.5 Hz, 1H), 4.72 (d, J = 6.9 Hz, 2H), 2.33 (s, 1H), 1.44 – 1.14 (m, 16 H), 0.87 (dt, J = 12.1, 6.9 Hz, 6H), 0.37 (s, 9H).

2-(2-butyloctyl)-4-(3-fluoro-5-(trimethylsilyl)thiophen-2-yl)-7-(5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 5.5) To the solution of Compound 5.4 (0.63 g, 1.21 mmol) and (4-fluoro-5-(trimethylstannyl)thiophen-2-yl)trimethylsilane (0.46 g, 1.36 mmol), Pd(PPh₃)₂Cl₂ (0.042 g, 0.06 mmol) was added under argon. The reaction mixture was purged with argon for 20 min before being refluxed for 48 hr. The solvent was removed. The crude product was purified by silica gel column chromatography with hexanes : dichloromethane = 14 : 1 as eluent. Yield, yellow solid, 0.60 g, 81%. ¹H NMR (400 MHz, Chloroform-d) δ 8.14 (d, J = 3.5 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 3.5 Hz, 1H), 7.06 (s, 1H), 4.77 (d, J = 6.3 Hz, 2H), 2.30 (q, J = 6.2 Hz, 1H), 1.47 – 1.19 (m, 16H), 0.95 – 0.78 (m, 6H), 0.38 (s, 9H), 0.37 (s, 9H). ¹⁹F NMR (376 MHz, chloroform-d) δ -126.26.

4-(5-bromo-3-fluorothiophen-2-yl)-7-(5-bromothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (Compound 5.6) To the solution of Compound 5.5 (0.60 g, 0.98 mmol) in dichloromethane (20 mL) and acetic acid (4 mL), NBS was added. The reaction was stirred in dark at r.t. for 38 hr. Then the reaction was poured into water, and the product was extracted with
dichloromethane for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The crude product was purified by silica gel column chromatography with hexanes : dichloromethane = 15 : 1 as eluent. The product was recrystallized in ethanol for further purification. Yield, yellow solid, 0.33 g, 55%. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.84 (d, $J = 7.7$ Hz, 1H), 7.79 (d, $J = 3.9$ Hz, 1H), 7.57 (d, $J = 7.7$ Hz, 1H), 7.13 (d, $J = 3.9$ Hz, 1H), 4.74 (d, $J = 6.5$ Hz, 2H), 2.33 – 2.23 (m, 1H), 1.47 – 1.22 (m, 16H), 0.89 (dt, $J = 19.0, 7.0$ Hz, 6H). $^{19}$F NMR (376 MHz, chloroform-d) $\delta$ -121.78.

2-(2-butyloctyl)-4-(4-fluoro-5-(trimethylsilyl)thiophen-2-yl)-7-(5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 5.5′) To the solution of Compound 5.4 (0.78 g, 1.50 mmol) and (3-fluoro-5-(trimethylstannyl)thiophen-2-yl)trimethylsilane (0.58 g, 1.72 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.031 g, 0.045 mmol) was added under argon. The reaction mixture was purged with argon for 20 min before being refluxed overnight. The solvent was removed. The crude product was purified by silica gel column chromatography with hexanes : dichloromethane = 30 : 1 to 15 : 1 as eluent. Yield, yellow solid, 0.68 g, 73%. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.17 (d, $J = 3.5$ Hz, 1H), 7.87 (d, $J = 1.1$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.33 (d, $J = 3.5$ Hz, 1H), 4.77 (d, $J = 6.4$ Hz, 2H), 2.33 (q, $J = 6.3$ Hz, 1H), 1.50 – 1.16 (m, 16H), 0.90 (dt, $J = 20.4, 6.9$ Hz, 6H), 0.41 (s, 9H), 0.40 (s, 9H).

4-(5-bromo-4-fluorothiophen-2-yl)-7-(5-bromothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (Compound 5.6′) To the solution of Compound 5.5′ (0.68 g, 1.10 mmol) in dichloromethane (25 mL) and acetic acid (3 mL), NBS was added. The reaction was stirred in dark at r.t. for overnight. Then the reaction was poured into water, and the product was extracted with dichloromethane for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The crude product was
purified by silica gel column chromatography with hexanes : dichloromethane = 4 : 1 as eluent. The product was recrystallized in ethanol for further purification. Yield, yellow solid, 0.30 g, 44%.

\[ \text{1H NMR (400 MHz, Chloroform-d) \( \delta \) 7.80 (d, } J = 3.9 \text{ Hz, 1H), 7.73 (s, 1H), 7.55 – 7.48 (m, 2H), 7.13 (d, } J = 4.0 \text{ Hz, 1H), 4.74 (d, } J = 6.6 \text{ Hz, 2H), 2.30 (q, } J = 6.3 \text{ Hz, 1H), 1.46 – 1.20 (m, 16H), 0.88 (dt, } J = 18.3, 7.0 \text{ Hz, 6H).} \]

\[ \text{19F NMR (376 MHz, chloroform-d) \( \delta \) -125.36.} \]

4-bromo-2-(2-butyloctyl)-5,6-difluoro-7-(4-fluoro-5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Compound 5.8) was the byproduct of the Stille coupling reaction for preparation of 4'-FT-FTAZ (Chapter 4). **Compound 5.8** was characterized with \(^1\)H and \(^{19}\)F NMR to confirm the chemical structure. \(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 8.02 (d, \( J = 0.9 \text{ Hz, 1H), 4.69 (d, } J = 6.8 \text{ Hz, 2H), 2.29 (s, 1H), 1.48 – 1.17 (m, 16H), 0.87 (dt, } J = 13.2, 6.9 \text{ Hz, 6H), 0.40 (s, 9H).} \]

\[ \text{19F NMR (376 MHz, Chloroform-d) \( \delta \) -119.65, -128.80 (d, } J = 18.5 \text{ Hz), -131.98 (d, } J = 18.5 \text{ Hz).} \]

\[ \text{19F NMR (376 MHz, chloroform-d) \( \delta \) -117.58.} \]

2-(2-butyloctyl)-5,6-difluoro-4-(4-fluoro-5-(trimethylsilyl)thiophen-2-yl)-7-(5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (Chemical 5.9) To the solution of **Compound 5.8** (0.34 g, 0.59 mmol) and **Compound 5.2** (0.23 g, 0.71 mmol), Pd(PPh\(_3\)_2Cl\(_2\) (0.012 g, 0.018 mmol) was added under argon. The reaction mixture was purged with argon for 20 min before being refluxed overnight. The solvent was removed. The crude product was purified by silica gel column chromatography with hexanes : dichloromethane = 40 : 1 as eluent. Yield, yellow solid, 0.37 g, 96%. \(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 8.35 (d, \( J = 3.6 \text{ Hz, 1H), 8.05 (s, 1H), 7.36 (dd, } J = 3.6, 1.8 \text{ Hz, 1H), 4.74 (d, } J = 6.4 \text{ Hz, 2H), 2.28 (q, } J = 6.2 \text{ Hz, 1H), 1.46 – 1.19 (m, 16H), 0.93 – 0.78 (m, 6H), 0.40 (s, 9H), 0.39 (s, 10H).} \]

\[ \text{19F NMR (376 MHz, Chloroform-d) \( \delta \) -119.75, -133.68 (d, } J = 15.2 \text{ Hz), -134.21 (d, } J = 15.1 \text{ Hz).} \]
4-(5-bromo-4-fluorothiophen-2-yl)-7-(5-bromo thiophen-2-yl)-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (Compound 5.10) To the solution of Compound 5.9 (0.31 g, 0.48 mmol) in dichloromethane (10 mL) and acetic acid (2 mL), NBS was added. The reaction was stirred in dark at r.t. for overnight. Then the reaction was poured into water, and the product was extracted with dichloromethane for 3 times. The combined organic solution was washed with water for 2 times and Brine for 1 time, and then was dried over magnesium sulfate. The crude product was purified by silica gel column chromatography with hexanes : dichloromethane = 10 : 1 as eluent. The product was recrystallized in ethanol for further purification. Yield, yellow solid, 0.22 g, 70%. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.05 (d, \(J = 4.1\) Hz, 1H), 7.96 (s, 1H), 7.19 (dd, \(J = 4.1, 1.5\) Hz, 1H), 4.73 (d, \(J = 6.5\) Hz, 2H), 2.26 (s, 1H), 1.47 – 1.20 (m, 16H), 0.89 (m, 6H). \(^19\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) -126.98, -133.49 (d, \(J = 14.9\) Hz), -134.12 (d, \(J = 14.9\) Hz).

