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# **Doctoral Dissertation**

# An Investigation of Molecular Designs of Donor-Acceptor Copolymers Incorporating Benzotrithiophene and Benzobisthiazole Units Toward High-Performance Organic Photovoltaics

(有機太陽電池の高効率化を指向したベンゾトリチオフェン あるいはベンゾビスチアゾールを有するドナー・アクセプ ター共重合体の分子設計に関する研究)

Eman Rashid Said Al-Naamani

January 2018

Department of Applied Chemistry, Graduate School of Engineering, Osaka University

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### PREFACE

This dissertation presents the studies conducted under the supervision of Associate Professor Akinori Saeki at Department of Applied Chemistry, Graduate School of Engineering, Osaka University and Professor Shu Seki, presently at Department of Molecular Engineering, Graduate School of Engineering, Kyoto University.

The objective in this dissertation is to provide insights into the semiconducting low bandgap polymers utilizing benzotrithiophene and benzobisthiazole units. The study includes synthesis, characterization, and solar cell fabrication using the designed polymers. The author hopes the findings of this work to contribute to the molecular design of organic semiconducting polymers for the photovoltaic applications.

Eman Al-Naamani

Department of Applied Chemistry Graduate School of Engineering Osaka University, Japan January 2018

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#### ACKNOWLEDGMENTS

# Chapter 1: Introduction

 $E_{\mathrm{nergy}}$  production from resources alternatives to fossil fuels with an effective yield is one of the most important issues needed to be resolved in the 21<sup>st</sup> century. Environmental impact along with the depletion of fossil fuel resources leads to a new revolution in the energy industry. Dependency on renewable energy resources appears to be possible and the time of actual replacement is progressing. With almost of today's energy production based on fossil fuels, renewable resources are being developed with time as predicted by the "Global Solar Demand Monitor" for the first quarter of 2017 (Figure 1).<sup>1</sup> In addition to diminution of fossil fuels, the environmental effects especially CO<sub>2</sub> emissions necessitate improvement of safer energy resources. The annual report of the "World energy issues monitor" for the year 2014 summarizes energy-related challenges of three main issues; energy security, equity and environmental sustainability.<sup>2</sup> Solar energy is the most secure and abundant energy resource yet not fully utilized. More than half a century, researches on implementing solar energy resulted in the commercialization of inorganic solar cells. In particular, the power conversion efficiency (PCE) of silicon-based single-layer solar cells has been improved from 6% in 1954 by Chapin<sup>3</sup> to about 27%.<sup>4</sup> Although inorganic solar cells achieved good efficiencies, they yet suffer from high production costs caused by high processing temperature. The discovery of conducting and semi-conducting polymers facilitates a possible replacement of inorganic materials in the active layer of solar cells.

Organic solar cell (OSC) uses flexible organic molecules such as semiconducting polymers or small organic molecules. Semiconducting organic molecules have the ability to absorb sunlight and convert it to electricity by the photovoltaic effect. The flexibility and lightweight of organic molecules is advantageous for cost-effective roll-to-roll processing. As well as, wider implementation possibilities due to the elastic nature of organic molecules. In addition, the photovoltaic properties of organic molecules can be rationally manipulated through molecular engineering. Nevertheless, given the low efficiency of OSCs compared to inorganic solar cells, there is still wide opportunity for improvements.



**Figure 1.** Global solar market shifts expectation until 2022. Source: Global Solar Demand Monitor Q1 2017.

The first organic photovoltaic (OPV) device was reported in 1986 by C. W. Tang. The device was fabricated in a bilayer structure consisting of copper phthalocyanine and perylene materials achieving only 1% PCE.<sup>5</sup> The significant improvement in OPV devices began after the invention of bulk heterojunction (BHJ) solar cell structure by Heeger and coworkers in 1995.<sup>6</sup> The enhanced performance of the BHJ design is due to the increased short circuit current (*J*<sub>SC</sub>) of the device as a result of the improved interfaces of the p-type (positive denoting electron donor) and n-type (negative denoting electron acceptor) materials. The device incorporating poly(2-methoxy-5-(2'ethyl-hexyloxy)1,4-phenylenevinylene) (MEH-PPV) as the p-type material with fullerene molecule as the n-type material achieved PCE of 2.9%. Further developments focused on device structure and its constituents of hole and electron transporting buffers along with the molecular design of the p-type polymers and the n-type materials resulted in PCE exceeding11%.<sup>7-11</sup>

#### 1-1 Bulk-heterojunction OPV devices

The bulk-heterojunction (BHJ) is the active layer in an OPV consisting of a blend of p- and n- type materials, where free carriers are generated and transport to the buffer/electrodes. Figure 2 shows a schematic diagram of the optoelectronic process that occurs in a BHJ. Upon light absorption with photon energy efficient to excite an electron from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) levels of the polymer, an exciton is formed, and then migrates to the p/ninterface. The exciton dissociates into free carriers at the p/n interface, which diffuse to the corresponding electrodes. Thus, polymer orientation, stacking in the  $\pi$  direction and its domain size in the microscale strongly alter charge dissociation process at the interface.<sup>12-14</sup> In Chapter 4, the impact of the nanoscale morphology is discussed in more details. The morphology of the BHJ can significantly affect the performance of the OPV device. Therefore, p/n interfaces are manipulated by different polymer molecular designs, processing conditions and solvent additives in order to optimize charges separation and minimize recombination rates. Throughout the study presented in this thesis, the optimum OPV performance was investigated at different processing conditions including solvent, solvent additives, annealing and active layer thickness.



**Figure 2.** Schematic diagram of photocurrent generation mechanism in organic photovoltaic; step 1: excitation and exciton diffusion to p/n interface, step 2: electronhole separation, and step 3: free charges transport to the electrodes.

#### 1-2 JV characterization

The conversion of the photon energy of the light into electric current is observed via the current density versus voltage (JV) curve of the device. A schematic diagram of the JV curve is represented in Figure 3. The performance parameters of an OPV device found from the produced JV curve under a certain illumination are the open circuit voltage ( $V_{\rm OC}$ ), short circuit current ( $J_{\rm SC}$ ) and fill factor (FF).  $V_{\rm OC}$  and  $J_{\rm SC}$  are the voltage and the current density at zero output power denoting the cross points at the two axes of the JV curve. FF is a parameter that compares the maximum output power to the power that can be obtained at  $V_{\rm OC}$  and  $J_{\rm SC}$ . High FF value means the maximum output power is close to the boundary and thus indicates high carriers' collection efficiencies at the electrodes. The power conversion efficiency PCE of the device is obtained as the product of the three parameters  $V_{\rm OC}$ ,  $J_{\rm SC}$  and FF over the incident light power  $P_{\rm in}$  (AM1.5G, 100 mWcm<sup>-2</sup>).



Figure 3. Schematic diagram of the *JV* curve of an OPV device.

#### 1-3 p/n materials and interfaces

The widely investigated OPV structure consists of the p/n blend BHJ as an active layer responsible for light absorption and generation of free carriers.<sup>15</sup> The implemented p-type materials are mostly the low bandgap conjugated copolymers consisting of alternating weak donor (D) and strong acceptor (A) monomers.<sup>16,17</sup> The underlying strategy of DA copolymers is its benefits to obtain high electron and hole mobility derived by the different electron affinity monomers providing a push-pull electronic nature in the polymer backbone. Therefore, DA copolymers can effectively enhance the intramolecular charge transfer in the polymer backbone.<sup>18-20</sup> In addition, DAtype copolymers facilitate narrow optical bandgap that can harvest broad sunlight spectrum in the visible and near infrared regions.<sup>21</sup> Numerous examples of DA copolymers are found in the literatures.<sup>22,23</sup> The optical band gap of DA copolymer is mainly dependent on the HOMO of donor moiety and

LUMO of the the acceptor moiety. Optimization of DA polymers requires matching their HOMO - LUMO energy levels with that of the acceptor fullerene in order to achieve optimum LUMO offset,24 Figure 4. These designs allow for enhancing dissociation charges and minimizing recombination. On the other hand, the difference between HOMO of the polymer and LUMO of fullerene needs to be maintained high in order to achieve high  $V_{\rm OC}$ in the device.

In addition to the energy levels of polymers, morphology is proved to have a significant impact on the device performance.<sup>25,26</sup> Therefore, polymer molecular weight, planarity and solubility



**Figure 4.** HOMO and LUMO energy levels of polymer aligning with respect to that of fullerene material for V<sub>OC</sub> and LUMO offset optimization are important factors to optimize charges transfer in the p/n BHJ. High performing DA copolymers were synthesized using benzodithiophene (BDT), cyclopentaditiophene (CPDT), or napthodithiophene (NDT) as a donor moiety with benzothiadiazole (BT), or thiazolothiazole (TTz) as an acceptor moiety. The literature is rich with plentiful examples of donor and acceptor moieties.<sup>27</sup> High mobility semiconducting polymers such as poly(3hexylthiophene) (P3HT) with the n-type fullerene derivative 6,6-phenyl- $C_{61/71}$ -butyric acid methyl ester (PC<sub>61/71</sub>BM) has shown PCE 4-5% in a BHJ device. <sup>28-32</sup> Yang et al. reported morphology control by varying the growth rate of the polymer layer. The study showed the solidification time resulted in increased hole mobility after allowing the polymer to self-organize in the blend film. On the other hand, Nelson et al. suggested that the vertical arrangement of the polymer molecules toward the electrodes can potentially improve exciton dissociation, charges transport and electrode selectivity. Another successful example of DA copolymer is polythieno[3,4-b]-thiopheneco-benzodithiophene (PTB7), the PCE of which approached 9 % in 2012.<sup>33-35</sup> The series of PTB polymers have revealed the beneficial effect of the reduced domain sizes that allowed PCBM molecules to intercalate and increase the interfacial distance with the polymer molecules. Furthermore, the nanoscale morphology of the BHJ can be manipulated using solvent additives such as 1,8-diiodooctane (DIO) to ensure forming of pure crystalline phases of the polymer and PCBM molecules in order to minimize charges recombination. Deibel et al. found that using DIO additive in PTB7 devices resulted in a reduction of the non-geminate recombination and increased charges collection efficiencies therefore obtained higher FF.<sup>36,37</sup> Subsequently, the crystalline pure and intermixed regions of p/n molecules in the BHJ facilitate the required medium for better hole mobility and exciton dissociation, respectively. Therefore, crystalline polymers with a distinct orientation are preferable. Stingelin *et al.* investigated the role of the intermixed phases on the optoelectronic properties of P3HT:PCBM blends. To compare between high and low weight-averaged molecular weights  $(M_w)$  of the crystalline P3HT

they probed the dissociated polaron yield using a microsecond-transient absorption experiments. The results showed about 30-40% increase in the dissociated polaron yields in favor to the high  $M_{\rm w}$  P3HT. Furtherly, when PCBM content was raised in the high  $M_{\rm w}$  P3HT, the dissociation was improved due to the formation of PCBM aggregates that facilitates better charges separation.<sup>38</sup> A schematic illustration of the P3HT:PCBM microstructure is represented in Figure 5 for the high and low  $M_{\rm w}$  P3HT. The illustrated image of high  $M_{\rm w}$  P3HT emphasizes the importance of three regions in a BHJ; the crystalline pure polymer, PCBM aggregations, and an intermixed PCBM intercalation between the polymer chains. For ordered and disordered domains in a BHJ, Neher *et al.* showed high local charge mobilities in the high  $M_{\rm w}$  P3HT indicating that the crystalline phase of the polymer is the main contributor to charge transport.<sup>39,40</sup> Similarly, Salleo et al. suggested that the coexistence of crystalline ordered structures and amorphous regions in the microstructure of the BHJ causes the carriers to be confined in the ordered region, which forces the carriers to hop between different regions with a high energy barrier. Thus, the presence of domain inter-connection between the ordered structures is required to increase

charge carrier mobility.<sup>41,42</sup> These results and others<sup>43·47</sup> highlight the importance of p/n interfaces for efficient charges separation as in addition to the polymer stacking in the  $\pi$ direction for high carrier mobility. In the work presented in this thesis, the crystallinity and orientation of the designed polymers are investigated using 2D-grazing incidence X-ray diffraction (2D-GIXRD) experiments.



**Figure 5.** Low and high  $M_w$ P3HT polymer chains. (Represented from ref.39)

#### 1-4 Optimum $V_{\rm OC}$ of an OPV device

In p/n BHJ OPV devices the  $V_{\rm OC}$  is widely known to be limited by the effective bandgap of the blend  $(E_{
m g}^{
m eff})$  denoting the difference of HOMO of the p-type and LUMO of the n-type.<sup>48-51</sup> Barbec *et al.* investigated the origin of  $V_{\rm OC}$  by varying the LUMO level of fullerene derivative materials. The results showed a degreasing linear correlation of Voc with the reduction of acceptor LUMO levels. <sup>48</sup> However, due to the complex nature of the p/n interfaces bound electron-hole pairs are formed resulting in the depletion of  $V_{\rm OC}$ . In most OPV devices the  $V_{\rm OC}$  encounters energy loss ( $E_{\rm g}^{\rm eff}$  -  $V_{\rm OC}$ ) of about 0.4-0.6 eV.<sup>52-</sup> <sup>54</sup> The existence of charge transfer (CT) state across the p/n interface as an intermediate in the charges dissociation process has referred a significant impact in the reduction of  $V_{\rm OC}$ .<sup>55-58</sup> Figure 6 shows a schematic representation of the formation of CT state in comparison with the  $E_{g}^{eff}$  in a p/n BHJ. Heeger et al. studied the transient absorption spectroscopy (TAS) of the pristine and BHJ samples of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4b]dithiophene)alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT). Probing the ultrafast (t<200 fs) charge separation process in the blend films advocated the appearance of a new photoinduced absorption band in the blended samples. The new absorption band in the blends declares formation of a CT state of bound electron on the PCBM and hole on the PCPDTBT molecules.<sup>59</sup> The significant variation in the charge separation indicates the CT dependence on the molecular structure and stacking orientation in the blend.<sup>60,61</sup> With the ever-advancing techniques, it became possible to evaluate the energy of the CT state of a p/n BHJ.<sup>62,63</sup> To investigate the role of CT state energy on the  $V_{\rm OC}$ , Ohkita *et al.* evaluated the CT state energy for samples containing different fullerene derivatives. The results indeed showed the primary impact of the CT state energy in the obtained V<sub>OC</sub>.<sup>64</sup> Therefore, high CT state energy consequently lead to improved  $V_{\rm OCS}$ .<sup>65,66</sup>