**Synthesis of polymers**

BnDT monomer (1.000 eq), TAZ monomers (1.000eq), Pd\(_2\)(dba)\(_3\)·CHCl\(_3\) (0.02 eq) and P(\(o\)-tol)\(_3\) (0.16 eq) were charged into a 10 mL vial designed for microwave reactor. The mixture was evacuated and refilled with argon for three cycles before addition of anhydrous o-xylene under argon stream. The reaction was heated up to 200 °C and hold in a CEM microwave reactor for 10 min for 3’-FT-T-HTAZ and 20 min for 4’-FT-T-HTAZ and 4’-FT-T-FTAZ. After the polymerization, the crude polymer was dissolved in hot chlorobenzene and precipitated into stirring methanol. The collected polymer was extracted via a Soxhlet extractor with EtOAc, hexanes, and chloroform. The polymer solution in chloroform was concentrated via rotavap. The collected polymer was re-dissolved into hot chlorobenzene and precipitated into methanol. The polymer was then collected via filtration and dried under vacuum.
CHAPTER 6

EFFECT OF CYANO SUBSTITUTION ON CONJUGATED POLYMERS FOR BULK HETEROJUNCTION SOLAR CELLS

6.1 Introduction

Tailoring the structure of the polymers has been one of the most important approaches to adjust the properties of polymers and improve the efficiency of the OPV devices.\textsuperscript{6, 7} Chapter 4 and Chapter 5 show that for the PBnDT-TAZ polymers, incorporation of fluorine substituents on the thiophene units effectively improves the \( V_{oc} \) and \( FF \) values through tuning the HOMO levels and charge transport properties respectively. However, the \( J_{sc} \) values of the OPV devices are limited by the large bandgaps (1.9 – 2.0 eV), and fluorine substitution on thiophene units does not significantly affect the absorption properties of the polymers. Thus, design of low bandgap polymers based on PBnDT-TAZ is of interest to further boost the efficiency of photovoltaic devices. According to the “donor-acceptor” concept, adding strong electron withdrawing groups to the acceptor unit can decrease the LUMO energy level of the polymer by a larger degree than decreasing the HOMO level, leading to a smaller bandgap. Cyano (CN) group is a strong electron withdrawing group. There have been studies showing that adding CN groups to the acceptor units can effectively decrease the optical bandgaps of the polymers.\textsuperscript{17} For example, Casey \textit{et al.} added one and two CN substituents to the benzo thiadi azole (BT) unit of the polymers based on dithienogermole (DTG) and di(thiophen-2-yl)-2,1,3-benzo thi di azole (DTBT) unit, and the bandgap of the polymers was decreased by ~ 0.15 eV by each cyano substituent.\textsuperscript{121} In our group, Li \textit{et al.} found for polymer PBnDT-PyCNTAZ with a single CN substituent on tri azolo[4,5- c]py-
ridine unit and for polymer PBnDT-diCNTAZ with two CN substituents on benzotriazole unit, a red-shift of the absorption spectra by 70 -80 nm was observed for both of them.\textsuperscript{122} PBnDT-PyCNTAZ achieved a high $PCE$ of $\sim 8.4\%$ due to the improved $V_{oc}$ and $J_{sc}$. However, for PBnDT-diCNTAZ, the $J_{sc}$ was significantly lower than that of the device based on PBnDT-PyCNTAZ despite the similar absorption spectra of the two polymers.

In this study, we prepared a new PBnDT-TAZ polymer, PBnDT-monoCNTAZ, with a single CN substituent on the benzotriazole unit. By comparing this new polymer with two structurally similar polymers, PBnDT-HTAZ with no CN substituent and PBnDT-diCNTAZ with two CN substituents, we systematically studied the effect of CN substitution on the properties of the polymers and the related OPV devices. The strong electron withdrawing cyano groups effectively decrease the HOMO levels of the polymers, leading to the noticeably higher $V_{oc}$. In addition, the CN substituents reduce the bandgaps of the polymers as intended. Interestingly, with a single CN substitution, the $J_{sc}$ of the monoCNTAZ based OPV devices was significantly improved due to the smaller bandgap, and the $FF$ was also noticeably improved due to the enhanced hole mobility. Thus, the best efficiency of $\sim 8.6\%$ was achieved by monoCNTAZ. With two CN substituents, even though the bandgap of diCNTAZ was further decreased compared to monoCNTAZ, the $J_{sc}$ of diCNTAZ based devices was dramatically reduced. The low hole mobility of diCNTAZ may increase the bimolecular recombination in the devices, causing loss of $J_{sc}$. Given the high $V_{oc}$ of diCNTAZ based devices, we would expect a high charge transfer (CT) state, which may induce low driving force for charge splitting and increase geminate recombination.\textsuperscript{123} We are currently investigating the interfacial energetics of the devices to figure out if the charge generation efficiency is affected and accountable for the low $J_{sc}$ of diCNTAZ based devices.
6.2 Design and Synthesis

For clarity, we will use HTAZ, monoCNTAZ and diCNTAZ to represent the polymers and use m-HTAZ, m-monoCNTAZ and m-diCNTAZ to represent the corresponding TAZ based monomers in the following discussion.

The synthesis of m-monoCNTAZ and m-diCNTAZ is shown in Scheme 6.1 and Scheme 6.2, respectively. The PyCNTAZ and diCNTAZ monomers were prepared through a general methodology developed by Li et al; however, we could not find suitable precursors to apply the methodology to prepare m-monoCNTAZ. Instead, in this study, m-monoCNTAZ was prepared from 3,4-diaminobenzonitrile (Compound 6.1). Compound 6.1 underwent oxidative bromination with potassium bromide, hydrogen bromide acid and tert-butylhydroperoxide to achieve Compound 6.2. Compound 6.2 was cyclized to obtain Compound 6.3, followed by alkylation of N-2 position of Compound 6.3 to achieve Compound 6.4, which was then subjected to Stille coupling reaction to achieve Compound 6.5, which was subsequently brominated by excessive N-bromosuccinimide (NBS) to obtain the m-monoCNTAZ. Please note that the substitution of one CN group on the TAZ unit significantly reduces the reactivity of Compound 6.5. Excessive NBS together with an extended time was needed. Reaction details were included in Experiment Section. Even though m-diCNTAZ can be prepared by the general methodology by Li et al., it involves six steps to the common precursor and two more steps to the final monomer. In this study, a new synthetic approach was developed to get m-diCNTAZ from m-FTAZ via nucleophilic aromatic cyanation as shown in Scheme 6.2. After we succeeded to prepare m-diCNTAZ through the new reaction approach with an elegant yield of ~ 60%, Casey et al. reported a similar synthetic approach. More reaction details can be found in Experiment Section.
Scheme 6.1. Synthesis of m-monoCNTAZ.

Scheme 6.2. Synthesis of m-diCNTAZ.

The polymers were synthesized based on Stille coupling polymerization under microwave heating. The molecular weight of each polymer, ranging from 50 to 70 kg/mol, was optimized by adjusting the monomer ratios.\textsuperscript{80} HTAZ and diCNTAZ have good solubility in common solvent such as chloroform and chlorobenzene at elevated temperature. However, monoCNTAZ has significantly reduced solubility, only partially soluble in chloroform and chlorobenzene at elevated temperature, but fully soluble in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene at elevated temperature.