**Figure 6.** A schematic representation of the effective bandgap and the formation of CT state in p/n BHJ.

#### 1-5 Donor and acceptor monomers

#### 1-5-1 Benzotrithiophene

Benzotrithiophene (BTT) donor unit is a member of seven isomers according to the sulfur position structured by fusing three thiophenes into a central benzene ring. The research in the photophysical properties of BTT molecules began with the interest on the star-shape oligothiophenes. The large core of the planar conjugated star-like molecule resulted in the enhanced electron delocalization.<sup>67</sup> The different isomers of BTT molecules encounter diverse molecular curvature and planarity.<sup>68</sup> With the trade-off between elongating the conjugation length to improve charges mobility and the curvature of the core to ensure solubility of the conjugated polymer, the asymmetric BTT unit with narrow bandgap is commonly used for optoelectronic applications.<sup>69</sup> BTT polymers with thiophene (T) and thieno[3,2-b]thiophene (TT) showed highly ordered and crystalline conformation with enhanced charge mobilities when utilized in organic field effect transistors (OFET).<sup>70</sup> The polymer structures are shown in Figure 7. Schroeder et al. studied alkyl chain direction effect in polymer packing of BTT-T polymers; tail-to-tail (tt) and head-to-head (hh). Results revealed a

significant impact of the chains direction with enhanced polymer packing resulted in about four times higher mobility for BTT-2Ttt.<sup>71</sup> The OPV devices of BTT polymers generally show low to moderate PCE. Ma *et al.* studied two of BTT polymers alkyl- and acyl-BTT based polymers, shown in Figure 7. The electron deficient acyl group in BTT polymers caused lowering the HOMO/LUMO energy levels allowing for higher  $V_{OC}$  and PCE achieved 4.2% (2.5% for the alkyl-BTT).<sup>72</sup> In addition, Wei *et al.* showed PCE of 5.6% for BTT-4BT polymer after annealing at 150°C (PCE of 4.4% before annealing).<sup>73</sup>



Figure 7. Examples of BTT polymers

#### 1-5-2 Benzobisthiazole

Conjugated polymers incorporating fused cyclic rings are known to improve  $\pi$ -stacking and the conjugation length of a polymer. Benzobisthiazole (BBT) molecule is a benzene ring fused with two thiazole units in a planar configuration. For the crystalline nature of BBT polymers they exhibit high thermal stability (> 300 °C).<sup>74,75</sup> Saeki *et al.* studied co-polymers of BBT donor monomer with different acceptor monomers, Figure 8. By manipulating alkyl chain on the thiophenes adjacent to the BBT ranging from linear octyl and branched hexyldecyl to linear dodecyl the PCE was found to significantly improve from 0.9% to 3.8% for the longer linear alkyl chain polymer. In addition when the device was changed to the inverted structure the PCE increased to 6.5%.<sup>76,78</sup>



R=DT (PCE= 3.8%~6.5)

Figure 8. BBT polymers previously studied for OPV devices.

#### 1-5-3 Naphthobisthiadiazole

Naphthobisthiadiazole (NTz) monomer is a heterocycle consisting of two fused benzothiadiazole (BT) structure. Thus, compared to the BT monomer NTz is a stronger acceptor with extended  $\pi$ -conjugation that leads to narrowing of the bandgap of the polymer.<sup>79,80</sup> Osaka *et al.* has intensively studied the optoelectronic and photovoltaic performance of NTz polymers with 10%PCE.<sup>81</sup> In addition to the enhanced electronic properties of the NTz polymers, they also showed improved crystallinity with dominating face-on orientation. The alkyl chain length has also showed a significant impact of the morphology and OPV performance of NTz polymers.<sup>82,83</sup> In the copolymer of NTz with thiazolothizole (PTzNTz), shown in Figure 9, the shorter alkyl chain combination of ethylhexyl butyloctyl resulted in PCE of 9% as a result of  $\pi$ - $\pi$  stacking in the face-on direction.<sup>83</sup>



Figure 9. PTzNTz polymer structure.

#### 1-6 Measurements to study p/n blends

#### 1-6-1 Time-resolved microwave conductivity (TRMC)

Photoconductivity of the p/n blends is investigated using TRMC measurement. In this technique the transient charge carriers generated in the material upon exposure to a light pulse are probed using a resonant cavity.<sup>84,85</sup> Using white light pulse of Xenon lamp and laser pulses (355 nm and 500 nm), photoconductivity ( $\triangle \sigma$ ) and/or pseudo-photoconductivity ( $\phi \Sigma \mu$ ) are obtained with a high sensitivity for the blend film of polymer/PCBM.86,87 Therefore it allows for electrodeless evaluation of blend films prior to device fabrication. The measured photoconductivity revealed a good correlation with the OPV device performance.<sup>88</sup> In addition,  $\phi \Sigma \mu$ , the kinetic traces evaluated by TRMC accounts for the charges generation efficiency (*ø*) multiplied by the summation of positive and negative charges ( $\sum \mu = \mu_{+} + \mu_{-}$ ), which is sensitive the crystallinity and optoelectronics of the polymer.<sup>89,90</sup> TRMC to measurements were conducted for the investigated polymers in this thesis to examine the best blend ratios prior to device fabrication. In addition, the strong correlation of TRMC photoconductivity with the device performance allowed for understanding the different optoelectronic behavior of polymers based on local charge mobility and generation efficiency.

#### 1-6-2 2D-grazing incidence X-ray diffraction (2D-GIXRD)

Polymer molecule orientation in the bulk of pristine and in the heterojunction in addition to the orientation relative to the device substrate is a sensitive matter that governs exciton dissociation and intermolecular charge transfer. Polymer molecules tend to pack/stack in unique pattern can be considered as a fingerprint that changes not only between different polymers but also for the same polymer when processed in various conditions. This makes the study of polymer stacking an important subject. Nevertheless, the parameters related to the molecular structure that facilitate polymer orientation are still not fully developed. Factors such as the polymer backbone and the density of the side groups are known to impact the polymer orientation.<sup>91-94</sup> The 2-dimensional grazing incidence X-ray diffraction (2D-GIXRD) pattern can provide an estimated image according to the peak

intensities in the out-of-plane (OOP) and in the in-plane (IP) directions. The peaks appearance and intensities can therefore describe the face-on and edgeon stacking of the polymer in the crystallite sites. In addition the  $\pi$ - $\pi$  stacking and the lamellar distances can be calculated. Figure 10 shows a schematic representation of the 2D-GIXRD pattern for face-on and edge-on orientation. In chapter 4 the effect of alkyl chain length on polymer crystallinity and orientation is examined using 2D-GIXRD patterns.



Figure 10. Schematic representation of face-on and edge-on patterns in the 2D-GIXRD

#### 1-7 Outline of this thesis

An effective approach toward high performing organic photovoltaic (OPV) devices is a rational molecular design of a p-type polymer. A DA polymer is formed by covalent coupling of electron-donating and -accepting units in an alternative fashion, which ensures delocalizing holes in the polymer backbone as well as narrowing the bandgap and tuning the energy levels.<sup>95</sup> Inherently, molecular structure alters the energy levels relative to those of the n-type fullerene derivative, which greatly affects the device  $V_{\rm OC}$ . <sup>66,48</sup> In addition, polymer orientation and intermolecular stacking have major impacts on the  $J_{SC}$  of an OPV device.<sup>96</sup> In this dissertation, the author copolymers based demonstrates new on benzotrithiophene and benzobisthiazole monomers for photovoltaic applications. The optoelectronic, electric and morphological properties of the designed polymers are investigated to accomplish understanding of molecular structure for high performance OPV devices.

*Chapter 1* introduces the basis of bulk heterojunction (BHJ) OPV devices, p- and n-types materials, and the general criteria for optimized device characteristics. This chapter also includes a brief literature review of the three main monomers used in this study; benzotrithiophene (BTT), benzobisthiazole (BBT) and naphthobisthiadiazole (NTz).

Chapter 2 illustrates the design, synthesis and photovoltaic characterization of BTT-based polymers. BTT monomer is copolymerized with three types of electron accepting monomers to vary the HOMO levels of the obtained polymers. In addition, BTT polymers exhibit different effective bandgaps, which is discussed in conjunction with the  $J_{\rm SC}$  and  $V_{\rm OC}$ .

Chapter 3 provides an insight into the origin of  $V_{\rm OC}$  from the aspect of energy losses due to the formation of charge transfer (CT) state in the exciton dissociation process. Despite  $V_{\rm OC}$  approaching as high as 1.0 V in BTT polymers, phase segregation and lack in distinct orientation of polymer backbone caused drastic decrease in  $J_{SC}$  and hence unsatisfactory PCE of 2.7%.

Chapter 4 discusses the importance of alkyl chain length in newlydesigned polymers. Optimizing morphology in the BHJ enhances charges separation and transport, therefore plays a vital role to achieve high PCE. Accordingly, the symmetric, planar BBT donor and NTz acceptor-based polymers are synthesized with different combination of alkyl chains, which show significant improvement in PCE from 2.5% to 6.6%. This increased PCE owing to alkyl chain engineering is rationalized through the detailed investigation on the charge carrier generation, charge mobility and lifetime obtained using time-resolved microwave conductivity (TRMC). The morphological variations in the synthesized polymers are observed via atomic force microscopic images (AFM) and 2-dimentional grazing-incident X-ray diffraction (2D-GIXRD).

Chapter 5 addresses the achievements and conclusions of this dissertation. The D-A manipulation in BTT polymers resulted in a cascade of HOMO levels and allowed for investigating the major influence of CT state in the device performance. On the other hand, alkyl side chain engineering in BBT-NTz polymers revealed importance in determining the charge transport mechanism in a BHJ to a similar extent of the design of  $\pi$ -conjugated backbone.

This work illustrates how the design of polymer backbone and side alkyl chains affects the energetics, charge transport associated with mobility, and morphology as well as the polymer orientation. The author hopes the present findings to contribute in the comprehensive understanding of the molecular engineering of p-type polymers in the development of OPV devices.

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### Chapter 2: Benzotrithiophene Based Low Bandgap Polymers

#### 2-1 Introduction

Bulk heterojunction (BHJ)-based organic photovoltaics (OPV) that typically consist of polymeric materials as electron donor with fullerene derivatives as electron acceptor are studied intensively.<sup>1-3</sup> Polymers applied in OPVs are mostly made of two alternating monomers with different electron affinities.<sup>4</sup> Hence, the polymer backbone has repeating units of electron donor (D) and electron acceptor (A) molecules, referred to as DA copolymers. Utilizing DA copolymers is an effective strategy to narrow optical bandgap via intramolecular charge transfer (CT) band.<sup>5-7</sup>

The optical band gap of DA copolymer is mainly dependent on the highest occupied molecular orbital (HOMO) of donor moiety and the lowest unoccupied molecular orbital (LUMO) of the acceptor moiety. Therefore, selection of D and A monomers has a direct impact on the device efficiency. Optimization of DA polymers requires matching of their HOMO–LUMO energy levels with that of the acceptor fullerene in order to enhance charge dissociation and minimize recombination. On the other hand, the difference between HOMO of the polymer and LUMO of fullerene needs to be maintained large in order to achieve high open circuit voltage ( $V_{\rm OC}$ ). In addition to the energy alignment, the morphology of the blend films plays a significant role in the device performance.<sup>10-12</sup> Therefore, molecular weight, backbone planarity, and solubility are important factors need to be considered.

In this work, photovoltaic properties are investigated for BHJ incorporating DA-type copolymers based on benzotrithiophene (BTT) unit (Figure 1). BTT is a donor moiety characterized as electron-rich constituent in low bandgap copolymers. It is a fused terthiophene with sulfur rich, planar and extended  $\pi$  conjugated system that brings the advantage of intermolecular  $\pi$  stacking.<sup>27</sup> Based on quantum chemical calculations it is predicted that BTT unit has similar donor strength as the well-known

benzodithiophene (BDT).<sup>28,29</sup> However, slightly bent structure of BTT molecule leads to backbone curvature which enhances the solubility and flexibility of the polymers.<sup>30</sup> An intrigued feature of BTT is the possibility to form seven structural isomers.<sup>14</sup> Among them,  $C_{2v}$ -symmetric benzo[1,2-*b*:3,4-*b*:5,6-*c*']



Figure 11. BTT monomer

trithiophene (*bbc*-BTT) and asymmetric benzo [1,2-b:-3,4-b:5,6-b'']trithiophene (BTT) have been often incorporated into backbone of pconjugated polymers. The rare example of the former *bbc*-BTT is a BTT-BT (benzothiadiazole) polymer which has shown a high field-effect transistor (FET) hole mobility.<sup>15</sup> On the other hand, the latter BTT has been polymerized with many kinds of electron accepting units for OPV applications, including

thiazolothiazole (TTz) (PCE = 1.4%),<sup>17</sup> BT (PCE = 2.2%),<sup>16</sup> diketopyrrolo pyrrole (PCE = 5.1%),<sup>18</sup> bisthiazole (PCE = 5.1%),<sup>19</sup> benzooxadiazole (PCE = 6.2%),<sup>20</sup> and benzothiadiazole-5,6- dicarboxylic imide (PCE = 8.3%).<sup>21</sup> In addition to the asymmetry, the slightly bent structure of BTT molecule leads to backbone curvature which enhances the solubility of polymers.<sup>22</sup>

In this investigation BTT monomer was copolymerized with three strong acceptor monomers thiadiazolopyridine (TP), difluorothiadiazole (FT) and naphthobisthiadiazole  $(NT_Z)$ units (Figure 12).

The optical, electrochemical,





Difluorothiadiazole (FT)



Naphthobisthiadiazole (NTz)



**Figure 12.** Acceptor monomers copolymerized with BTT; TP, FT and NTz units.

morphological and photovoltaic properties of BTT copolymers are investigated. In this study, the synthesized BTT copolymers achieved  $V_{\rm OC}$  as high as 1.0 V. Results show that these polymers exhibit small and constant energy loss of about 0.4 eV as compared to their  $E_{\rm g}^{\rm eff}$ . Power conversion efficiency for BTT polymers/ PC<sub>61</sub>BM BHJ was studied. Fabrication conditions such as blend ratio and solvent additives were optimized. Charge carrier lifetime, mobility and density were examined by the time resolved microwave conductivity (TRMC) technique.