Scheme 6.3. Stille coupling based polymerization for the three polymers.
6.3 Optical and Electrochemical Properties

The optical properties of the polymers were investigated with UV-Vis absorption of the polymer solution in 1,2-dichlorobenzene (o-DCB) and of the films of the polymer (Figure 6.1). A gradual bathochromic shift of the UV-Vis absorption with more cyano substituents was observed: for each cyano substituent, the absorption edge shows a red-shift by 30 – 40 nm, and the optical bandgap decreases by ~ 0.1 eV. The UV-Vis absorption spectra of the polymers in solution at r.t. are almost the same with that of thin films, which means the polymer chains already aggregate in the solution at r.t. It is interesting that though the solubility of the monoCNTAZ is significantly lower than the other two polymers, no extra aggregation peaks or intensified aggregation absorption were observed in the absorption spectra of monoCNTAZ. The UV-Vis absorption of the polymers in DCB solutions at elevated temperature was also investigated (Figure 6.3). At ~110 °C, the aggregation peak of HTAZ fully disappears, and the aggregation peaks of monoCNTAZ and diCNTAZ still exist, but the intensity of the aggregation peak of diCNTAZ is stronger than the monoCNTAZ, which indicates that the amounts of the cyano group significantly affects the aggregation intensity of the polymers; the aggregation of polymers is stronger with more cyano substituents.

Table 6.1. Molecular weight, optical and electrochemical properties of the three polymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>(M_n) (kg/mol)</th>
<th>(D) ((M_w/M_n))</th>
<th>Absorption onset (nm)</th>
<th>HOMO(^a) (eV)</th>
<th>LUMO(^b) (eV)</th>
<th>Band Gap(^c) (opt, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>44.1</td>
<td>3.0</td>
<td>616</td>
<td>-5.47</td>
<td>-3.46</td>
<td>2.01</td>
</tr>
<tr>
<td>monoCNTAZ</td>
<td>52.0</td>
<td>3.5</td>
<td>658</td>
<td>-5.58</td>
<td>-3.70</td>
<td>1.88</td>
</tr>
<tr>
<td>diCNTAZ</td>
<td>50.6</td>
<td>3.3</td>
<td>693</td>
<td>-5.60</td>
<td>-3.81</td>
<td>1.79</td>
</tr>
</tbody>
</table>

\(^a\) HOMO levels were estimated by cyclic voltammetry; \(^b\) LUMO = HOMO + optical bandgap; \(^c\) Bandgap = optical bandgap, were estimated from the onset of absorption of the polymer films.
The electrochemical properties of the polymers were investigated with cyclic voltammetry (CV) (Figure 6.2). The HOMO energy levels of the polymers are estimated to be -5.48, -5.58 and -5.60 eV based on the onset of the oxidation peaks. It is clear that adding electron withdrawing groups on the acceptor units also affect the HOMO energy levels. However, the degree of the HOMO level decreasing by adding the second CN substituent is much smaller than by adding the first CN substituent.

Figure 6.1. UV-Vis of (a) polymer solutions in 1,2-dichlorobenzene and (b) polymer films.

Figure 6.2. Cyclic voltammetry curves of the three polymers.
Figure 6.3. Temperature dependent UV-Vis absorption spectra of (a) HTAZ, (b) monoCNTAZ and (c) diCNTAZ in o-DCB.

6.4 Photovoltaic Properties

Figure 6.4. (a) Representative $J$-$V$ curves and (b) EQE curves of the BHJ devices.
The photovoltaic properties of the three polymers were investigated in the bulk heterojunction (BHJ) solar cells with a normal device configuration: indium doped tin oxide (ITO)/ copper(I) thiocyanate (CuSCN)/polymer:phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM)/Ca/Al. The weight ratio of the polymer:PC$_{61}$BM was 1:2 for all the three polymer blends. Because of the deep HOMO energy levels of the polymers, CuSCN was selected as the hole transporting layer. The $J$-$V$ curves and EQE curves of optimized devices are presented in Figure 6.4, respectively, with the related device characteristics summarized in Table 6.2. For good comparison of device performance at similar thickness, devices at two thickness ($\sim$ 200 nm and $\sim$ 300 nm) are provided in Table 6.2. The best performance is achieved by monoCNTAZ based OPV devices with the $PCE$ values almost doubling that of HTAZ based devices. With the addition of the second cyano group, diCNTAZ only observes a significant drop of $J_{sc}$ in its devices, leading to a significant decrease in $PCE$. However, the $V_{oc}$ is further improved by the second cyano group.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$PCE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>205</td>
<td>10.55±0.21</td>
<td>0.752±0.001</td>
<td>56.9±1.1</td>
<td>4.52±0.18</td>
</tr>
<tr>
<td></td>
<td>249</td>
<td>11.10±0.25</td>
<td>0.741±0.001</td>
<td>53.3±1.3</td>
<td>4.39±0.17</td>
</tr>
<tr>
<td>monoCNTAZ</td>
<td>219</td>
<td>14.01±0.26</td>
<td>0.938±0.002</td>
<td>63.5±2.0</td>
<td>8.35±0.34</td>
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<tr>
<td></td>
<td>333</td>
<td>14.97±0.40</td>
<td>0.932±0.001</td>
<td>61.6±1.1</td>
<td>8.60±0.27</td>
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<tr>
<td>diCNTAZ</td>
<td>172</td>
<td>10.12±0.37</td>
<td>1.001±0.005</td>
<td>58.6±1.5</td>
<td>5.94±0.32</td>
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<tr>
<td></td>
<td>282</td>
<td>11.30±0.33</td>
<td>0.998±0.008</td>
<td>49.6±1.5</td>
<td>5.59±0.28</td>
</tr>
</tbody>
</table>

*Open Circuit Voltage ($V_{oc}$).* The $V_{oc}$ values are significantly improved as the HOMO level is decreased with CN substitution on TAZ unit, especially from HTAZ to monoCNTAZ. The
increase of the $V_{oc}$ from HTAZ to monoCNTAZ is nearly three times that from monoCNTAZ to diCNTAZ (0.19 V vs 0.07 V), implying that the second CN group has much less impact than the first CN group has. Though the deeper HOMO levels of monoCNTAZ and diCNTAZ explain well the higher $V_{oc}$ values, we plan to measure the charge transfer (CT) state energy, which is more directly related to the $V_{oc}$.\(^9\)

**Short Circuit Current ($J_{sc}$).** With CN substitutions, the absorption spectra of the polymers show a red-shift by ~40 nm by each CN group, thus we would expect higher $J_{sc}$. Indeed, the $J_{sc}$ of the monoCNTAZ based devices is remarkably improved compared to that of HTAZ at similar thickness. In addition to the bathochromic shift of the absorption spectra, the corresponding EQE values of monoCNTAZ based devices are also slightly higher over the whole absorption range. In contrast to the increase of $J_{sc}$ with one CN substitution, the $J_{sc}$ of the diCNTAZ based devices noticeably reduces to the level comparable to that of HTAZ based devices at similar thickness. The EQE values of the corresponding devices are the lowest among the three polymers over the whole absorption range. The hole mobilities of the BHJ blends were measured to check the effect of the hole mobilities on the $J_{sc}$. The hole mobility of monoCNTAZ:PC$_{61}$BM blend is (1.08 $\times 10^{-3}$ cm$^2/(V\cdot s)$), which is much higher than that of HTAZ:PC$_{61}$BM blend (0.17$\times 10^{-3}$ cm$^2/(V\cdot s)$) and diCNTAZ:PC$_{61}$BM blend (0.05$\times 10^{-3}$ cm$^2/(V\cdot s)$). This trend of hole mobility matches well with that of $J_{sc}$ and EQE; the low hole mobility of diCNTAZ may cause severe non-geminate recombination in devices and thus lead to dramatically reduced $J_{sc}$. Given the low HOMO level and the high $V_{oc}$ of diCNTAZ, we would expect a high charge transfer (CT) state energy at the polymer:PC$_{61}$BM interface, which may cause insufficient driving force for charge splitting or energy back transfer to the singlet of PC$_{61}$BM, leading to severe gemination recombination and
reducing the charge generation efficiency.\cite{123} We are currently investigating the interfacial energetics to further understand the low $J_{sc}$ in the diCNTAZ based devices.

**Fill Factor (FF)** As we discussed in Chapter 4 and Chapter 5, for PBnDT-TAZ based polymers, the hole mobility strongly influences the FF. For these three polymers, the FF is also impacted by the hole mobility. For the monoCNTAZ, its hole mobility in devices is above the threshold (~ $1\times10^{-3}$ cm$^2/(V\cdot s)$), which explains the decent FF (over 60%); the noticeably lower hole mobility for diCNTAZ and HTAZ accounts for the lower FF of the devices.

6.5 Morphology

In addition to the inherent properties of the polymers such as the optical properties and the energy levels, the morphology of the blends of polymers with PCBM plays an important role in determining the PSC performance.

![2D GIWAX patterns](image)

**Figure 6.5.** 2D GIWAX patterns of (a) HTAZ, (b) monoCNTAZ, (c) diCNTAZ, (d) HTAZ:PC$_{61}$BM, (e)monoCNTAZ:PC$_{61}$BM and (f)diCNTAZ:PC$_{61}$BM.
We utilized grazing incidence wide angle X-ray scattering (GIWAXS) to investigate the polymer packing of the neat polymer films and in the polymer blends with PC_{61}BM (Figure 6.5). For the pure polymer films, the (010) and (100) scattering peaks of HTAZ simultaneously appears in the out-of-plane direction, indicating the formation of rolling-log crystallites that adopt statistically random orientations with the backbone direction locked within the plane parallel with the substrate.\textsuperscript{109} This behavior of HTAZ is similar to that of FTAZ, 3’-FT-HTAZ and 3’-FT-FTAZ. With CN substitution, the polymers tend to adopt more face-on orientation as the (100) peaks tend to be stronger in the in-plane direction and the (010) peaks are in the out-of-plane direction. These

**Figure 6.6.** 1D profiles of neat polymer films along (a) q_{xy} axis and (b) q_{z} axis, of polymer: PC_{61}BM blends (c) along q_{xy} axis and (d) along q_{z} axis.
packing features of the polymers are maintained in the blends with PC$_{61}$BM. The $\pi$-$\pi$ stacking distances of the polymers in blends are 3.98 Å, 3.92 Å and 3.85 Å for HTAZ, monoCNTAZ and diCNTAZ respectively, gradually decreasing with more cyano substituents and indicating the strengthened $\pi$-$\pi$ stacking by cyano substitution. The coherence length of the (010) peaks of the three polymers in blends is similar to each other, meaning the difference in the polymer crystallinity is minimal. The intensified $\pi$-$\pi$ and the more “face-on” orientation explains the remarkably enhanced hole mobility of monoCNTAZ:PC$_{61}$BM blend. However, it couldn’t explain the lowest hole mobility of diCNTAZ:PC$_{61}$BM blend, which has the smallest $\pi$-$\pi$ stacking distance and most significant “face-on” orientation.

Since GIWAXS detects only the crystalline part of the samples, we utilized resonant soft X-ray scattering (RSoXS) to inspect the domain information in the polymer:PC$_{61}$BM blends.$^{111,112}$ The domain spacing of the three polymer:PC$_{61}$BM blends is very similar. Specifically, monoCNTAZ blend has relatively smaller domain spacing of ~ 36 nm than the other two polymer:PC$_{61}$BM blends (~ 46 nm). Since the weight ratio of the polymers to PC$_{61}$BM is 1:2 for all samples, the domain sizes of the polymers are estimated to be 12 – 15 nm, which are all in the range of the exciton diffusion distance. We do not believe the minor difference in the domain size is primarily responsible for the change in $J_{sc}$ and EQE of the three polymers. The domain purity of the monoCNTAZ:PC$_{61}$BM blends is the highest among the three polymer:PC$_{61}$BM blends, which may also contribute to the highest $FF$ in addition to the highest hole mobility for the monoCNTAZ based devices.

Overall, the morphology of all the three polymer:PC$_{61}$BM blends are similar, which indicates that CN substituents on the TAZ units would not strongly affect the morphology of the blends.
The lowest $J_{sc}$ of diCNTAZ based devices does not seem to be caused by the morphological features of the blends.

<table>
<thead>
<tr>
<th>Polymer:PC$_{61}$BM</th>
<th>$\pi-\pi$ stacking distance (Å)</th>
<th>(010) peak coherence length (Å)</th>
<th>Domain spacing (nm)</th>
<th>Relative domain purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ:PC$_{61}$BM</td>
<td>3.98</td>
<td>31.22</td>
<td>45.73</td>
<td>0.533</td>
</tr>
<tr>
<td>monoCNTAZ:PC$_{61}$BM</td>
<td>3.92</td>
<td>27.84</td>
<td>36.59</td>
<td>1</td>
</tr>
<tr>
<td>diCNTAZ:PC$_{61}$BM</td>
<td>3.85</td>
<td>27.84</td>
<td>48.21</td>
<td>0.771</td>
</tr>
</tbody>
</table>

**Figure 6.7.** Lorentz-corrected R-SoXS scattering profiles of the blends of polymer:PC$_{61}$BM at 283.2 eV.

### 6.6 Conclusion

In this study, we added a different number of strong electron withdrawing groups (CN) to the acceptor unit. With CN substitution, the HOMO levels are effectively decreased, and the $V_{oc}$ is noticeably improve to $\sim$ 1 eV. The CN substituents also effectively reduce the bandgaps of the polymers. With a single CN substituent, monoCNTAZ based devices achieve noticeably improved $J_{sc}$, $FF$ and thus best $PCE$ of $\sim$ 8.6%. However, with two CN substituents, diCNTAZ based devices
suffers from the low $J_{sc}$ values. The lowest hole mobility of diCNTAZ may increase the non-geminate recombination in the devices and thus decrease the $J_{sc}$. Other reasons may also contribute to the decreased $J_{sc}$ of diCNTAZ based devices, which is currently under exploration. Overall, this study proves the usefulness of CN substituents in tailoring the energy levels, bandgaps and charge transport properties of the polymers and provides some guidelines for the design of materials with strong electron-withdrawing substituents to simultaneously achieve high $V_{oc}$, high $J_{sc}$ and high $FF$.

6.7 Experiment Section

Chemicals and methods All chemicals were purchased from commercial sources and were utilized as received except when specified.

Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Agilent PL220 instrument with TCB as the eluent (stabilized with 250 ppm BHT) at 160 °C. The obtained molecular weight is relative to the polystyrene standard. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometers (400 MHz, 500 MHz or 600 MHz). Mass Spectrometry was run on a Q Exactive Orbitrap (ThermoFisher, Bremen, Germany) mass spectrometer and analyzed via Xcalibur (ThermoFisher, Breman, Germany). UV-visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments).

Cyclic Voltammetry (CV). CV measurements were carried out on solid films using a Bioanalytical Systems (BAS) Epsilon potentiostat with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, Ag reference electrode and Pt counter electrode were used. Films were drop-cast onto the glassy carbon electrode from hot chloroform
solution (2 mg/mL, with tetrabutylammonium hexafluorophosphate added at 100% wt% relative to polymers) and dried using a heat gun. 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were carried out under argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential ($E_{ox}$) according to the following equation:

$$HOMO = -[4.8e + e(E_{ox} - E_{Fc/Fc^+})]$$

**Device fabrication** Glass substrates coated with patterned indium doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. About 150 nm sputtered ITO pattern had a resistivity of 20Ω/□. Prior to use, the substrates were ultrasonicated in deionized water, acetone, and then 2-propanol for 15 minutes each. The substrates were dried under a stream of nitrogen gas and subjected to the treatment of UV-Ozone for 15 min. CuSCN was used as the hole transport layer for all three polymers. The CuSCN was dissolved in diethylsulfide with the concentration 23 mg/mL under stirring for 1 h. Then the CuSCN solution was filtered by 0.2 µm poly(tetrafluoroethylene) (PTFE) filter and spun-cast on the cleaned ITO substrates at 6000 rpm for 60 s and then baked at 100 °C for 10 min in air to give a thin film with a thickness of about 40 nm. Blends of polymer:PC$_{61}$BM (1:2 w/w) were dissolved in 1,2,4-trichlorobenzene with heating at 130 °C for 6h. All the solutions were filtered through a 5.0 µm PTFE filter and spun-cast at an optimized rpm for 60 seconds onto the HTL layer. The substrates were transferred into vacuum chamber immediately after spin-coating and then dried at 30 mmHg below atmosphere for 30 mins. The devices were finished for measurement after thermal deposition of a 30 nm film of calcium and a 70 nm aluminum film as the cathode for at base pressure of $2 \times 10^{-6}$ mbar.
The concentrations of the polymer and PC$_{61}$BM solution in 1,2,4-trichlorobenzene are as follows: 10 mg/mL for HTAZ, 6 – 7 mg/mL for monoCNTAZ and 7 – 8 mg/mL for diCNTAZ.