#### 2-2 Synthesis of monomers and polymers

BTT monomer was synthesized according to the literature.<sup>30</sup> The synthesis route is shown in Scheme 1. Starting with Friedel-Crafts acylation of 2,3-dibromothiophene results in ketone (1) which then through Suzuki-Miyaura cross-coupling with thiophene-3-boronic acid gives trithiophene system, compound (2) Scheme 1. The resultant undergo subsequent oxidative ring closure with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone to form benzo[1,2-b:3,4-b':6,5-b"]trithiophen, compound (3). Then a second octyle chain is added via Grignard reaction. After that, compound (4) is reduced by lithium aluminum hydride in the presence of aluminum chloride. Finally, compound (5) is lithiated at the two  $\alpha$ -positions with tert-butyl lithium and the resultant dilithiated species is guenched with trimethyltin chloride to afford the 2,8-distannylated BTT ((5-(heptadecan-9-yl)benzo[1,2-b:3,4-b':6,5b"]trithiophene-2,8-diyl)bis(trimethylstannane)). Monomers 4.7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine  $(TP)^{31}$ , and 5,6-difluoro-4,7diiodobenzo[c][1,2,5]thiadiazole  $(FT)^{32}$  were synthesized according to previous reports. Monomer 5,10-bis(5-bromo-4-(tricosan-11-yl)thiophen-2yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (NTz) was synthesized by the group of Professor Osaka Itaru at Center of Emergent Science at RIKEN Institute.

Polymers BTT-TP, BTT-FT and BTT-NTz were synthesized via Stille coupling reaction as illustrated in Scheme 2.

Synthesis of BTT-TP. A solution of (5-(heptadecan-9-yl)benzo[1,2-b:3,4-b':6,5-b'']trithiophene-2,8-diyl)bis(trimethylstannane) (14 mg, 0.0543 mmol) and 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (18 mg, 0.0543 mmol) in anhydrous chlorobenzene (1 mL) was degassed via "freeze-pump-thaw" cycles. Tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) (1 mg, 0.025 mmol, 97% pure purchased from Sigma Aldrich) and tri(o-tolyl)phosphine (1.65 mg, 0.1 mmol) were added to the degassed solution under nitrogen gas flow. Then the reaction mixture was refluxed at 110°C for 3 hours. Followed end-capping by

subsequent addition of bromobenzene (0.1 mL) and trimethyltinbenzene (0.1 mL) and refluxed for 1 hour after each addition. The resulted reaction mixture was diluted in chlorobenzene and precipitated in methanol. The precipitate was filtered and dried in a vacuum desiccator overnight. The filtered was dissolved in chloroform and purified by column chromatography packed with acid silica and alternating NH silica and NH<sub>2</sub> silica followed by celite filtration. The solution was concentrated, precipitated in acetone, filtered and dried to afford the final dark blue product (10 mg) (43% yield). ( $M_w$ ) = 70,370 g mol<sup>-1</sup>, ( $M_n$ ) = 16,740 g mol<sup>-1</sup>, polydispersity index (PDI) = 4.2.

Synthesis of BTT-FT. A solution of (5-(heptadecan-9-yl)benzo[1,2-b:3,4-b:6,5-b"]trithiophene-2,8-diyl)bis(trimethylstannane) (47.6 mg, 0.0622 mmol) and 5,6-difluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (62 mg, 0.0622 mmol) in anhydrous chlorobenzene (1 mL) was degassed via "freeze-pump-thaw" cycles. Pd<sub>2</sub>(dba)<sub>3</sub> (1.34 mg, 0.025 mmol) and tri(o-tolyl)phosphine ( 2 mg, 0.1 mmol) were added to the degassed solution under nitrogen gas flow. Then the reaction mixture was refluxed at 110°C for 24 hours. The reaction mixture was monitored by GPC. End capping and purification processes were conducted as described above to afford the final product as dark green solid (60 mg) (50% yield).  $M_w$ = 24,770 g mol<sup>-1</sup>,  $M_n$ = 20,050 g mol<sup>-1</sup>, PDI = 1.24.

Synthesis of BTT-NTz. A solution of (5-(heptadecan-9-yl)benzo[1,2-b:3,4b::6,5-b"]trithiophene-2,8-diyl)bis(trimethylstannane) (46 mg, 0.0350 mmol) and 5,6-difluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (42.5 mg, 0.0350 mmol) in anhydrous chlorobenzene (2 mL) was degassed via "freeze-pump-thaw" cycles. The mixture transferred to a microwave reactor vail and tetrakis-(triphenylphosphine) palladium (2 mg, 0.05 mmol) was added to the degassed solution under argon gas flow. Then in the microwave reactor the solution was heated to 180°C for 70 minutes. After end capping the product was purified as described above to afford the final product as dark green solid (40 mg) (81% yield).  $M_w$ = 62,720 g mol<sup>-1</sup>,  $M_n$ = 39,970 g mol<sup>-1</sup>, PDI = 1.5.





Scheme 2. Synthesis of polymers BTT-TP (purple), BTT-FT (blue), and BTT-NTz (green).

#### 2-3 Results

#### 2-3-1 DFT calculation results for monomers

DA type copolymers are intensively studied as donor materials in OPV devices with fullerene derivatives as acceptor materials. Alternating building blocks with different electron affinities in DA copolymers enhances intramolecular charge transfer characteristics. In addition, DA copolymers facilitate narrow band gap which in turn broaden the absorption in UV/Vis and in near-IR regions.<sup>6,35</sup> A successful example of DA type copolymer is polythieno[3,4-b]-thiophene-co-benzodithiophene (PTB7)whose PCE approached 9% recently.<sup>9</sup> The improvement in PCE utilizing PTB7 which contains benzodithiophene (BDT) in its backbone as donor moiety has initiated the study of benzotrithiophene (BTT) copolymers.<sup>27-29,36-37</sup> Theoretical calculations show that BTT and BDT have similar donor ability which makes it a promising candidate for DA copolymers.<sup>26</sup> BTT unit has three thiophene units fused to the central benzene resulting in highly planar and electron rich molecule beneficial to be used as donor in DA copolymer. In addition, the larger BTT core enhances intermolecular  $\pi$ - $\pi$ \* stacking. Energy levels of BTT in comparison with BDT and cyclopentadithiophene (CPDT) obtained by DFT calculations are summarized in Figure 13. The results reveal that BTT unit exhibit deeper HOMO level which is advantageous to rise its  $E_{\rm g}^{\rm eff}$  when blended with PC<sub>61</sub>BM and hence gaining higher  $V_{\rm OC}$ . On the other hand, due to the deep HOMO level of BTT unit it is copolymerized with strong acceptor units to yield polymers with narrow band gap. Three acceptor units are selected; thiadiazolopyridine (TP), difluorothiadiazole (FT) and naphthothiadiazole (NTz) units. Energy levels of the three acceptor units estimated from DFT calculations are illustrated in Figure 13. Figure 14 shows planarity difference of trimer units for BTT-TP, BTT-FT and BTT-NTz.



**Figure 13.** Energy levels of monomers benzotrithiophene (BTT), benzodithiophene (BDT), cyclopentadithiophene (CPDT), thiadiazolopyridine (TP), difluorothiadiazole (FT) and naphthothiadiazole (NTz) units, obtained by DFT calculations using B3LYP6-31 G\*.



Figure 14. Planarity of trimer units of BTT polymers estimated from DFT calculations.

#### 2-3-2 Optical properties of BTT polymers

The UV/Vis absorption spectra for BTT-TP, BTT-FT and BTT-NTz in dilute chloroform solution and in thin films are shown in Figures 15 (a and b, respectively). The absorption peaks in solution appeared at 560 nm, 570 nm and 613 nm for BTT-TP, BTT-FT, and BTT-NTz, respectively. Whereas, in thin film samples the absorption peaks were slightly red shifted, indicating the ordering of the molecules and/or the  $\pi$ - $\pi^*$  interchain interaction. The absorption band edge (absorption onset) of BTT-NTz showed a clear red shift compared to BTT-TP and BTT-FT indicating a better conjugated structure of BTT-NTz. The optical band gaps of the polymers were calculated from the absorption onset of the thin film sample and found to be 1.75 eV, 1.78eV and 1.68eV for BTT-TP, BTT-FT, and BTT-NTz, respectively (Figure 16). HOMO levels were determined by photoelectron yield spectroscopy (PYS) to be -5.6 eV, -5.5 eV and -5.4 eV, respectively. Accordingly, LUMO levels were calculated to be -3.85 eV, -3.74 eV and -3.73 eV respectively. The weightaveraged molecular weights and polydispersity indices characterized by gel permeation chromatography (GPC) were 16.4 kg mol<sup>-1</sup> (1.59) for BTT-TP, 24.8 kg mol<sup>-1</sup> (1.24) for BTT-FT, and 62.7 kg mol<sup>-1</sup> (1.57) for BTT-NTz, respectively (vs. polystyrene standards in tetrahydrofuran eluent). The results are tabulated in Table 1.

Polymer	$\lambda_{max}^{abs}$ /nm		$\lambda_{onset}^{abs}$ /nm	$E_g^{opt}$	HOMO	LUMO	Mw	DDIe
	Solution	Film	Film	/eV <sup>a</sup>	$/eV^b$	$/eV^{c}$	/ kg mol $^{-1}$ d	FDI
BTT-TP	560	613	708	1.75	-5.60	-3.85	16.4	1.59
BTT-FT	570	600	696	1.78	-5.52	-3.74	24.8	1.24
BTT-NTz	615	650	738	1.68	-5.41	-3.73	62.7	1.57

**Table 1.** Summary of electrochemical and polymeric properties of BTT-based polymers.

<sup>a</sup> Optical bandgap determined from photoabsorption onset in the film states.<sup>b</sup> Measured by photoelectron yield spectroscopy. <sup>c</sup> HOMO +  $E_g^{opt}$ . <sup>d</sup> Weight-averaged molecular weight. <sup>e</sup> Polydispersity index.


**Figure 15.** Normalized UV/Vis absorption spectra for BTT-TP, BTT-FT, and BTT-NTz (a) in chloroform solution and (b) in thin films.



Figure 16. Energy diagram of polymers BTT-TP, BTT-FT, BTT-NTz and  $PC_{61}BM$ .

#### 2-3-3 Time-resolved microwave conductivity measurement

Time-resolved microwave conductivity (TRMC) experiments were conducted in order to predict the best photovoltaic performing polymer to  $PC_{61}BM$  ratio prior to device fabrication. The photoconductivity transient maxima ( $\Delta \sigma_{max}$ ) obtained from TRMC experiments provide information about the charge carrier lifetime, mobility and density.<sup>27</sup> The results of film processed from CB for all polymers show that photoconductivity maximized upon mixing with  $\sim 75\%$  PC<sub>61</sub>BM content for BTT-TP,  $\sim 50\%$  for BTT-FT and BTT-NTz, yellow region in Figure 17 (a, b, and c, respectively).  $PC_{61}BM$ content required to increase  $\Delta \sigma_{max}$  is higher for BTT-TP is indicating low charge carrier mobility/ density for this polymer. For the pristine polymer film  $\Delta\sigma$  is highest for BTT-FT indicating its higher local charge carrier mobility than BTT-TP and BTT-NTz (Figure 18). The higher  $\Delta\sigma_{max}$  for BTT-FT is due to the electronegative fluorine modification resulted in better polymer packing which therefore enhanced intramolecular charge transport. OPV devices for the three polymers are studied for blend ratios giving maximum  $\Delta \sigma_{max}$ , the highlighted regions in Figure 8. The high PC<sub>61</sub>BM loading of 70-80% is sometimes required to maximize PCE<sup>6</sup> and  $\Delta \sigma_{max}^{27}$  in amorphous or semi-crystalline low bandgap polymers (LBPs). This is assumed due to an essential role of electron delocalization in PCBM aggregates for efficient charge separation. In the case of crystalline polymers such as poly(3hexylthiophene)<sup>33,34</sup> and high performing LBPs,<sup>35</sup> the 1:1 blend ratio (50 wt%) is often optimal, because self-assembling nature of polymer concurrently promotes the growth of PCBM aggregates. In the present case, BTT-TP is amorphous, while BTT-FT and BTT-NTz are more crystalline, as evidenced by X-ray diffraction (*vide infra*). Therefore, the trend in p/n blend ratio of these polymers is consistent with the previous OPV polymers.



**Figure 17.** The plot of photoconductivity transient maxima ( $\Delta \sigma_{max}$ ) versus wt. % of PC<sub>61</sub>BM for (a) BTT-TP, (b) BTT-FT and (c) BTT-NTz. The yellow area represents the optimal blend ratio to maximize  $\Delta \sigma_{max}$ .



**Figure 18.** Kinetic traces of transient photoconductivity ( $\Delta \sigma$ ) for 1 : 1 blend ratio of polymer : PC<sub>61</sub>BM.

#### 2-3-4 J-V characteristics

The photovoltaic performance of BTT-TP, BTT-FT and BTT-NTz p-type polymers with  $PC_{61(71)}BM$  were investigated at blend ratios corresponding to the maximum  $\Delta \sigma_{\rm max}$  of TRMC experiments. All OPV devices were fabricated as inverted structure and measured under m AM1.5G illumination (100 mW cm  $^{-}$ <sup>2</sup>). Table 2 summarizes the photovoltaic performance of the three polymers. They showed the high  $V_{\rm OC}$  of 1.0 V, 0.9 V and 0.8 V for BTT-TP, BTT-FT and BTT-NTz respectively (Figure 19 a). Although BTT-TP showed the highest Voc yet it exhibited the very low PCE of about 0.35%. On the other hand, BTT-FT showed remarkably higher PCE  $\sim$  1.4%. The increased molecular weight as well as enhanced polymer packing due to fluorine modification in BTT-FT resulted in enhanced intra- and intermolecular charge transport as dictated from TRMC experiments. This led to a higher  $J_{\rm SC}$  in BTT-FT devices (2.15 mA cm<sup>-2</sup>) compared to 0.74 mA cm<sup>-2</sup> for BTT-TP. BTT-NTz polymer showed the highest PCE of 1.87% (average: 1.41%) with PC<sub>61</sub>BM and improved to 2.78% (average: 2.57%) with PC<sub>71</sub>BM. The increased efficiency of BTT-NTz is attributed to the higher molecular weight of this polymer and the improved  $\pi$ - $\pi$  interaction in this polymer as revealed from the UV-vis absorption spectra. In addition, external quantum efficiency (EQE) spectra (Figure 19 b) indicate the same order of PCE. BTT-NTz showed the maximum EQE of ~ 30% at wavelength range 300 nm to 550 nm. However, in the wavelength region from 550 nm to 800 nm, the EQE spectrum of BTT-NTz device dropped to less than 20 %, which is understood by the less efficient exciton migration in polymer to the polymer/fullerene interface compared to that in PC<sub>61</sub>BM domain. Solvent, solvent additives and annealing effects were studied for BTT-NTz performance effect. The results are summarized in Tables (3-5) in the experimental section. DIO concentration has been examined in the range 1 - 5 vol. %. Increasing DIO concentration above 3 vol. % did not cause any significant difference in the performance, however, lowering to 1 vol. % DIO led to decreasing the performance by about 50%. In addition, Annealing at 120°C for 10 minutes caused a drop in the device

performance by about 50%.