There were 8 devices per substrate, with an active area of 13 mm$^2$ per device. Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW/cm$^2$ (Oriel 91160, 300 W) calibrated by an NREL certified standard silicon cell. Current density versus voltage (J-V) curves was recorded with a Keithley 2400 digital source meter. EQE was detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode (Model No.: Newport 71580). All fabrication steps after adding the PEDOT:PSS or CuSCN layer onto ITO substrate, and characterizations were performed in gloveboxes under nitrogen atmosphere.

**Grazing Incidence Wide Angle X-ray Scattering.** GIWAXS was measured at beamline 7.3.3 of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.$^{115}$ The 10 keV. X-ray beam was incident at a grazing angle of 0.13°, which maximized the scattering intensity from the samples and minimized the scattering intensity from the substrate. The scattered intensity was detected with a Dectris Pilatus 1M photon counting detector.

**Resonant Soft X-ray Scattering.** R-SoXS was measured at beamline 11.0.1.2 of the ALS$^{72}$ on blend films. Data were acquired at the photon energy of 283.6 eV where the contrast between polymer and fullerene is relatively high enough for these materials, yet does not lead to beam damage or background fluorescence.

**Synthesis of monomers**

For reactions that was ran under argon, the flask was evacuated and refilled with argon before reactants were charged.
3,4-diamino-2,5-dibromobenzonitrile (Compound 6.2) (under argon) The solution of 3,4-diaminobenzonitrile (Compound 6.1, 2.66 g, 20.0 mmol) and potassium bromide (31.65 g, 266 mmol) in 300 mL methanol was purged with argon for 20 min. 62% hydrogen bromide solution (3.54 mL) was added at 0 °C slowly. 70% tert-butylhydroperoxide solution (1.74 mL) was added and stirred at r.t. for 6 hr. Then a second portion of 70% tert-butylhydroperoxide solution (1.74 mL) was added and stirred for 6 hr before the third portion of 70% tert-butylhydroperoxide solution (1.74 mL) was added and stirred overnight. The reaction mixture poured into water and filtered. The red solid was washed with water and dried over phosphorus pentoxide under low pressure. Yield, 3.31 g, 56.9%. \(^1\)H NMR (600 MHz, MeOD) δ 7.22 (1H).

4,7-dibromo-2H-benzo[d][1,2,3]triazole-5-carbonitrile (Compound 6.3) To the solution of Compound 6.2 (2.33 g, 8.0 mmol) in 18 mL acetic acid, sodium nitrite (0.91 g, 13.2 mmol) in 14 mL water was added at 0 °C. The reaction was stirred at r.t. for 1.5 hr before being poured into water. The product was extracted with ethyl acetate for three times, and the combined organic solution was washed with water for two times and brine. The organic solution was then dried over magnesium sulfate, filtered, and the solvent was removed with rot-vap. Yield, dark red solid, 2.1 g, 86.9%. \(^1\)H NMR (600 MHz, MeOD) δ 7.98.

4,7-dibromo-2-(2-butylctyl)-2H-benzo[d][1,2,3]triazole-5-carbonitrile (Compound 6.4) (under argon) To the solution of Compound 6.3 (2.1 g, 6.95 mmol) and triphenylphosphine (2.73 g, 10.43 mmol) in anhydrous THF, 2-butyl-1-octanol (1.94 g, 10.43 mmol) was added at 0 °C, and then diisopropyl azodicarboxylate (DIAD) (2.67 g, 13.20 mmol) was added at 0 °C. The reaction was slowly warmed to r.t. and stirred overnight. Then the reaction mixture was poured into water, and the product was extracted with ethyl acetate for three times. The combined organic solution was washed with water for two times and brine for one time. The organic solution was dried over
magnesium sulfate and filtered. The solvent was removed with rot-vap, and the crude product was purified via silica column chromatography with hexanes : ethyl acetate = 15 : 1 as eluent. Yield, colorless oil, 1.11 g, 34.0%. \( ^{1} \text{H NMR} \ (600 \text{ MHz, Chloroform-}d) \ \delta 7.72 \ (s, 1H), 4.72 \ (d, J = 7.1 \text{ Hz, 2H}), 2.33 \ (m, 1H), 1.40 – 1.15 \ (m, 16H), 0.87 \ (m, 6H). \ \ ^{13} \text{C NMR} \ (151 \text{ MHz, Chloroform-}d) \ \delta 144.69, 143.27, 130.78, 117.59, 116.36, 113.74, 111.34, 61.72, 39.27, 31.79, 31.24, 30.96, 29.53, 28.33, 26.09, 22.95, 22.73, 14.22, 14.10. 

2-(2-butyloctyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-5-carbonitrile

(Compound 6.5) (under argon) To the solution of Compound 6.4 (1.30 g, 2.76 mmol) and trimethyl(thiophen-2-yl)stannane (1.70 g, 6.91 mmol) in anhydrous toluene, Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.058 g, 0.083 mmol) was added under argon stream, and the solution was purged with argon for 20 min. The reaction was refluxed for 48 hr. The solvent was removed via rot-vap. And the product was purified via silica column chromatography with hexanes : dichloromethane = 10 : 1 to 4 : 1 as eluent. Yield, yellow oil, 0.93 g, 70.7%. \( ^{1} \text{H NMR} \ (600 \text{ MHz, Chloroform-}d) \ \delta 8.21 \ (dd, J = 3.8, 1.1 \text{ Hz, 1H}), 8.12 \ (dd, J = 3.7, 1.1 \text{ Hz, 1H}), 7.83 \ (s, 1H), 7.63 \ (dd, J = 5.1, 1.1 \text{ Hz, 1H}), 7.47 \ (dd, J = 5.1, 1.1 \text{ Hz, 1H}), 7.26 \ (m, 1H), 7.21 \ (dd, J = 5.1, 3.7 \text{ Hz, 1H}), 4.77 \ (d, J = 6.6 \text{ Hz, 2H}), 2.31 \ (h, J = 6.4 \text{ Hz, 1H}), 1.47 – 1.15 \ (m, 16H), 0.88 \ (m, 6H). \ \ ^{13} \text{C NMR} \ (151 \text{ MHz, Chloroform-}d) \ \delta 142.83, 142.54, 137.93, 135.00, 130.58, 129.69, 129.04, 128.45, 128.35, 127.78, 127.23, 125.45, 124.69, 119.82, 105.73, 60.62, 39.29, 31.94, 31.54, 31.28, 29.66, 28.59, 26.33, 23.07, 22.78, 14.24, 14.20.

4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole-5-carbonitrile

(m-monoCNTAZ) (under argon) To the solution of Compound 6.4 (0.92 g, 1.93 mmol) in 50 mL dichloromethane and 18 mL acetic acid, NBS (0.72 g, 4.05 mmol) was added in dark. The reaction was stirred in dark at r.t. for 40 hr. The second portion of NBS (0.12 g, 0.68 mmol) was added and
stirred in dark at r.t. for 50 hr. The third portion of NBS (0.21 g, 1.16 mmol) was added and stirred overnight. Then the fourth portion of NBS (0.16 g, 0.79 mmol) was added and stirred overnight. The fifth portion of NBS (0.18 g, 1.0 mmol) was added and stirred overnight. The sixth portion of NBS (0.05 g, 0.28 mmol) was added and stirred overnight. The reaction was tracked with $^1$H NMR until the dibromination was complete. The reaction was then poured into water, and the product was extracted with dichloromethane for three times. The combined organic solution was washed with water for two times and brine for one time. The organic solution was dried over magnesium sulfate and filtered. The solvent was removed via rot-vap. And the product was purified with silica column chromatography with hexanes : dichloromethane = 4 : 1 as eluent and was then recrystallized in ethanol. Yield, yellow solid, 0.96 g, 78.4%. $^1$H NMR (600 MHz, Chloroform-$d$) δ 8.01 (d, $J = 4.1$ Hz, 1H), 7.79 (d, $J = 4.0$ Hz, 1H), 7.71 (s, 1H), 7.21 (d, $J = 4.1$ Hz, 1H), 7.16 (d, $J = 4.0$ Hz, 1H), 4.77 (d, $J = 6.5$ Hz, 2H), 2.28 (p, $J = 6.3$ Hz, 1H), 1.47 – 1.21 (m, 16H), 0.89 (m, 6H). $^{13}$C NMR (151 MHz, chloroform-$d$) δ 142.43, 142.11, 139.11, 136.50, 131.23, 130.71, 130.68, 128.21, 127.96, 125.00, 123.93, 119.46, 118.04, 115.27, 105.22, 60.60, 39.36, 31.96, 31.54, 31.31, 29.70, 28.60, 26.32, 23.10, 22.81, 14.25, 14.23. [M + H]$^+$ (ESI) calculated 633.035135, measured 633.03567.

4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole-5,6-dicarbonitrile (m-diCNTAZ) (under argon) The solution of m-FTAZ (0.97 g, 1.5 mmol), potassium cyanide (0.59 g, 9.0 mmol) and 18-crown-6 ether (0.221 g, 0.9 mmol) in 65 mL THF and 11 mL DMF was purged with argon for 20 min. The reaction was refluxed for 48 hr. The reaction mixture was poured into water. The product was extracted with ethyl acetate for three times, and the combined organic solution was washed with water for two times and brine for one time. The aqueous solution was treated with excessive sodium hypochlorite solution to oxidize the

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residue potassium cyanide before being poured into waste container. The organic solution was
dried over magnesium sulfate and filtered. The solvent was removed via rot-vap. The product was
purified via silica column chromatography with hexanes : dichloromethane = 3 : 2 as eluent and
was recrystallized in ethanol for further purification. Yield, yellow solid, 0.66 g, 66.0%. $^1$H NMR
(600 MHz, Chloroform-d) δ 8.07 (d, $J = 4.1$ Hz, 2H), 7.24 (d, $J = 4.1$ Hz, 2H), 4.80 (d, $J = 6.4$
Hz, 2H), 2.27 (p, $J = 6.3$ Hz, 1H), 1.49 – 1.21 (m, 16H), 0.90 (m, 6H). $^{13}$C NMR (151 MHz,
chloroform-d) δ 142.51, 134.81, 132.15, 130.98, 129.91, 119.78, 116.77, 107.54, 61.04, 39.46,
31.95, 31.50, 31.27, 29.68, 28.56, 26.29, 23.09, 22.80, 14.24, 14.23. [M]$^+$ (ESI), calculated
657.023107, measured 657.02739.

**Synthesis of polymers**

BnDT monomer (1.030 eq for $m$-HTAZ, 1.020 eq for $m$-monoCNTAZ and 1.015 eq for $m$-
diCNTAZ), TAZ monomers (1.000eq), Pd$_2$(dba)$_3$·CHCl$_3$ (0.02 eq) and P(o-tol)$_3$ (0.16 eq) were
charged into a 10 mL vial designed for microwave reactor. The mixture was evacuated and refilled
with argon for three cycles before addition of anhydrous o-xylene under argon stream. The reaction
was heated up to 200 °C and hold in a CEM microwave reactor for 10 min. After the
polymerization, the crude polymer was dissolved in hot chlorobenzene (use 1,2-dichlorobenzene
for monoCNTAZ polymer) and precipitated into stirring methanol. The collected polymer was
extracted via a Soxhlet extractor with EtOAc, hexanes, and chloroform. The polymer solution in
chloroform was concentrated via rotavap. The collected polymer was re-dissolved into hot
chlorobenzene and precipitated into methanol. The polymer was then collected via filtration and
dried under vacuum. For the Soxhlet extraction of monoCNTAZ, after chloroform, chlorobenzene
was used. Some insoluble polymer solid floated in chlorobenzene was transferred into the
chlorobenzene solution carefully with pipet. The chlorobenzene fraction was combined with the
chloroform fraction. The solvent was removed, and the polymer was redissolved in dichlorobenzene, precipitated into methanol, filtered and dried under vacuum.
CHAPTER 7
CONCLUSION AND FUTURE DIRECTION

7.1 Conclusion

Design of new polymer structure has played an important role in improving the performance of polymer solar cells. Many polymers have been introduced into this field in the past fifteen years, but fine-tuning of the chemical structure of the high-performance polymers is still of great importance to further boost the efficiency of PSCs. This dissertation was dedicated to the rational design of polymer structure and development of synthetic approaches to achieve those structures, with the goal of adjusting specific properties of the polymer. Chapter 2 introduced a methodology for synthesizing regio-regular terpolymers and regio-random terpolymers in order to extend the absorption bandgap. In Chapter 3, we developed wide bandgap polymers with two electron rich units (D-D polymers) which achieved high $V_{oc}$ values. In Chapter 4 and Chapter 5, we developed an elegant approach to controlling the position of fluorine substituents on the $\pi$-linker thiophene units of PBnDT-TAZ based polymers. Eight novel PBnDT-TAZ based polymers were designed and prepared in these two chapters, and the efficiencies of the polymers were effectively improved by the fluorinated thiophene unit. In Chapter 6, we decreased the bandgap of the polymers through introducing strong electron withdrawing cyano groups to the backbone. The efficiency of PSC devices was further improved to $\sim 8.6\%$. Several conclusions can be drawn based on the strategies for tuning polymer properties developed in this dissertation.

1) Both regio-regular terpolymers and regio-random terpolymers composed of the chemical units from polymers with complementary absorption spectra can extend the
absorption range of the polymers. However, in order to achieve high efficiency with the benefit of extended absorption range, compatibility of the monomer units needs to be considered. Forcing the chemical units onto the same polymer chains, especially for regio-regular terpolymers, may lead to poor aggregation of polymer chains, which may cause low local mobility, suppress charge generation and increase the non-geminate recombination.

2) Large bandgap polymers can be developed by copolymerizing two electron-rich units. High $V_{oc}$ was achieved by the “donor-donor” copolymers based on BnDT and dithenylbenzene units.

3) Fluorine substituents on the $\pi$ linker thiophene units between the donor unit and acceptor unit of a D-A copolymer can effectively improve the $\pi-\pi$ stacking and increase hole mobility of the polymer:PC$_{61}$BM blends. Considering many polymers are based on “donor-thiophene-acceptor-thiophene” pattern, we believe incorporation of fluorine substituents on the linker thiophene unit can further improve the efficiency of PSCs.

4) Hole mobility is important for the $FF$ of the PSC devices. High hole mobility will reduce the non-geminate recombination and improve the charge extraction efficiency, thus improve the $FF$. For the PBnDT-TAZ based polymers, a threshold hole mobility of $1 \times 10^{-3}$ cm$^2$/V•s is important for high $FF$ (> 65%) of 300 nm devices.

5) Adding electron withdrawing cyano groups can effectively lower the HOMO levels and decrease the bandgaps of the polymers, thus, the $V_{oc}$ and the $J_{sc}$ values are improved. High efficiency of ~ 8.6% was achieved by the monoCNTAZ polymer.
7.2 Future Direction

7.2.1 Control the regio-regularity of the asymmetric polymers

The photovoltaic properties of the four asymmetric polymers, monoFTAZ, 3’-FT-T-HTAZ, 4’-FT-T-HTAZ and 4’-FT-T-FTAZ are strongly affected by the number of the fluorine substituent. Interestingly, the fluorine position on the polymer backbones does not noticeably affect the properties of these polymers. However, symmetric fluorination seems to have a strong effect on the properties of the polymers and often leads to higher device efficiency. Given that the lack of the regio-regularity in these asymmetric polymers may pose negative effect on the morphology of the BHJ blends, control of the regio-regularity of the polymers may improve the efficiency of the asymmetric polymers based devices.

![Image of regio-random and regio-regular polymers]

**Figure 7.1.** Illustration of control of the regio-regularity of the asymmetric polymers.
7.2.2 Extend the series of polymers with fluorinated thiophene unit

We have proven that the fluorinated thiophene unit is an efficient approach to improve the efficiency of the TAZ polymer based PSC devices. Is the “efficiency enhancing” effect of fluorinated thiophene units applicable to the other D-A copolymers based on “donor-thiophene-acceptor-thiophene” pattern? We have designed several polymers of the “donor-thiophene-acceptor-thiophene” pattern (Figure 7.2), including TAZ based polymers and other acceptors (BT and TPD) based polymers. It will be interesting to apply this strategy to more polymers and carefully investigate them.

Figure 7.2. Designed polymers with fluorinated thiophene unit.