**Figure 19.** (a) J-V characteristic under 1 sun illumination for BTT-based polymers: PC<sub>61</sub>BM; BTT-TP, 0.38% PCE (purple dashed line), BTT-FT, 1.4% PCE (blue solid line), BTT-NTz, 1.87% PCE (green dotted line) (b) EQE spectra for the three devices.

Table 2. Summary of photovoltaic performance for BTT-TP, BTT-FT and BTT-NTz with  $PC_{61}BM$ , solvent additive DIO 3 vol. % <sup>a</sup>

Donor Polymer	p∶n	Thickness / nm	$J_{\rm SC}$ / mA cm <sup>-2</sup>	$V_{\rm OC}$ / V	FF	PCE / %
BTT-TP	1:3	165 - 230	0.74 (0.78)	1.00 (1.01)	0.44 (0.49)	0.33 (0.38)
BTT-FT	$1 \cdot 2$	85 - 165	2.15 (2.59)	0.89 (0.92)	0.59 (0.65)	1.14 (1.4)
BTT-NTz	$1 \cdot 2$	96 - 200	3.68 (4.31)	0.78 (0.80)	0.49 (0.55)	1.41 (1.87)
BTT-NTz/	1:1	90 - 125	5 98 (5 88)	0.75 (0.74)	0 61 (0 59)	2 78 (2 57)
$PC_{71}BM$	1.1	00 120	5.56 (5.66)	0.10 (0.14)	0.01 (0.00)	2.10 (2.01)

<sup>a</sup> Averaged values for at least three devices. Maximum values are in brackets.

#### 2-4-5 Morphology

The morphology of the active layers of the best-performing devices were examined by atomic force microscopy (AFM) (Figure 20). The AFM images of BTT-TP: PC<sub>61</sub>BM showed the large spherical aggregations ~ 600 nm in size with the surface roughness of 12 nm (Figure 20a). In sharp contrast, BTT-FT: PC<sub>61</sub>BM blend showed the fiber-like structure with the very less surface roughness of 2 nm, which is consistent with the high  $J_{SC}$  (Figure 20b). However, AFM images of BTT-NTz: PC<sub>61</sub>BM device showed again the large aggregates of ~ 260 nm in size along with the surface roughness of ~ 25 nm (Figure 20c). Despite the high surface roughness and large aggregates in BTT-NTz: PC<sub>61</sub>BM, it showed the highest PCE of 1.87 % among the three polymers. This indicates a possibility of improvement by optimizing the morphology. Whereas BTT-NTz: PC<sub>71</sub>BM device showed less surface-roughness ~ 17 nm and smaller aggregation sizes ~ 190 nm than those of BTT-NTz: PC<sub>61</sub>BM

Two-dimensional grazing-incidence X-ray diffraction analysis (2D-GIXRD) was performed to study polymer orientation in pristine film. The percentages of polymer face-on orientation is roughly estimated from signal intensities of interlamellar diffractions in the out-of-plane and in-plane directions. The results showed the random nature of BTT-TP polymer, which may be associated with the disordered structure in its PC<sub>61</sub>BM blend (Figure 21a). Conversely, BTT-FT showed semicrystalline nature with ~ 40 % face-on orientation and the  $\pi$ - $\pi$  stacking distance of 3.68 Å (Figure 21b). The 2D-GIXRD pattern of BTT-NTz showed ~ 60 % face-on orientation with the  $\pi$ - $\pi$ stacking distance of 3.74 Å (Figure 21b). Accordingly, BTT-NTz has the most suitable polymer orientation for the hole transport in the vertical direction, which contributes to the higher  $J_{SC}$  of the devices. However, less crystallinity and coarse BHJ morphology (large aggregates) limits a further boost in  $J_{SC}$ .



**Figure 20.** AFM phase images (upper panel) and height (lower panel) (2µm<sup>2</sup>). Scale bar is 500 nm.



**Figure 21.** 2D-GIXRD of pristine polymers; (a) BTT-TP/CF, (b) BTT-FT/CF, (c) BTT-NTz/CF. Corresponding GIXRD patterns are shown in lower panel.

## 2-4 Conclusions

Three BTT-based copolymer were designed and synthesized; BTT-TP, BTT-FT, and BTT-NTz. The polymers showed deep HOMO and LUMO levels of -5.4 ~ -5.6 eV and -3.7 ~ -3.9 eV, respectively. Owing to these electrochemical properties, high  $V_{OC}$  of 0.79–0.99 V were obtained. However, the PCEs were constrained to stay at low values (0.4–1.8 %), mainly due to the low  $J_{SC}$ . The low  $J_{SC}$  is readily explained by the extremely coarse BHJ morphology with several hundred nanometer-sized aggregates. The BTT-NTz showed the best PCE of 2.73% by the use of visible light absorbing PC<sub>71</sub>BM. The higher molecular weight, lower bandgap, and slightly-improved face-on orientation are responsible for the higher PCE of BTT-NTz. It should be noted that the large phase separation in BTT-NTz:PCBM was unable to be alleviated by either solvent mixture or additive concentration. In light of observed high  $V_{OC}$ , there is a great possibility for BTT-based polymers to improve the efficiency by controlling morphology via alkyl side-chain and/or molecular weight.

## 2-5 Experimental section

#### 2-5-1 Materials and instruments

All chemicals were purchased from Sigma Aldrich, Wako or Tokyo Chemicals Inc. (TCI) and used as received. PCBM (purity > 99.5%) was obtained from Frontier Carbon Inc. <sup>1</sup>H NMR was recorder on a JEOL 400SS (400 MHz) spectrometer, and all spectra were recorded in a CDCl<sub>3</sub> solution using TMS as the internal reference standard. Monomers were purified by recycle preparative HPLC system (Japan Analytical Industry Co., Ltd., LC-9210NEXT with JaiGel-1H/-2H) using CHCl<sub>3</sub> as eluent. Microwave experiments were conducted in Anton Paar Monowave 300. Weight average and number average molecular weights ( $M_w$  and  $M_n$ , respectively) were determined via Gel Permeation Chromatography (GPC) using tetrahydrofuran (THF) as eluent at flow rate of 1 mL min<sup>-1</sup> at 40°C, on a HITACHI L-2130, L-2455, L-2530 chromatography instrument with Shodex KF-804L/KF-805L (Shodex Co., Japan) connected to a refractive index detector. Ultraviolet – visible light (UV - Vis) steady state absorption spectra were recorded on a Jasco V-570 UV-vis spectrophotometer. Photoelectron yield spectroscopy (PYS) experiments were conducted on a RIKEN Keiki Co., Ltd., model AC-3. AFM surface morphologies of the devices were obtained from a Seiko Instruments, Inc., model Nanocute OP, and Nanonavi II.

# 2-5-2 Time-resolved microwave conductivity (TRMC) measurement

TRMC experiment was conducted in order to study the photovoltaic performance of polymer/ PCBM blends prior to device fabricating. Blend samples were prepared by drop-casting chlorobenzene solution of polymer/ PCBM onto quartz plate and dried under vacuum. To maintain high degree of sensitivity in conductivity measurement a resonance cavity was used. The resonance frequency and microwave power were set at ca. 9.1 GHz and 3 mW, respectively, in order to keep the electric field of the microwave sufficiently small not to disturb motion of charge carriers. Nanosecond laser pulse at 500 and 680 nm from an optical parametric oscillator (Continuum, Panther) seeded by third-harmonic generation (THG; 355 nm) of a Nd:YAG laser (Continuum, Surelite II, 5 – 8 ns pulse duration, 10 Hz) or microsecond whitelight pulse from a Xe flash lamp was used as an excitation source. The photoconductivity  $\Delta\sigma$ was obtained by  $\Delta P_r/(AP_r)$ , where  $\Delta P_r$ , A, and  $P_r$  are the transient power change of reflected microwave power, respectively. The nanosecond laser intensities at 500 and 680 nm were set at 2.5 mJ cm<sup>-2</sup> pulse<sup>-1</sup> ((6.4 and 8.7) × 10<sup>15</sup> photons cm<sup>-2</sup> pulse<sup>-1</sup>), respectively. The power of the white light pulse was 0.3 mJ cm<sup>-2</sup> pulse<sup>-1</sup>. All TRMC measurement were conducted at ambient conditions.

#### 2-5-3 Photovoltaic device fabrication and characterization

Inverted structure of organic solar cells in bulk heterojunction architecture, Figure 22, were fabricated on indium tin oxide (ITO) coated glass substrates. Prior to fabrication, ITO-coated substrates were subsequently washed by ultrasonication in series of solvents; diluted detergent, water, acetone and isopropanol alcohol. Then dried using air stream and treated under UV/Ozone for 10 minutes. ZnO precursor solution prepared by the reported sol-gel method<sup>33</sup> (0.1 g/mL zinc acetate dihydrate and 0.028 g/mL ethanolamine in 2-methoxyethanol) was spin coated and annealed at 200°C for 30 minutes. A solution of polymer and PC<sub>61</sub>BM or PC<sub>71</sub>BM stirred at 80°C for at least 2 hours under oxygen-free atmosphere. The hot polymer/ PCBM blend was spin-coated from different solvents on top of ZnO layer inside glove box at 25°C. The substrates were then kept in an ultrahigh vacuum chamber for 1 hour to evaporate solvent additives. Finally, 10 nm of MoO<sub>3</sub> and 100 nm Ag layers were sequentially thermally deposited on top of the active layer using a shadow mask. The resulted device configuration was ITO (120–160 nm)/ Al mask (100 nm)/ ZnO (30 nm)/ BHJ active layer/MoO<sub>3</sub> (10 nm)/ Ag (100 nm) with an active area of 7.1 mm<sup>2</sup>. Current-voltage (J-V) curves were measured using a source-measure unit (ADCMT Corp., 6241A) under AM 1.5 G solar illumination at 100 mW cm<sup>-2</sup> (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250 KD) from a 300 W solar simulator (SAN-EI Corp., XES-301S). The EQE spectra were measured by a Bunko Keiki model BS-520BK equipped with a Keithley model 2401 source meter. The monochromatic light power was calibrated by a silicon photovoltaic cell, Bunko Keiki model S1337-1010BQ. Temperature dependent J-V characteristics in dark was measured in a vacuum chamber whose temperature was controlled by a He-cooler and monitored by a thermos-coupler.



Figure 22. OPV device were fabricated in inverted solar cell structure.

OPV device optimization for BTT-NTz

> Effect of solvent additive (DIO) concentration



Figure 23. DIO effect on BTT-NTz device performance, 1:2 blend ratio with  $PC_{61}BM$ .

**Table 3.** DIO solvent additive concentration effect on BTT-NTz :  $PC_{61}BM OPV$  device performance at 1: 2 p:n ratio.

DIO /	Thickness /	Ing/mA am <sup>-2</sup>	Va a / V	FF	PCE / %	
vol.%	nm	JSC7 IIIA CIII 2	VOC/ V	гг		
1	146	2.79	0.69	0.52	1.00	
L	130	2.56	0.58	0.49	0.73	
9	176	4.31	0.79	0.55	1.87	
ర	157	$J_{\rm SC}$ / mA cm $^{-2}$ $V_{\rm OC}$ / VFFPC2.790.690.5212.560.580.4904.310.790.5513.970.770.5514.20.80.4814.70.80.481	1.69			
~	262	4.2	0.8	0.48	1.6	
G	250	4.7	0.8	0.48	1.8	



**Figure 24** DIO concentration effect on morphology of BTT-NTz: PC<sub>61</sub>BM (1:2) OPV devices. AFM phase images (left column) and topography (right column); (a,c) 1 vol.% DIO/ CB/ PCE 1.0%, (b,d) 5 vol.% DIO / CB/ PCE 1.8%, 3 vol.% DIO Scale is 2×2µm. Scale bars are 500 nm length.

#### Effect of solvent and annealing

**Table 4.** Solvent and annealing effect on BTT-NTz :  $PC_{61}BM$  OPV device performance at 1: 2 p:n ratio and 3 vol.% DIO

solvent	annealing	Thickness / nm	$J_{ m SC}$ / mA cm $^{-2}$	V <sub>oc</sub> / V	FF	PCE / %
CF + CB	no annealing	150	3.32	0.79	0.55	1.46
CF	no annealing	530	4.78	0.79	0.47	1.76
CB	annealed	146	2.8	0.67	0.52	0.98



**Figure 26.** Solvent and annealing effect on morphology of BTT-NTz:  $PC_{61}BM$  (1:2) OPV devices. AFM phase images (top panel) and topography (lower panel), (a,d) CF+CB (30%+70%)/ PCE 1.46%. (b,e) CF/ PCE 1.76%, (c,f) CB/ PCE 0.98% / annealed at 120°C for 10 minutes, all with 3 v.% DIO. Scale is  $2 \times 2\mu$ m. Scale bars are 500 nm length.



Figure 25 Annealing temperature effect on kinetic traces of transient photoconductivity ( $\Delta \sigma$ ) for 1 : 1.5 blend ratio of BTT-NTz : PC<sub>61</sub>BM.

#### OPV device performance for BTT-NTz and BTT-FT with $PC_{71}BM$

p∶n		Thickness / nm	$J_{ m SC}$ / mA cm <sup>-2</sup>	$V_{ m OC}$ / V	FF	PCE / %
	1 • 1	85	3.28	0.89	0.49	1.45
	110	3.19	0.88	0.48	1.37	
	1 . 0	140	1.9	0.9	0.6	1.03
	$1 \cdot 2$	155	2.07	0.89	0.56	1.04
N	N 1 · 1	90	5.87	0.73	0.58	2.52
LZ 1:1	125	5.98	0.75	0.6	2.73	
-LLB 1	1 • 0	170	3.36	0.66	0.39	0.88
	$1 \cdot 2$	160	3.82	0.75	0.43	1.22

**Table 5.** Photovoltaic performance for BTT-FT and BTT-NTz with  $PC_{71}BM$  using 3 vol.% DIO



**Figure 27.** J - V characteristic under 1 sun illumination for BTTbased polymers: PC<sub>71</sub>BM; BTT-FT, 1.4% PCE, BTT-NTz, 2.73% PCE.



Figure 28. AFM phase images (left column) and topography (right column) OPV devices of BTT-FT and BTT-NTz with  $PC_{71}BM$  (a,b) BTT-NTz (1 :1)/ PCE 2.73%, (c,d) BTT-NTz (1 :2)/ PCE 1.22%, (e,f) BTT-FT (1 :2)/ PCE 1.0%, (g,h) BTT-FT (1 :1)/ PCE 1.4%, all with 3 vol.% DIO. Scale is  $2 \times 2\mu m$ .

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# Chapter 3: Energy Loss in OPV Devices of BTT Polymers

## **3-1 Introduction**

Dynamics of charge carriers in polymer-fullerene bulk heterojunction (BHJ) photovoltaic devices play a substantial role in altering power conversion efficiency (PCE).<sup>1-3</sup> Each step from photoexcitation to charge collection is significantly contributing to the overall device efficiency. Due to the low dielectric constant of organic materials, exciton (a pair of hole–electron) at the p-type (p) and n-type (n) heterojunction leads to the formation of a bound charge transfer (CT) state.<sup>4,5</sup> A large portion of CT excitons is allowed to separate into free carriers at the p/n interface,<sup>6</sup> by virtue of excess energy,<sup>7</sup> electronic coupling,<sup>8</sup> charge delocalization,<sup>9</sup> local mobility,<sup>10</sup> and energy gradient.<sup>11</sup> However, the separation efficiency is mostly material-specific, and therefore, the ambiguous nature of the p/n interfaces in the BHJ requires deep investigations on the factors controlling exciton separation.<sup>12</sup>

It has been well established that the maximum open circuit voltage  $(V_{\rm OC})$  is limited by the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor referred to as effective band gap  $(E_{\rm g}^{\rm eff})$ .<sup>13-16</sup> However, in most of the organic photovoltaic (OPV) devices,  $V_{\rm OC}$ s are lowered from  $E_{\rm g}^{\rm eff}$  by 0.8 - 1.3 eV which is considered as energy loss.<sup>17-19</sup> Whereas in inorganic solar cells, the energy loss is only 0.3 - 0.5 V.<sup>20</sup> The larger energy loss in OPV has been rationally linked to the excitonic nature of photogenerated excitons which gives rise to the CT state at p/n interface as an intermediate in charge separation process.<sup>21</sup> The CT energy,  $E_{\rm CT}$  has been reported as efficiency-limiting factor in OPV,<sup>22,23</sup> and thus theoretical and experimental approaches to exemplify the relationship between  $E_{\rm CT}$  and  $V_{\rm OC}$  has been intensively explored for different p/n combinations.<sup>24-26</sup> Accordingly, quantitative evaluation of  $E_{\rm CT}$  is necessary to understand the origin of loss in  $V_{\rm OC}$ , in order to pave the way toward efficient OPVs.<sup>27</sup>

The synthesis and characterization of benzotrithiophene (BTT)-based low bandgap polymers by combining three kinds of electron-withdrawing (TP), difluorobenzothiadiazole thiadiazolopyridine (FT)units. and naphthobisthiadiazole (NTz) affording BTT-TP, BTT-FT and BTT-NTz, respectively, are reported in the previous chapter (Scheme 2, Chapter 2).<sup>28</sup> The comparatively weak electron donating ability of BTT led to the deep HOMO levels (-5.4 - -5.6 eV) and typical optical bandgap of 1.7 - 1.8 eV, resulting in moderate PCEs of 0.4 - 1.9 % when blended with methano[60]fullerene (PCBM). The best PCE of 2.7% was achieved for BTT-NTz: methano[70]fullerene (PC[70]BM), while the interest of this chapter is in the high  $V_{\rm OCS}$  of 0.79 - 0.99 V, which in turn implies a low energy loss. The mechanistic insight underlying the small energy loss and how the charge carrier dynamics and energetic factors contribute to  $V_{
m OC}$  are utmost important issues to be addressed.

In this chapter the contribution of  $E_{\rm CT}$  and pre-exponential factor ( $J_{00}$ ) of Shockley diode model to the  $V_{\rm OC}$  of OPV devices is studied by measurements of dark saturation current at low temperature (ca. 100-300 K). It was found that  $E_{\rm CT}$  is directly correlating to the obtained  $V_{\rm OC}$  for the three polymer devices, while the recombination factor associated with  $J_{00}$  also deviates the total energy loss. Dark saturation current analysis at low temperatures allows an intuitive approach to revealing the significance of charge recombination and CT energy at polymer/fullerene heterojunctions.

#### 3-2 Results and discussion

Electrochemical properties for the synthesized BTT polymers are summarized in Figure 29(a). The optical band gaps ( $E_g$ ) estimated from the absorption onset in the film state are 1.75, 1.78, and 1.68 eV for BTT-TP, BTT-FT, and BTT-NTz, respectively. They exhibit deep HOMO levels of -5.60, -5.52, and -5.41 eV, respectively. As a consequence, assuming the LUMO levels of PCBM at -4.2 eV,<sup>32</sup> effective band gaps ( $E_g^{eff}$ ) defined by the difference between donor HOMO and acceptor LUMO<sup>18</sup> are 1.4, 1.3, and 1.2 eV for BTT-TP, BTT-FT, and BTT-NTz when blended with PCBM, respectively.



**Figure 29.** (a) Energy level diagram illustrating  $V_{OC}$  loss in BTT-polymers OPV devices, (b)  $V_{OC}$  vs. effective band gap for BTT-based polymers: PC<sub>61</sub>BM.

The processing conditions of the polymer:PCBM blends were screened by Xe-flash time-resolved microwave conductivity (TRMC),<sup>33</sup> which were further validated by device characterization.<sup>28</sup> Figure 29(b) displays the JVcurves of 1 sun illuminated OPV devices fabricated at the optimal conditions (chlorobenzene solutions with 3 vol.% DIO). The BTT-TP, BTT-FT, and BTT-NTz exhibited 0.32, 1.4, and 1.5% PCE with the high  $V_{OCS}$  of 0.99, 0.92 and 0.78 V, respectively (Table 6). These PCEs are slightly different from the previous best performances (0.35, 1.0, 1.9%),<sup>28</sup> arisen from unexpected processing variation. However, it is noted that the  $V_{OCS}$  were unchanged, and moreover, comparison between  $V_{OCS}$  in light and those derived from dark saturation current was performed for the identical devices to secure the consistency. Notably, as shown in Figure 29(b), the  $V_{\rm OC}$  is in proportion to  $E_{\rm g}^{\rm eff}$  (slope = 1) with relatively small energy loss (intercept = 0.4 eV, note that the intercept depends on the assumed LUMO level of PCBM).<sup>19</sup>

Figure 30(a) shows *JV* curves in dark for BTT-NTz:PCBM from 296 to 106 K. Each curve was analyzed by the least-square-mean fit of Shockley diode equation<sup>25, 34</sup> given by

$$J = J_0 \left[ \exp\left(\frac{q(V - JR_s)}{nk_BT}\right) - 1 \right] + \frac{V - JR_s}{R_p}$$
(1)

where  $J_0$  is the saturation current density in dark, q is the elementary of charge,  $k_{\rm B}$  is the Boltzmann's constant, n is the ideality factor,  $R_{\rm s}$  is the series resistance in W.cm<sup>2</sup> unit,  $R_{\rm p}$  is the parallel resistance in W.cm<sup>2</sup> unit, and T is the absolute temperature. The  $J_0$  is expressed as Arrhenius type equation incorporating activation energy  $\triangle E$  and pre-exponential factor,  $J_{00}$ , as follows.<sup>26, 35</sup>

$$J_0 = J_{00} \exp\left(-\frac{\Delta E}{nk_B T}\right) \tag{2}$$

Whereas  $J_{00}$  is considered as an indication of the electronic coupling of the donor and acceptor.  $\triangle E$  is the energy required for charges separation at the p/n interface and regarded as being identical to charge transfer state energy,  $E_{\rm CT}$ .<sup>26</sup> Note that the ideality factor (*n*) is included in the exponential part of Eq. (2), which is excluded in some cases.<sup>25</sup> The  $J_{00}$  and  $\triangle E$  were determined as the slope and the intercept of the Arrhenius plot in Figure 30(b), respectively. The resultant parameters for BTT-TP, BTT-FT and BTT-NTz devices are summarized in Table 6.

At open circuit condition (V = 0, J equal to the short circuit current density,  $J_{sc}$ ),  $V_{OC}$  is formulated by Eq. (3) using approximations of  $V_{OC} \ll J_{sc}R_{p}$  and  $J_0 \ll J_{sc}$ .

$$qV_{OC} = nk_B T ln\left(\frac{J_{sc}}{J_0}\right) \tag{3}$$

Combination of Eq. (2) and Eq. (3) leads to Eq. (4).

$$qV_{OC} = \Delta E - nk_B T ln\left(\frac{J_{00}}{J_{sc}}\right) \tag{4}$$



**Figure 30.** (a) *J*-*V* curves of BTT-NTz:PCBM (1:2) in dark at low temperature. (b) Arrhenius plot of logarithmic dark saturation current density,  $n\ln(J_0)$  vs.  $1/(k_B T)$  to evaluate D*E* (slope) and  $J_{00}$  (intercept) for BTT-TP:PCBM (triangles), BTT-FT:PCBM (diamonds), and BTT-NTz:PCBM (circles). The dotted lines are linear fitting curves (blue and green lines are almost overlapped).

Given that  $\triangle E$  equals  $E_{\rm CT}$ ,<sup>26</sup> Eq. 4 indicates that  $E_{\rm CT}$  sets as the upper limit of  $V_{\rm OC}$  as temperature approaches 0 K.<sup>35</sup> Therefore, JV characteristics in the dark for OPV devices provide an overview of the origin of  $V_{\rm OC}$  loss. By inserting experimentally-determined n,  $\triangle E$ ,  $J_{00}$ , and  $J_{\rm SC}$  into Eq. 4, the first (energetic) and the second (kinetic) terms of  $V_{\rm OC}$  are evaluated.

Figure 31 illustrates the contributions of  $\triangle E$  and  $J_{00}$  to the device  $V_{0C}$ . The largest values of both  $\triangle E$  and  $V_{0C}$  are seen for BTT-TP, and the  $\triangle E$  decreases with the decrease of  $V_{0C}$  in BTT-FT and BTT-NTz. Such a positive correlation between  $\triangle E$  and  $V_{0C}$  has been justified in other polymer/fullerene systems.<sup>21-27</sup> In the work by Yamamoto *et. al*, origin of  $V_{0C}$  was studied for OPV devices based on poly(3-hexylthiophene), P3HT, blended with different types of fullerene derivatives.<sup>25</sup> They found that  $\triangle E$  is the main contributor to  $V_{0C}$  of the device with a non-negligible effect of charge recombination in some of the devices. The more predominant effect of  $\triangle E$  than LUMOs of fullerene derivatives has been reported for P3HT-based solar cells.<sup>31</sup> Most interestingly,  $\triangle E$  of BTT-FT device is equal to the obtained  $V_{0C}$ s with a small difference of 0.08 eV. On the other hand,  $\triangle E$  of BTT-TP deviates from Voc by ~ 0.2 eV as a result of the higher charge recombination evidenced from the four orders of magnitude larger  $J_{00}$  than BTT-FT (Table 6). These results suggest that BTT-TP undergoes significant reduction of  $V_{0C}$  due to charge recombination, and adversely has a potential to enhance its performance if charge recombination is minimized. A pronounced impact of  $J_{00}$  on  $V_{0C}$  has been revealed in thermal annealing of poly(3alkylthiophene):PCBM.<sup>36</sup> Indeed, BTT-TP indicates the lowest  $J_{SC}$  (0.78 mA cm<sup>-2</sup>), a low crystallinity, random orientation, and micrometer-scale phase segregation of polymer and PCBM. As for the BTT-NTz showing a low energy loss, its  $J_{SC}$  is still unsatisfactory (3.44 mA cm<sup>-2</sup>) due to the coarse BHJ morphology comprising hundreds of nanometer-scale polymer domains, which was unable to be mediated by solvent additive. Controlling morphology and tailoring face-on orientation<sup>37,38</sup> is other crucial factors to achieve high PCE, in addition to rendering the energy loss minimized.

From the illustrated contribution of the two terms of  $V_{\rm OC}$  (Eq. 4) in Figure 31, it can be concluded that  $\triangle E$  is the primary factor to impact  $V_{\rm OC}$ and  $J_{00}$  is the secondary one, although the  $J_{00}$  is not completely negligible. In particular, the OPV device of BTT-TP showed  $J_{00}$  term almost 40% as high as the  $\triangle E$  term. Wherein,  $J_{00}$  has been discussed as an indicator of intermolecular electronic coupling between donor and acceptor.<sup>25</sup> Increasing the electronic coupling among LUMOs of p- and n-materials is important to enhance charge dissociation. Conversely, excessive electronic coupling between HOMO of p- and LUMO of n-materials induce charge recombination at the interface. The large energy loss attributed to a large  $J_{00}$  in BTT-TP might be linked to the electronic coupling varied by TP unit in the backbone.



Figure 31. Contribution of  $nE_{CT}$  and  $nk_BTln(J_{00}/J_{SC})$  to  $V_{0C}$  according to equation (5), the term  $n\Delta E$  is illustrated in dark gray bars, the term  $nk_BTln(J_{00}/J_{SC})$  is illustrated in light gray bars, x-axis shows the three polymers.

**Table 6.** Activation energy  $(\Delta E)$ , pre-exponential factor  $(J_{00})$  and the ideality factor (n) evaluated from dark current analysis

Polymer	Blend ratio	$J_{ m SC}$ / mA cm <sup>-2</sup>	Voc/ V	FF	PCE / %	riangle E /eV	$J_{00}$ / mA cm <sup>-2</sup>	п
BTT-TP	1:3	0.78	0.98	0.42	0.32	1.26	$9.1  imes 10^7$	1.5
BTT-FT	1:2	2.59	0.86	0.65	1.4	0.99	$5.9 imes10^3$	1.4
BTT-NTz	1:2	3.44	0.78	0.56	1.5	0.96	$5.0  imes 10^3$	1.5

## 3-3 Conclusions

Photovoltaic performance of three BTT polymers; BTT-TP, BTT-FT and BTT-NTz, was investigated and discussed with respect of CT state energy. The dark current analysis at low temperature identified the determinant factors of  $V_{\text{OC}}$ , revealing major contribution of activation energy ( $\triangle E$ ) rather than the pre-exponential factor ( $J_{00}$ ) associated with charge recombination channel, in a good agreement with the reported studies. In contrast to BTT-TP devices, BTT-FT and BTT-NTz devices showed relatively low  $J_{00}$  and therefore resulted in low energy loss. Consequently, a successful approach toward high performing OPV devices is to increase CT energy and lower  $J_{00}$ for maximized  $V_{\text{OC}}$  and  $J_{\text{SC}}$ , as well as optimization of BHJ network.