7.2.3 Study non-fullerene acceptor based devices with the novel PBnDT-TAZ polymers.

Non-fullerene acceptors (NFAs) are the key development in this filed accompanied by rapidly increasing efficiencies. With the development of non-fullerene acceptor units that have significantly improved absorption properties over the fullerene derivatives, $J_{sc}$ values of the solar cells are remarkably improved. Indeed, the record high efficiency (12% - 13%) of single junction PSCs were all achieved by the NFAs based devices.5, 126, 127 Current studies are focused on
optimization of the structure of the NFAs, yet continuing the development of high performance polymers to pair with NFAs is of equal importance. Subtle change in the structure of the polymers may have a significant effect on the device performance. High efficiency was achieved by FTAZ when it was blended with non-fullerene acceptors.\textsuperscript{126, 128} Since several novel polymers (3’-FT-HTAZ, 4’-FT-HTAZ and 4’-FT-FTAZ) achieved comparable or even higher efficiency than FTAZ in PC\textsubscript{61}BM based devices, we will further explore them by pairing them with NFAs.

\textbf{Figure 7.3.} An example of high performance non-fullerene acceptor with FTAZ (Reference\textsuperscript{126}).
1. Supplementary X-Ray diffraction figures

**Figure A 1.** Raw high-q R-SoXS images for all blended samples, with the vertical and horizontal axes displayed in terms of the reciprocal space scattering vector, q. The images also show the wedges wherein the sector averages were calculated, which are ±10° wide.
Figure A 2. Results of least-squares peak fitting analysis for all samples. The green line in all fits is a constant baseline, which was kept the same in all samples. For each sample, the q-range was kept constant for both the vertical and horizontal sectors.
Figure A 3. Results of GIWAXS experiments on BD:PCBM, BH:PCBM, BD:BH:PCBM, Ra-BDH:PCBM, and Re-BDH:PCBM. The dashed purple line represents a linear sum of the BD:PCBM and BH:PCBM sector averages.

2. NMR spectra of chemicals
Appendix for Chapter 3

1. NMR spectra of compounds

[Image of NMR spectra with chemical structures and ppm values]
Appendix for Chapter 4

1. Elemental analysis results of the four polymers

Table A 1. Elemental analysis results of the four polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>C</th>
<th></th>
<th>H</th>
<th></th>
<th>N</th>
<th></th>
<th>S</th>
<th></th>
<th>F</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cal</td>
<td>Exp</td>
<td>Cal</td>
<td>Exp</td>
<td>Cal</td>
<td>Exp</td>
<td>Cal</td>
<td>Exp</td>
<td>Cal</td>
<td>Exp</td>
</tr>
<tr>
<td>3'-FT-HTAZ</td>
<td>71.56</td>
<td>71.77</td>
<td>8.43</td>
<td>8.39</td>
<td>4.04</td>
<td>3.93</td>
<td>12.31</td>
<td>12.14</td>
<td>3.65</td>
<td>3.55</td>
</tr>
<tr>
<td>4'-FT-HTAZ</td>
<td>71.56</td>
<td>71.51</td>
<td>8.43</td>
<td>8.41</td>
<td>4.04</td>
<td>3.92</td>
<td>12.31</td>
<td>12.11</td>
<td>3.65</td>
<td>3.57</td>
</tr>
<tr>
<td>3'-FT-FTAZ</td>
<td>69.17</td>
<td>69.29</td>
<td>7.96</td>
<td>7.94</td>
<td>3.90</td>
<td>3.88</td>
<td>11.91</td>
<td>11.79</td>
<td>7.06</td>
<td>6.90</td>
</tr>
<tr>
<td>4'-FT-FTAZ</td>
<td>69.17</td>
<td>69.05</td>
<td>7.96</td>
<td>7.89</td>
<td>3.90</td>
<td>3.81</td>
<td>11.91</td>
<td>11.73</td>
<td>7.06</td>
<td>7.03</td>
</tr>
</tbody>
</table>

2. DFT calculation results

![BnDT-HTAZ](image1)

![BnDT-FTAZ](image2)

![BnDT-3'-FT-HTAZ](image3)

![BnDT-3'-FT-FTAZ](image4)
Figure A 4. Computed conformational structure and electron distribution of one repeating unit of polymers.

3. Photoluminescence quenching

Figure A 5. Photoluminescence curves of polymers and polymer: PC61BM blends.
Table A 2. PL quenching results of four new polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Polymer PL (a.u., ×10^7)</th>
<th>Polymer Absorption (a.u.)</th>
<th>Polymer:PCBM PL (a.u., ×10^6)</th>
<th>Polymer:PCBM absorption (a.u.)</th>
<th>PL Quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>3’-FT-HTAZ</td>
<td>10.0</td>
<td>0.552</td>
<td>9.64</td>
<td>0.578</td>
<td>91%</td>
</tr>
<tr>
<td>3’-FT-FTAZ</td>
<td>10.9</td>
<td>1.278</td>
<td>2.35</td>
<td>1.247</td>
<td>98%</td>
</tr>
<tr>
<td>4’-FT-HTAZ</td>
<td>7.65</td>
<td>0.604</td>
<td>5.70</td>
<td>0.666</td>
<td>93%</td>
</tr>
<tr>
<td>4’-FT-FTAZ</td>
<td>8.31</td>
<td>0.523</td>
<td>3.04</td>
<td>0.587</td>
<td>96%</td>
</tr>
</tbody>
</table>

4. Additional photovoltaic data

Table A 3. Best photovoltaic properties of devices with PEDOT : PSS as HTL

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>HTL</th>
<th>Thickness (nm)</th>
<th>J_sc (mA/cm^2)</th>
<th>V_oc (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>TCB</td>
<td>PEDOT</td>
<td>227</td>
<td>10.11±0.31</td>
<td>0.750±0.005</td>
<td>52.7±0.7</td>
<td>3.99±0.13</td>
</tr>
<tr>
<td>FTAZ</td>
<td>TCB</td>
<td>PEDOT</td>
<td>208</td>
<td>11.44±0.15</td>
<td>0.801±0.003</td>
<td>70.0±1.7</td>
<td>6.41±0.17</td>
</tr>
<tr>
<td>3’-FT-HTAZ</td>
<td>CB+3% DIO</td>
<td>PEDOT</td>
<td>237</td>
<td>11.72±0.28</td>
<td>0.879±0.009</td>
<td>67.3±1.3</td>
<td>6.94±0.25</td>
</tr>
<tr>
<td>3’-FT-FTAZ</td>
<td>CB+3% DIO</td>
<td>PEDOT</td>
<td>182</td>
<td>5.61±0.34</td>
<td>0.875±0.022</td>
<td>44.4±1.0</td>
<td>2.18±0.19</td>
</tr>
<tr>
<td>4’-FT-HTAZ</td>
<td>TCB</td>
<td>PEDOT</td>
<td>168</td>
<td>11.69±0.43</td>
<td>0.641±0.010</td>
<td>56.6±1.2</td>
<td>4.24±0.17</td>
</tr>
<tr>
<td>4’-FT-FTAZ</td>
<td>TCB</td>
<td>PEDOT</td>
<td>191</td>
<td>11.71±0.29</td>
<td>0.728±0.011</td>
<td>63.5±1.1</td>
<td>5.40±0.12</td>
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</tbody>
</table>

Table A 4. Photovoltaic properties of devices at 200 nm

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>HTL</th>
<th>Thickness (nm)</th>
<th>J_sc (mA/cm^2)</th>
<th>V_oc (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>205</td>
<td>10.55±0.21</td>
<td>0.752±0.001</td>
<td>56.9±1.1</td>
<td>4.52±0.18</td>
</tr>
<tr>
<td>FTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>233</td>
<td>11.48±0.25</td>
<td>0.812±0.002</td>
<td>69.0±1.1</td>
<td>6.43±0.23</td>
</tr>
<tr>
<td>3’-FT-HTAZ</td>
<td>CB+3% DIO</td>
<td>CuSCN</td>
<td>220</td>
<td>10.28±0.20</td>
<td>0.925±0.001</td>
<td>67.0±0.7</td>
<td>6.37±0.16</td>
</tr>
<tr>
<td>3’-FT-FTAZ</td>
<td>CB+3% DIO</td>
<td>CuSCN</td>
<td>193</td>
<td>6.16±0.12</td>
<td>0.981±0.006</td>
<td>48.6±0.6</td>
<td>2.94±0.05</td>
</tr>
<tr>
<td>4’-FT-HTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>200</td>
<td>12.02±0.58</td>
<td>0.820±0.001</td>
<td>69.3±0.9</td>
<td>6.82±0.32</td>
</tr>
<tr>
<td>4’-FT-FTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>223</td>
<td>12.39±0.41</td>
<td>0.922±0.003</td>
<td>67.8±2.9</td>
<td>7.74±0.36</td>
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</tbody>
</table>
### Table A 5. Photovoltaic properties of devices at 300 nm