#### **3-4 Experimental section**

**Materials.** The synthesis and characterization of thee three polymers; BTT-TP, BTT-FT and BTT-NTz are reported in Chapter 2.<sup>28</sup> The weight-averaged molecular weights and polydispersity indices characterized by gel permeation chromatography (GPC) were 16.4 kg mol<sup>-1</sup> (1.59) for BTT-TP, 24.8 kg mol<sup>-1</sup> (1.24) for BTT-FT, and 62.7 kg mol<sup>-1</sup> (1.57) for BTT-NTz, respectively (vs. polystyrene standards in tetrahydrofuran eluent). PCBM and solvents were purchased from Frontier Carbon Inc. and Kishida Kagaku Corp. or Tokyo Chemical Inc. (TCI), respectively, and used as received.

**OPV** device fabrication and measurements. OPV devices were fabricated according to the optimal condition illustrated in Chapter 2.<sup>28</sup> The polymers and PCBM were dissolved in chlorobenzene with 3 vol% 1,8-diiodeoctane (DIO). The polymer: PCBM blend ratios were 1:3 for BTT-TP, 1:2 for BTT-FT, and 1:2 for BTT-NTz. The inverted solar cell structures were fabricated according to the report.<sup>29,30</sup> The BHJ layers were cast on ZnO layer by spincoating in a N<sub>2</sub> glovebox and subsequently electrodes were deposited in a vacuum evaporator without pre-thermal annealing process. The inverted device configuration was ITO (120-160 nm)/ZnO (30 nm)/ BHJ active layer/MoO<sub>3</sub> (10 nm)/ Ag (100 nm) with an active area of 7.1 mm<sup>2</sup>. Currentvoltage (JV) curves were measured using a source meter unit (ADCMT Corp., 6241A) with/without AM 1.5 G solar illumination at 100 mW cm<sup>-2</sup> (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250KD) using a 300 W solar simulator (SAN-EI Corp., XES-301S). Temperature-dependent JVcharacteristics in dark were measured in a vacuum chamber whose temperature is controlled by a He-cooler and monitored by a thermoscoupler.<sup>31</sup>

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## Chapter 4: Alkyl Chain Impact on Benzobisthiazole Polymers

## **4-1 Introduction**

The nanoscale morphology obtained upon the intermixing of a polymer p-type (p) and a fullerene n-type (n) in a bulk heterojunction (BHJ) governs charge separation and transport, and hence the performance of organic photovoltaic devices (OPVs).<sup>1-3</sup> Recent advances in state-of-the-art material design and characterization allow for power conversion efficiencies (PCEs) exceeding 10%.<sup>4-7</sup> Unlike organic field-effect transistors (OFETs),<sup>8</sup> face-onoriented  $\pi$ -stacked polymers contribute to improvements in the PCE of a sandwiched OPV device structure.<sup>9</sup> Generally, symmetric and planar  $\pi$ conjugated polymer backbones facilitate the formation of ordered crystallites in the film state, which simultaneously assists domain purity, prompt charge separation, and charge carrier mobility.<sup>10</sup> Conversely, symmetric polymers suffer from poor solubility and thus, alkyl chain engineering that balances solubility and crystallinity is key to optimal BHJ morphology.<sup>11,12</sup> However, predicting which alkyl chain is best is still difficult and specific to individual polymer backbones.

The morphologies and p/n interactions modulated by alkyl chains not only greatly impact the short-circuit current density ( $J_{SC}$ ) but also the opencircuit voltage ( $V_{OC}$ ),<sup>13·15</sup> the latter of which is primarily determined by the donor's highest occupied molecular orbital (HOMO) and the acceptor's lowest unoccupied molecular orbital (LUMO).<sup>16·19</sup> Interestingly, the electrochemical properties of a polymer are affected by the insulating alkyl chain that can change the LUMO offset (LUMO[A] – LUMO[D]) essential for the escape of charge carriers from geminate recombination.<sup>20·23</sup> Regarding the shapes of alkyl chains, Beaujuge *et al.* showed that a benzodithiophene (BDT)thienopyrrolodione (TPD) polymer (PBDTTPD) with a pair of branched and linear alkyl chains outperformed those with all-linear chains (PCE = 8.5 % vs. 3.2–4.1%).<sup>24,25</sup> With respect to the chain lengths, Janssen *et al.* reported that the long linear alkyl chains of the BDT-benzothiadiazole (BT) polymer, despite improving solubility, causes a decrease in PCE due to increased bimolecular recombinations.<sup>26</sup> Osaka *et al.* demonstrated that a thiazolothiazole (Tz) and naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz)<sup>27,28</sup> polymer (PTzNTz) gave the highest PCE of 9.0% with the shortest branched alkyl chains (ethylhexyl and butyloctyl), along with excellent thermal stability.<sup>29</sup>

This chapter reports the effects of the alkyl chains in new conjugated polymers composed of benzobisthiazole (BBT) and NTz (a "PBBT-NTz"). NTz is an analogue of the benchmark BT acceptor in which the  $\pi$ -plane has been extended with a naphthalene unit, and has been copolymerized with various donor moieties for OPV applications.<sup>27-34</sup> On the other hand, the weak BBT donor, when incorporated in a BBT-BT polymer<sup>35,36</sup> and its difluorinated analogue (PBBT-FBT) exhibited PCEs of 6.5 and 6.4%,<sup>37</sup> respectively. The interest in this work is the systematic investigation of the role that alkyl chains play in the OPV performance and associated properties of PBBT-NTz polymers. Six PBBT-NTz polymers are synthesized bearing pairs of the following alkyl chains: *n*-dodecyl (C12), 2-decyltetradecyl (DT), 2-octyldodecyl (OD), 2-hexyldecyl (HD), and 2-butyloctyl (BO), as shown in Scheme 3. Hereafter, PBBT-NTz polymers are simply abbreviated by the combination of their alkyl chains (e.g., C12-DT). The pristine and blended films with [6,6]phenyl-C61(71)-butyric acid methyl ester ( $PC_{61(71)}BM$ ) are evaluated by photoabsorption spectroscopy, two-dimensional X-ray diffraction (2D-GIXRD), flash-photolysis time-resolved microwave conductivity (TRMC) and techniques.<sup>38-40</sup> This chapter highlights the superior performance of the polymers composed of linear and branched chains over those composed of only all-branched chains, which is a consequence of their enhanced crystallinities, in contrast to previous observations of the analogous PTzNTz and PTzTz polymers.<sup>29,41</sup>

## 4-2 Results and discussion

#### 4-2-1 Density functional theory (DFT) of BBT-NTz

DFT calculations were performed in order to evaluate the planarity of the PBBT-NTz backbone and charge delocalization over its HOMO and LUMO. A model three-repeating unit (BBT-NTz-BBT) bearing methyl substituents exhibits a planar backbone with a twist angle of almost 0° (Figure 32(a)). This excellent planarity is similar to those reported for the analogous polymers, PBBT-BT<sup>36</sup> and PBBT-FBT.<sup>35</sup> The HOMO is delocalized mostly over the entire molecule, whereas the LUMO is localized on the electron withdrawing NTz unit (Figure 32(b)). These observations are typical for a p-type polymer in which the localized LUMO density facilitates electron transfer to the PCBM.<sup>42</sup>



**Figure 32.** (a) Chemical structure and geometry-optimized PBBT-NTz molecule (BBT-NTz-BBT) calculated by DFT (B3LYP/6-31+G). Alkyl chains have been replaced by methyl groups for simplicity. (b) Pictorial representations of the HOMO (upper) and LUMO (lower).

#### 4-2-2 Synthesis and optical/electrochemical properties

The BBT and NTz monomers were synthesized following previous reports.<sup>29,36</sup> Note that synthetic procedures for BBT monomers bearing branched alkyl chains are slightly modified from that of the linear-chain monomer (C12) (Experimental section).<sup>36</sup> The monomers were polycondensed by Stille coupling in a microwave reactor (Scheme 3) to afford six polymers (C12-DT, C12-OD, C12-HD, HD-HD, HD-BO, and BO-BO) with mid-to-high molecular weights ( $M_w$ s) of 33–175 kg mol<sup>-1</sup> (Table 7). These polymers are soluble in hot chlorobenzene (CB) at 120 °C, except for C12-HD which was insufficiently soluble and, therefore, not subjected to OPV characterization. The five polymers were subjected to DSC evaluations and showed small shoulder at ~ 145 °C ascribed to glass transition (Figure 34). Up to 300 °C, neither decomposition nor melting were observed, exhibiting a good thermal stability.

Figure 33(a) depicts the photoabsorption spectra of the pristine PBBT-NTz films. They exhibit mostly similar, but slightly different bandgaps ( $E_{g^{opt}}$ ) in the region of 1.68–1.74 eV, depending on the alkyl chains (Table 7). The HOMO levels of these films were evaluated using photoelectron yield spectroscopy (PYS) and found to lie between -5.44 eV (BO-BO) and -5.57 eV (HD-HD) (the spectra are provided in Figure 35). The resulting energy diagram is presented in Figure 33(b). The  $E_{g^{opt}}$  values and HOMO energy levels of PBBT-NTz are almost identical to those of PBBT-BT and PBBT-FBT.<sup>36,37</sup> In comparison with PTzNTz ( $E_{g^{opt}} = 1.58 \text{ eV}$ , HOMO = -5.28 eV in the film),<sup>29</sup> PBBT-NTz display a lower  $E_{g^{opt}}$  (by approximately 0.1 eV) and deeper HOMO levels (by ~0.2 eV). The deeper HOMO is due to the weaker donating ability of BBT that has a central benzene ring inserted into the thiazolethiazole (Tz) unit.



#### Six PBBT-NTz polymers: (C12-DT), (C12-OD), (C12-HD), (HD-HD), (HD-BO), and (BO-BO)

Scheme 3. Synthetic route and chemical structures of the PBBT-NTz polymers.



**Figure 33. (a)** Normalized UV-vis absorption spectra for PBBT-NTz-polymer films; C12-DT (purple-dotted line), C12-OD (blue-dashed line), C12-HD (green), HD-HD (red), HD-BO (yellow), BO-BO (dark blue), **(b)** Energy diagram of the PBBT-NTz polymers and methanofullerenes.

**Table 7.** Molecular Weights and Optical/Electrochemical Properties of PBBT-NTzPolymers.

Polymer /	$M_{ m n}{}^{ m a}$	$M_{ m w}$ a		$\lambda_{max} \ ^{b}$	$\lambda_{onset} \ ^{b}$	$E_{ m g}^{ m optc}$	$E_{ m HOMO}$ d	$E_{ m LUMO}$ d
	/kg mol <sup>-1</sup>	/kg mol <sup>-1</sup>	PDIα	/nm	/ nm	/ eV	/ eV	/ eV
C12-DT	33	69	2.1	680	726	1.71	-5.51	-3.80
C12-OD	58	98	1.7	675	715	1.73	-5.50	-3.77
C12-HD	88	175	2.0	671	713	1.74	-5.45	-3.71
HD-HD	34	48	1.4	650	720	1.72	-5.57	-3.85
HD-BO	51	66	1.3	644	733	1.69	-5.45	-3.76
BO-BO	25	33	1.4	615	738	1.68	-5.44	-3.76

<sup>a</sup> Number-averaged molecular weight ( $M_n$ ), weight-averaged molecular weight ( $M_w$ ), and polydispersity index (PDI =  $M_w/M_n$ ). <sup>b</sup> Photoabsorption maximum ( $\lambda_{max}$ ) and onset ( $\lambda_{onset}$ ) of the film. <sup>c</sup> Optical bandgap of the film. <sup>d</sup>  $E_{HOMO}$  was evaluated using a PYS in the film state.  $E_{LUMO}$  was calculated by adding  $E_g^{opt}$  to  $E_{HOMO}$ .



**Figure 34.** DSC profiles of (a) C12-DT, (b) C12-OD, (c) HD-HD, (d) HD-BO and (e) BO-BO at temperature ramp rate of 10 °C/ min. The upper direction is exothermic.  $T_{\rm g}$  represents a glass transition temperature.



**Figure 35.** PYS spectrum of (a) C12-DT, C12-HD, C12-OD, (b) HD-HD, HD-BO, and BO-BO films.
#### 4-2-3 Pre-evaluation by Xe-flash TRMC

The transient photoconductivities  $(\Delta \sigma)$  of PBBT-NTz and the PCBM blended films were evaluated using the Xe-TRMC technique, which provides a measure of local mobility, generation yield, and charge-carrier lifetimes upon exposure to a white-light pulse. The measured  $\Delta \sigma$  at different blend ratios, therefore, screens optoelectronic responses without an electrode and is well correlated with OPV performance.<sup>43-47</sup> attached, The photoconductivity maxima ( $\Delta \sigma_{max}$ ) at different blend ratios are presented in Figure 36(a); these curves are convex in shape, with peaks at PCBM = 60–70 wt%, which corresponds to a PBBT-NT:PCBM ratio of between 1:1.5 and 1:2. The  $\Delta\sigma$  transients at PBBT-NT:PCBM = 1:2 are shown in Figure 36(b), which exemplifies the order of  $\Delta \sigma_{\text{max}}$  such that C12-DT (8.9 × 10<sup>-8</sup> S cm<sup>-1</sup>) >> C12-OD  $(4.5 \times 10^{-8} \text{ S cm}^{-1}) > \text{HD-BO} (3.6 \times 10^{-8} \text{ S cm}^{-1}) \approx \text{BO-BO} (3.5 \times 10^{-8} \text{ S.cm}^{-1}) >>$ HD-HD  $(0.3 \times 10^{-8} \text{ S cm}^{-1})$ . Accordingly, it is expected that the optimal polymer: PCBM blend ratios are between 1:1.5 and 1:2, and that the best OPV performance is obtained for C12-DT.



**Figure 36.** Xe-flash TRMC evaluations of PBBT-NTz and the PCBM blends. (a) Photoconductivity maxima ( $\Delta \sigma_{max}$ ) of polymers at different PCBM concentrations. (b) Transient photoconductivities ( $\Delta \sigma$ ) of PBBT-NTz:PCBM = 1:2 blends.

#### 4-2-4 Solar cell performance

The photovoltaic performance of PBBT-NTz was evaluated in an inverted device structure (ITO/ZnO/BHJ/MoO<sub>x</sub>/Ag). Processing conditions including n-type material (PC<sub>61</sub>BM or PC<sub>71</sub>BM), active layer thickness, p/n ratio, processing solvent (CB or  $\sigma$ -dichlorobenzene: DCB), and solvent additive content (1,8-diiodooctane, DIO) were examined. Figures 37(a) and (b) display the best-performing current density–voltage curves (*J*–*V* curves) and the external quantum efficiency (EQE) spectra, respectively; the parameters along with the averaged PCEs are listed in Table 8. All polymers show almost identical *V*<sub>OC</sub> values of 0.81–0.87 V, with the exception of HD-HD:PC<sub>61</sub>BM that reached 0.93 V, consistent with its deep HOMO level. Despite the high *V*<sub>OC</sub> and fill factor (FF) (0.63) of HD-HD, its low *J*<sub>SC</sub> (4.32 mA cm<sup>-2</sup>) led to a low overall device efficiency (2.53%). HD-BO and BO-BO exhibit improved PCEs of 3.70 and 3.09%, respectively, although they in turn suffer from low FFs (0.49 and 0.43). There are no significant differences in PCE between the use of PC<sub>61</sub>BM and PC<sub>71</sub>BM.

In contrast to the all-branched polymers, the linear-branched PBBT-NTz polymers show greater PCEs for PC<sub>71</sub>BM than for PC<sub>61</sub>BM. While the PCE of C12-OD is still moderate (3.63%), C12-DT, bearing the longest linear and branched alkyl chains, exhibits the highest PCE (6.59%) by virtue of its high  $J_{SC}$  (13.3 mA cm<sup>-2</sup>) and relatively high  $V_{OC}$  (0.86 V). It is worth noting that the OPV results are in qualitative agreement with those from the TRMC pre-evaluation, where the highest and lowest PCEs were found for C12-DT and HD-HD, respectively, with optimal blend ratios between 1:1.5 and 1:2. Unfortunately, the FF (0.57) of C12-DT is lower than those of polymers previously reported (FF = 0.64–0.67 for PBBT-BT and PBBT-FBT, Table 8), which limits the overall PCE.

The reason for the low FF observed for PBBT-NTz was examined by measuring the dependences of  $J_{SC}$  on light intensity (Figure 37(c)). The analyses, using  $J_{SC} = AI^{a}$  (A is a scaling factor, I is the light intensity, and a

is an exponent) provide *a* values of 0.83–0.89 for the four evaluated polymers (C12-DT, HD-HD, HD-BO, and BO-BO). The parameter *a* is an indicator of bimolecular recombination, in which a value of unity for *a* indicates weak bimolecular recombination, and thus, a high FF.<sup>48</sup> The observed *a* values are rather low, consistent with the corresponding low FFs (0.4–0.6). Therefore, we conclude that the observed low FF is due to bimolecular recombination. Among the polymers, HD-HD shows the highest *a* (0.89) and FF (0.63), but its  $J_{SC}$  is low.



**Figure 37.** (a) *J*-*V* curves of the best-performing devices under pseudo sunlight (100 mW cm<sup>-2</sup>). (b) EQE spectra. (c) Dependence of  $J_{SC}$  on light intensity (*I*) for OPV devices; C12-DT (purple), HD-HD (red), HD-BO (yellow), and BO-BO (blue), with the fitting exponent a from  $J_{SC} = A I_{c}$ .

Active layer	Solvent	p/n	<i>L</i> /nm	J <sub>SC</sub> /mAcm <sup>-2</sup>	<i>V</i> oc / V	FF	PCE d / %
C12-DT:PC71BM	$CB^{b}$	1:1.5	210	13.3	0.861	0.575	6.59 (5.55)
C12-DT:PC <sub>61</sub> BM	DCB <sup>b</sup>	1:1.5	290	10.3	0.864	0.471	4.20 (3.79)
C12-OD:PC71BM	CB/DCB <sup>b</sup>	1.2	140	7.37	0.873	0.564	3.63 (3.35)
HD-HD:PC71BM	DCBb	1.2	120	4.15	0.836	0.548	1.90 (1.74)
HD-HD:PC <sub>61</sub> BM	DCBb	1.2	170	4.32	0.931	0.629	2.53 (2.35)
HD-BO:PC71BM	DCBc	1:1.5	60	7.93	0.848	0.533	3.59 (3.40)
HD-BO :PC <sub>61</sub> BM	DCBc	1:1.5	65	9.30	0.811	0.491	3.70 (3.41)
BO-BO:PC71BM	$CB^{c}$	1:1.5	160	7.74	0.839	0.451	2.93 (2.80)
BO-BO:PC <sub>61</sub> BM	$CB^{c}$	1:1.5	115	8.61	0.834	0.430	3.09 (2.90)
PBBT-BT:PC71BMf	$CB^{b}$	1.2	210	12.4	0.801	0.674	6.53
PBBT-FBT:PC71BMg	DCB	1:2	210	11.4	0.879	0.636	6.37 (6.21)

Table 8. Best PBBT-NTz:PCBM OPV performance.<sup>a</sup>

<sup>a</sup> Inverted device structure (ITO/ZnO/BHJ/MoOx/Ag) under pseudo-sunlight (100 mW cm<sup>-</sup><sup>2</sup>). <sup>b</sup> DIO = 3 vol%. <sup>c</sup> DIO = 1 vol%. <sup>d</sup> Values in brackets are averaged PCEs over at least eight devices. <sup>f</sup> Taken from Ref. 35. <sup>g</sup> Taken from Ref. 37.

**Table 9.** OPV performance for C12-DT, HD-BO and BO-BO at different BHJ layer thickness

Polymer	Fullerene	Solvent	p/n	<i>L</i> /nm	$J_{\rm SC}$	Voc	$\mathbf{FF}$	PCE e
					/IIIACIII -	1 V		1 70
	PC71BM	$CB^{c}$	1:1.5	126	7.79	0.866	0.661	4.46(4.27)
C12-D1	PC <sub>61</sub> BM	$CB^{c}$	1:1.5	190	8.70	0.860	0.530	3.97(3.65)
HD-BO	PC <sub>61</sub> BM	$\mathrm{DCB}^{\mathrm{d}}$	1:1.5	120	6.34	0.638	0.532	2.31(2.11)
BO-BO	PC <sub>61</sub> BM	$\operatorname{CB^d}$	1:1.5	170	7.27	0.808	0.439	2.58(2.49)

<sup>a</sup> Inverted structure (ITO/ZnO/BHJ/MoOx/Ag) under pseudo-sunlight (100 mW cm<sup>-2</sup>). <sup>c</sup> DIO = 3 vol%. <sup>d</sup> DIO = 1 vol%. <sup>e</sup> Values in the brackets are averaged PCE over at least 3 devices.

#### 4-2-5 Morphology, orientation, and crystallinity.

Atomic force microscope (AFM) images of the blended films are displayed in Figure 38 (upper panels, phase images; lower panels, height images). All-branched PBBT-NTz polymers form circular aggregates with domain sizes of 74.3, 49.5, and 31.2 nm for HD-HD, HD-BO, and BO-BO, respectively. In sharp contrast, the linear-branched C12-DT and C12-OD materials exhibit fibril structures with smaller domains. These morphologies account for the higher  $J_{\rm SC}$  values of the linear-branched polymers (7–13 mA cm<sup>-2</sup>) than those of the all-branched ones (4–9 mA cm<sup>-2</sup>). In particular, the coarsest morphology is observed for HD-HD, and this polymer has the lowest  $J_{\rm SC}$ . Notably, the domain-size order is consistent with the fluorescence quenching  $(\eta_Q)$  of the blended polymers relative to the pristine polymers (Figure 39). Since the difference in  $\eta_Q$  (59–75%) is less significant than that in  $J_{\rm sc}$ , the mobility and charge separation yield associated with the morphology plays determining roles in the overall PCEs, which is consistent with the TRMC evaluations. Thus, the AFM observations clearly indicate that the choice of alkyl chain significantly impacts on the morphology and  $J_{\rm SC}$  of the corresponding polymer.

Figures 40(a)-40(e) (upper panels) and Figures 40(f)-40(j) (lower panels) show the 2D-GIXRD images for the pristine and blended films, respectively. Inter-lamellar and  $\pi$ - $\pi$  stacking diffractions appear at scattering vectors (*q*) of approximately 0.2-0.4 Å<sup>-1</sup> and 1.7 Å<sup>-1</sup>, respectively. The in-plane (IP, *q*<sub>xy</sub>) and out-of-plane (OOP, *q*<sub>z</sub>) 2D-GIXRD profiles are shown in Figure 41. The pristine polymers with all-branched alkyl chains (HD-HD, HD-BO, and BO-BO) indicate no, or very weak,  $\pi$ - $\pi$  stacking diffractions, whereas C12-OD and C12-DT exhibit pronounced diffractions corresponding to  $\pi$ - $\pi$  stacking distances (*d*<sub> $\pi$ </sub>) of 3.48 and 3.64 Å, respectively (Table 10). These *d*<sub> $\pi$ </sub> values are comparable to, or even shorter than, those of PTzNTz bearing all-branched alkyl chains (3.69–3.80 Å).<sup>29</sup> However, the all-branched PBBT-NTz showed mostly random orientations (e.g. face-on = 45.4% and edge-on = 54.6% for BO- BO) and less crystallinity compared with face-on-favorable PTzNTz, in spite of their identical alkyl chains (BO-BO). Note that the percentage of face-on and edge-on is a simple, relative indicator for the orientation of polymer crystallites, which is calculated from the intensities of (100) diffraction in the out-of-plane ( $I_{OOP}$ ) and in-plane ( $I_{IP}$ ) directions (face-on% =  $I_{OOP}/(I_{OOP}+I_{IP}) \times$ 100). This treatment inclines the percentage more to either face-on or edgeon, compared to those in the previous report that divides the azimuthal profile into halves at 45° and compares the integrated intensities,<sup>49</sup> or that uses a Herman order parameter S (S = -0.5: perfect face-on, 0: random, 1: perfect edge-on).<sup>50,51</sup>

The insertion of the benzene ring into the Tz unit extends the size of the  $\pi$ -plane, which is expected to increase the crystallinity and facilitate  $\pi$ - $\pi$  stacking; however, the opposite is observed. This contradiction may be explained by a mismatch in the sizes of the D and A units. In particular, the size of the Tz unit, that includes two adjacent thiophenes, is comparable to that of NTz, while the BBT unit is larger than NT leading to steric repulsion between alkyl chains. This explanation is partly supported by the enhanced crystallinity and increased face-on orientation of the polymer when the branched alkyl chains are replaced by their less-sterically demanding linear counterparts (C12-DT).

C12-DT shows the most distinct diffraction pattern with a signature of a strong edge-on orientation (edge-on = 93.5%) together with a partial face-on orientation (face-on = 6.5%, Table 10). The interlamellar distances ( $d_{\rm IL}$ ) evaluated from the (100) diffractions in the OOP direction simply increase from 15.6 Å for the shortest alkyl-chain-bearing BO-BO, to 27.3 Å for C12-DT, which bears the longest alkyl chain. Upon mixing with PCBM at the deviceoptimized condition, neither  $d_{\pi}$  nor  $d_{\rm IL}$  significantly changes, indicating that PCBM does not intercalate into the polymer crystallites. The coherence lengths in the interlamellar and  $\pi$ - $\pi$  stacking directions ( $L_{100}$  and  $L_{010}$ , respectively) were evaluated using Scherrer's relation<sup>52</sup> (L~0.9 $\lambda$ ( $\Delta_{20}\cos\theta$ )<sup>-1</sup>, where  $\lambda$  is the wavelength of an X-ray,  $\Delta_{20}$  is the full width at half-maximum of the peak, and  $\theta$  is the diffraction angle). For simplicity and relative comparison, polarization correction in the projected polar coordinate is not applied.<sup>53</sup> As listed in Table 10, C12-DT shows unchanged or slightly increased values of  $L_{100}$  (9.7 to 11.6 nm) and  $L_{010}$  (2.9 to 3.1 nm) upon blending with PCBM, providing the highest solar cell PCE. However, the  $L_{010}$  of C12-OD decreases to approximately half of its unblended value (3.9 to 2.1 nm), and its diffraction intensities are also observed to decrease. These properties are likely to be responsible for its lower PCE (3.6%) compared to that of C12-DT (6.6%), in spite of their similar AFM morphologies (Figure 38). The higher crystallinity of C12-DT than C12-OD is also confirmed from the UV-vis absorption spectra in the blends, where the former shows a clear vibrational peak in the long wavelength region (Figure 42).

The all-branched PBBT-NTz polymers display weak edge-on, random orientations that remain mostly unchanged upon mixing with PCBM. The low crystallinity is also evident from the broad photoabsorption spectra in their blends (Figure 42). The intensities of the (100) diffraction in the blended films increase with the length of the alkyl chain (the longest HD-HD > the middle HD-BO > the shortest BO-BO), while the sizes of the aggregates determined by AFM also increase in the same order. Due to a balance between crystallinity and morphology, the best PCE of 3.7% was obtained for (midlength) HD-BO, followed by BO-BO (3.1%) and HD-HD (2.5%). Such an alkylchain-length trade-off effect was not observed in PTzNTz, where the PCEs are comparable among the polymers with short alkyl chains, but suddenly drops in value for that bearing the longest chain (ethylhexyl:EH-BO =  $9.0\% \approx$ EH-HD =  $8.8\% \approx BOBO = 8.8\% > BOHD = 5.2\%$ ).<sup>29</sup> The trend observed for PBBT-NTz shows a similarity to that of the PBDTTPD polymers,<sup>54</sup> rather than PTzNTz. The orientation of PTzNTz has been demonstrated to gradually change from face-on, to isotropic, and edge-on with increasing branched-alkylchain size, and the greatest face-on orientation is obtained when linear and branched chains are combined.<sup>54</sup> In addition to orientation, the alkyl-chain

length impacts on the generation of free charge carriers and their recombination,<sup>55</sup> which is further discussed in the next subsection.

			•				
Polymer	Pristine or blendª	Face- on /% <sup>b</sup>	Edge- on /% <sup>b</sup>	$d_{ m IL}$ /Åc	<i>L</i> <sub>100</sub> /nm <sup>c</sup>	$d_{\pi\pi}$ /Åd	<i>L</i> <sub>010</sub> /nm <sup>d</sup>
C19-DT	Pristine	6.5	93.5	27.3	9.7	3.64	2.9
01 <b>2</b> -D1	Blend (CB)	43.4	56.6	26.6	11.6	3.64	3.1
	Pristine	13.1	86.9	20.6	9.2	3.48	3.9
C12-OD	Blend (CB/DCB)	19.5	80.5	20.2	10.8	3.40	2.1
	Pristine	0.7	99.3	18.4	11.6	-e	-e
HD-HD	Blend (DCB)	2.8	97.2	18.8	17.1	-e	<b>-</b> e
	Pristine	6.4	93.6	17.8	8.2	-e	-e
пр.во	Blend (DCB)	38.4	61.6	19.2	10.3	3.65	5.2
DO-DO	Pristine	45.4	54.6	15.6	8.5	3.61	2.8
RO-RO	Blend (CB)	61.2	38.8	17.8	8.9	3.63	4.8

**Table 10.** Orientations and crystallite sizes of PBBT-NTz and its  $PC_{71}BM/PC_{61}BM$  blends evaluated by 2D-GIXRD.