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>HTL</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>249</td>
<td>11.10±0.25</td>
<td>0.741±0.001</td>
<td>53.3±1.3</td>
<td>4.39±0.17</td>
</tr>
<tr>
<td>FTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>308</td>
<td>12.02±0.25</td>
<td>0.805±0.001</td>
<td>68.0±1.0</td>
<td>6.58±0.21</td>
</tr>
<tr>
<td>3'-FT-HTAZ</td>
<td>CB+3% DIO</td>
<td>CuSCN</td>
<td>272</td>
<td>11.72±0.15</td>
<td>0.909±0.002</td>
<td>69.6±1.0</td>
<td>7.42±0.14</td>
</tr>
<tr>
<td>3'-FT-FTAZ</td>
<td>CB+3% DIO</td>
<td>CuSCN</td>
<td>281</td>
<td>4.57±0.05</td>
<td>0.947±0.005</td>
<td>39.2±1.0</td>
<td>1.70±0.06</td>
</tr>
<tr>
<td>4'-FT-HTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>291</td>
<td>12.41±0.45</td>
<td>0.812±0.003</td>
<td>65.1±3.6</td>
<td>6.56±0.40</td>
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<tr>
<td>4'-FT-FTAZ</td>
<td>TCB</td>
<td>CuSCN</td>
<td>299</td>
<td>12.28±0.51</td>
<td>0.910±0.003</td>
<td>64.0±1.4</td>
<td>7.15±0.32</td>
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</tbody>
</table>

### Table A 6. Photovoltaic results of high-molecular-weight 4'-FT-FTAZ (Mn = 37.1 Kg/mol, PDI = 2.91)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCB</td>
<td>262</td>
<td>11.55±0.55</td>
<td>0.821±0.001</td>
<td>65.4±1.2</td>
<td>6.20±0.28</td>
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<tr>
<td></td>
<td>216</td>
<td>11.03±0.36</td>
<td>0.823±0.004</td>
<td>67.1±1.8</td>
<td>6.10±0.22</td>
</tr>
<tr>
<td></td>
<td>187</td>
<td>10.45±0.38</td>
<td>0.827±0.001</td>
<td>68.6±1.4</td>
<td>5.92±0.23</td>
</tr>
</tbody>
</table>

### Table A 7. Photovoltaic results of high-molecular-weight 4'-FT-FTAZ (Mn = 26.0 Kg/mol, PDI = 2.40)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Condition</th>
<th>Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCB</td>
<td>Preheat to 95°C</td>
<td>260</td>
<td>12.90±0.45</td>
<td>0.913±0.001</td>
<td>62.4±0.6</td>
<td>7.35±0.30</td>
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<tr>
<td></td>
<td></td>
<td>218</td>
<td>11.29±0.28</td>
<td>0.922±0.002</td>
<td>63.5±1.2</td>
<td>6.61±0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>172</td>
<td>10.56±0.53</td>
<td>0.917±0.004</td>
<td>63.9±0.8</td>
<td>6.19±0.28</td>
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<tr>
<td>CB+3% DIO</td>
<td>Solvent annealing</td>
<td>123</td>
<td>9.74±0.15</td>
<td>0.895±0.005</td>
<td>51.2±1.9</td>
<td>4.46±0.20</td>
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<td></td>
<td></td>
<td>116</td>
<td>9.11±0.14</td>
<td>0.915±0.003</td>
<td>54.3±1.0</td>
<td>4.53±0.07</td>
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<tr>
<td></td>
<td></td>
<td>115</td>
<td>9.06±0.12</td>
<td>0.914±0.007</td>
<td>51.9±2.2</td>
<td>4.30±0.22</td>
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<tr>
<td>DCB+3% DIO</td>
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<td>10.65±0.18</td>
<td>0.900±0.004</td>
<td>54.6±1.7</td>
<td>5.23±0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.12±0.29</td>
<td>0.909±0.004</td>
<td>56.0±1.4</td>
<td>5.15±0.08</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>9.64±0.22</td>
<td>0.918±0.008</td>
<td>56.4±1.3</td>
<td>4.99±0.12</td>
<td></td>
</tr>
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</table>
5. High sensitivity EQE and CT state fitting

Figure A 6. High sensitivity EQE and CT state fitting.
6. Supplementary morphology data

Figure A 7. 2D GIWAXS patterns of (a-d) neat polymer films and (e-h) blends; pole figures of (100) and (010) peaks of (i-l) neat films and (m-p) blends.
Figure A 8. Diffraction profiles cut along the \( \sim q_z \) axis of the 2D GIXD images for polymer/PC61BM blend films (blue line), their fits (red line) fitted to pseudo-Voigt functions, and PC61BM (peak 1) and polymer \( \pi-\pi \) stacking (peak 2) peaks separated from the fits.
**Figure A 9.** Lorentz-corrected R-SoXS scattering profiles of the blends of polymer:PC61BM at 284.2 eV.

**Table A 8.** Morphological data of the polymers and polymer:PC61BM blends.

<table>
<thead>
<tr>
<th>Polymer: PC61BM</th>
<th>3'-FT-HTAZ (Å)</th>
<th>3'-FT-FTAZ (Å)</th>
<th>4'-FT-HTAZ (Å)</th>
<th>4'-FT-FTAZ (Å)</th>
<th>FTAZ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) peak</td>
<td>0.36</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>n.a.</td>
</tr>
<tr>
<td>(010) peak</td>
<td>1.56</td>
<td>1.62</td>
<td>1.66</td>
<td>1.68</td>
<td>n.a.</td>
</tr>
<tr>
<td>π-π stacking distance</td>
<td>4.03</td>
<td>3.88</td>
<td>3.78</td>
<td>3.74</td>
<td>n.a.</td>
</tr>
<tr>
<td>(010) fwhm</td>
<td>0.28</td>
<td>0.21</td>
<td>0.32</td>
<td>0.21</td>
<td>n.a.</td>
</tr>
<tr>
<td>Coherence length of π-π stacking (Å)</td>
<td>22.44</td>
<td>29.92</td>
<td>19.63</td>
<td>19.92</td>
<td>n.a.</td>
</tr>
<tr>
<td>PC61BM peak</td>
<td>1.36</td>
<td>1.36</td>
<td>1.35</td>
<td>1.35</td>
<td>n.a.</td>
</tr>
<tr>
<td>PC61BM fwhm</td>
<td>0.24</td>
<td>0.25</td>
<td>0.27</td>
<td>0.27</td>
<td>n.a.</td>
</tr>
<tr>
<td>PCBM Voigt shape parameter</td>
<td>0.91</td>
<td>0.62</td>
<td>1.67</td>
<td>1.69</td>
<td>n.a.</td>
</tr>
<tr>
<td>Domain spacing (nm)</td>
<td>71.4</td>
<td>n.a.</td>
<td>89.7</td>
<td>149.5</td>
<td>128.2</td>
</tr>
<tr>
<td>Relative domain purity</td>
<td>1</td>
<td>n.a.</td>
<td>0.70</td>
<td>0.56</td>
<td>0.62</td>
</tr>
<tr>
<td>Anisotropy parameter</td>
<td>0.15</td>
<td>n.a.</td>
<td>0.12</td>
<td>0.086</td>
<td>0.064</td>
</tr>
</tbody>
</table>
7. NMR

NMR of small molecules were taken in chloroform-d at r.t.. NMR of polymers were taken in 1,1,2,2-Tetrachloroethane-d$_2$ at 373 K.
1. NMR
Appendix for **Chapter 6**

1. GPC curves of the three polymers at 160 °C.

![GPC curves of the three polymers](image)

**Figure A 10.** GPC curves of the three polymers

2. NMR

![NMR spectrum](image)
REFERENCES