<sup>a</sup> The abbreviations in brackets represent the solvent. The blend films are identical to those of the best-performing OPV devices. <sup>b</sup> The portion of polymer orientation in crystallites evaluated from the relative intensities of the (100) diffraction in the out-of-plane ( $I_{OOP}$ ) and in-plane ( $I_{IP}$ ) directions. Face-on% =  $I_{OOP}/(I_{OOP}+I_{IP}) \times 100$ , edge-on% = 100 – (face-on%). <sup>c</sup> Interlamellar distance ( $d_{IL}$ ) and crystalline size ( $L_{100}$ ) evaluated from the out-of-plane (100) diffraction. <sup>d</sup>  $\pi$ - $\pi$ stacking distance ( $d_{\pi\pi}$ ) and crystalline size ( $L_{010}$ ) evaluated from the out-of-plane (010) diffraction. <sup>e</sup> Not observed.



**Figure 38.** AFM phase (upper panels) and height (lower panels) images of the best-performing devices (2  $\mu$ m<sup>2</sup>). Scale bar = 500 nm.



**Figure 39.** Fluorescence spectra of pristine (red) and blend (black) films for (a) C12-DT, (b) C12-OD, (c) HD-HD, (d) HD-BO, and (e) BO-BO polymers.  $\lambda_{ex} = 500$  nm.



**Figure 40.** 2D-GIXRD images for (a–e) pristine and (f–j) BHJ films under optimized conditions.



**Figure 41.** 2D-GIXRD profiles in the out-of-plane (OOP) and in-plane (IP) directions for (a–e) pristine and (f–j) BHJ films under optimized conditions.



**Figure 42.** UV-vis absorption spectra of the best-performing OPV devices for (a) C12-DT and C12-OD, and (b) HD-HD, HD-BO, and BO-BO polymers.

#### 4-2-6 Alkyl chain length discussion

The effect of the alkyl side chains on BBT-NTz polymers are discussed in aspects of crystalline structure, OPV performance, and TRMC photoconductivity of the polymers. Figure 44(a) depicts  $d_{\rm IL}$  as a function of the maximum alkyl-chain length ( $C_{\rm max}$ ), where the open and closed symbols represent the pristine and PBBT-NTz:PCBM blended films, respectively. A reasonable, positive, linear correlation between  $d_{\rm IL}$  and the maximum alkyl length is observed. However, the  $d_{\rm IL}$  of the most efficient C12-DT is about 20% larger than expected one based on the trend line from the other polymers. This is probably due to the longest alkyl chain of C12-DT being attached to the thiophenes on the NTz unit, while in the other polymers the longest alkyl chain is attached to the thiophenes on the BBT moiety. In other words, the alkyl chains adjacent to the NTz unit have a greater impact on  $d_{\rm IL}$  than those adjacent to BBT. A similar trend was observed in the plot of  $d_{\rm IL}$  against the average number of alkyl-chain length ( $C_{\rm avg}$ , Figure 43).



**Figure 43.** Interlamellar distances  $(d_{IL})$  for pristine polymers (open symbols) and blends (filled symbols) obtained from 2D-GIXRD as functions of the average number of carbons in the alkyl chain for each polymer ( $C_{avg}$ ).

Interestingly, PCE shows an increasing trend with  $d_{\rm IL}$ , suggesting that long alkyl chains are beneficial for solar cell performance (Figure 44(b)). Note that this trend is unlikely to be a direct correlation, but an indirect one because increasing alkyl chain length improves both the crystallinity of the polymer and the BHJ morphology; consequently performance increases.<sup>56-59</sup> Moreover, the PCE of the HD-HD polymer is far below the trend curve, indicating that the correlation between PCE and  $d_{\rm IL}$  is not general.

As clarified by the AFM and 2D-GIXRD experiments, HD-BO, with the mid-sized branched alkyl chains, exhibits the highest PCE among the allbranched polymers (HD-HD, HD-BO, and BO-BO), presumably as a result of a balance between morphology (domain size) and crystallinity (intensity of diffraction). Replacing the branched alkyl groups on the BBT units by linear ones, and extending the lengths of the branched chains on the NTz units brought about enhanced crystallinity and a fiber-like morphology, which results in improved PCE. In particular, C12-DT exhibits an edge-on orientation in both the pristine and blended films that is accompanied by a partial face-on orientation. These superior properties lead to increases in charge carrier mobility, charge generation efficiency, and/or charge carrier lifetime.

To investigate the charge-carrier lifetimes and generation efficiencies, laser-flash TRMC experiments were performed on the device-optimized blended films. Figure 44(c) depicts time-dependent kinetic traces of  $\phi \sum \mu$ , where  $\phi$  and  $\sum \mu$  are the charge-carrier-generation efficiency and the sum of the charge-carrier mobilities (=  $\mu_{+} + \mu_{-}$ ), respectively. C12-DT displays the highest  $\phi \sum \mu$  values, with a  $\phi \sum \mu$  maximum ( $\phi \sum \mu_{max}$ ) of 1.7 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, as well as the longest half-life ( $\tau_{1/2}$ ) of 1.62 µs, consistent with the highest PCE and  $\Delta \sigma_{max}$  values determined by Xe-flash TRMC (Figure 4). In contrast, HD-HD exhibits a very small  $\phi \sum \mu_{max}$  (5.6 × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) in good agreement with the lowest PCE among the materials in this study. C12-OD, HD-BO, and BO-BO show comparable values of  $\phi \sum \mu_{max}$  (~ 0.6 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), while the  $\tau_{1/2}$ s were observed to decrease from 0.88, to 0.31, and 0.22 µs, respectively. PCE divided by  $V_{\rm OC}$  (=  $J_{\rm SC} \times \rm FF$ ), when plotted against  $\phi \sum \mu_{\rm max}$ , shows a good linear correlation (Figure 44(d)), indicating that the comparable solar cell outputs of C12-OD, HD-BO, and BO-BO are due to similar local mobilities ( $\sum \mu$ ) and charge separation efficiencies ( $\phi$ ) rather than the  $\tau_{1/2}$  associated with charge transport efficiency. Indeed, the optimal thickness of these polymers is 60–140 nm; the PCEs are observed to decrease in thicker films (126–190 nm, Table 9). The relation between PCE( $V_{\rm OC}$ )<sup>-1</sup> is usually sublinear,<sup>43,44,60</sup> which is partly rationalized by a sublinear relation between the product of lifetime ( $\tau$ ) and mobility ( $\mu$ ) vs FF.<sup>61</sup> The present linear trend is caused by the very small TRMC signal of HD-HD in spite of its moderate PCE (2.5%). This is probably due to the lifetime is not considered in Figure 44(d), because of its small, noisy TRMC signal.

In contrast, the maximum PCE of C12-DT is observed in a relatively thick layer (6.6%, 210 nm), owing to its high crystallinity, partial face-on orientation, and long charge-carrier lifetime. A thinner C12-DT resulted in a PCE decrease to 4.5%, limited mainly by the decrease in  $J_{\rm SC}$  (13.3 mA cm<sup>-2</sup> to 7.79 mA cm<sup>-2</sup>, Table 9). Although the PCE and optimal thickness of C12-DT are almost identical to those of PBBT-BT (6.5%, 210 nm)<sup>35</sup> and PBBT-FBT (6.4%, 210 nm),<sup>37</sup> the FF (0.57) is lower than those of the analogous polymers (0.64–0.67, Table 8). Conversely, the  $\Delta \sigma_{\rm max}$  of C12-DT is approximately twice that of PBBT-FBT. This implies that the optoelectronic properties of C12-DT are potentially superior to those of PBBT-FBT, and that there is room for PCE improvement in these devices. A possible drawback of C12-DT is its molecular weight ( $M_{\rm w}$  = 69 kg mol<sup>-1</sup>), which is approximately one third of PBBT-FBT (237 kg mol<sup>-1</sup>).<sup>37</sup> A few batches of PBBT-NTz were synthesized; however, a higher molecular weight polymer was never obtained. A mismatch in the solubilities and/or diffusivities of the monomers may interfere with the growth of high molecular weight polymers. It should be noted that monomer purity is an unlikely reason for these observations. Since NTz polymers are among the most versatile acceptors in BHJ OPVs, we foresee that the impact of alkyl chains on crystallinity, orientation, and device parameters found in this study will be useful for molecular design during the further evolution of polymer solar cells.



Figure 44. (a) Interlamellar distances ( $d_{\rm IL}$ ) for pristine polymers (open symbols) and blends (filled symbols) obtained from 2D-GIXRD as functions of the number of carbons in the longest alkyl chain for each polymer ( $C_{\rm max}$ ). (b) Best PCE as a function of  $d_{\rm IL}$  (blends) (c) Laser TRMC kinetic traces of BHJ blends under the PBBT-NTz-polymer optimized conditions showing half-lives ( $\tau_{1/2}$ ) of the charge carriers. (d) PCE divided by  $V_{\rm OC}$  as a function of  $\varphi \Sigma \mu_{\rm max}$  of TRMC ( $\lambda_{\rm ex} = 355$  nm).

## **4-3 Conclusions**

Five PBBT-NTz polymers bearing linear-branched and all-branched alkyl chains (C12-DT, C12-OD, HD-HD, HD-BO, and BO-BO) were synthesized and their optical/electrochemical properties, crystalline structures in films, and OPV outputs were evaluated. The combination of linear (C12) and branched (DT) polymer units afforded the highest PCE (6.59%) owing to high  $J_{\rm SC}$  (13.3 mA cm<sup>-2</sup>) and  $V_{\rm OC}$  (0.86 V) values, despite the moderate FF (0.57). AFM experiments reveal nanometer-scale fibers in C12-DT and C12-OD, while the other all-branched polymers exhibit circle-shaped domains, and therefore low  $J_{\rm SC}$  values. From the 2D-GIXRD experiments, C12-DT and C12-OD were found to be composed of edge-on, with partial faceon, orientations and to have high crystallinities, which is in contrast to the randomly oriented, less-crystalline all-branched polymers (HD-HD, HD-BO, and BO-BO). The transient photoconductivities from Xe-flash and laser-flash TRMC experiments correlate with the outputs from the devices, with the most efficient C12-DT exhibiting the highest  $\varphi \Sigma \mu_{max}$  and longest lifetime, suggesting that lifetime plays a minor role among the all-branched polymers. Notably, the optimal alkyl chain for PBBT-NTz is different to that observed for the analogous PTzNTz polymers, despite the only difference between the two being the central benzene ring. It is anticipated that these findings will provide the foundations for the future directions of alkyl engineering.

## 4-4 Experimental section

Materials. All materials used in this study were purchased from Sigma-Aldrich, Wako Chemicals Inc., and Tokyo Chemical, Inc. (TCI). All chemicals purification. 2,6-bis(3-dodecvl-5were used without further (trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole), 2,6-bis(3-(2*hexyldecyl*)-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5d']bis(thiazole), 2,6-bis(3-(2-butyloctyl)-5-(trimethylstannyl)thiophen-2yl)benzo[1,2-d:4,5-d']bis(thiazole), 5,10-bis(5-bromo-4-(2*decyltetradecyl*)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole), 5,10-bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)naphtho[1,2-c:5,6c']bis([1,2,5]thiadiazole), 5,10-bis(5-bromo-4-(2-octyldodecyl)thiophen-2yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) were synthesized according to the previous reports.<sup>1,2</sup>

#### Synthesis of branched alkyl-chain BBT



2-formyl-3-(2-hexyldecyl)thiophene (1.62 g, 4.8 mmol), 2,5-diamino-1,4benzenedithiol dihydrochloride (0.6 g, 2.4 mmol) and tributylamine (0.9 g, 4.8 mmol) were dissolved into DMSO (40 mL) under nitrogen and the solution was refluxed at 195 ° C overnight. The reaction mixture was quenched with H<sub>2</sub>O *without* cooling down to room temperature. The product was extracted with chloroform and purified by column chromatography (silica gel, hexane : choloroform = 1 : 1) to give a yellow solid (0.76 g, 40 % yield).1H NMR (400 MHz, CDCl3):  $\delta$ = 8.46 (s, 2H), 7.41 (d, 2H), 7.03 (d, 2H), 3.03 (d, 4H), 1.83 (m, 2H), 1.2-1.5 (m, 48H), 0.86 (m, 12H).

#### <sup>1</sup>H NMR of stannylated BBT monomers

Reaction yield and <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) characteristics for the stannylated BBT monomers after HPLC purification:

BTT(C12). 2,6-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2d:4,5-d']bis(thiazole) (Yield:76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 8.47 (s, 2H), 7.08 (s, 2H), 3.07 (t, 4H), 1.79 (m, 4H), 1.1-1.5 (m, 36H), 0.87 (t, 6H), 0.42 (s, 18H).

BTT(HD). 2,6-bis(3-(2-hexyldecyl)-5-(trimethylstannyl)thiophen-2yl)benzo[1,2-d:4,5-d']bis(thiazole) (Yield:65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.46 (s, 2H), 7.03 (s, 2H), 3.03 (d, 4H), 1.83 (m, 2H), 1.2-1.5 (m, 48H), 0.86 (m, 12H), 0.42 (s, 18H).

BTT(BO). 2,6-bis(3-(2-butyloctyl)-5-(trimethylstannyl)thiophen-2yl)benzo[1,2-d:4,5-d']bis(thiazole) (Yield:67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.46 (s, 2H), 7.03 (s, 2H), 3.03 (d, 4H), 1.83 (m, 2H), 1.2-1.5 (m, 32H), 0.86 (m, 12H), 0.42 (s, 18H).

#### <sup>1</sup>H NMR of brominated NTz monomers

Reaction yield and <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) characteristics for the brominated NTz monomers after HPLC purification:

NTz(DT). 5,10-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.94 (s, 2H), 7.92 (s, 2H), 2.60 (d, 4H), 1.80 (m, 2H), 1.2-1.5 (m, 80H), 0.80-0.90 (m, 12H). NTz(OD). 5,10-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.94 (s, 2H), 7.92 (s, 2H), 2.60 (d, 4H), 1.80 (m, 2H), 1.2-1.5 (m, 64H), 0.80-0.90 (m, 12H). NTz(HD). 5,10-bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.94 (s, 2H), 7.92 (s, 2H), 2.60 (d, 4H), 1.80 (m, 2H), 1.2-1.5 (m, 48H), 0.80-0.90 (m, 12H). NTz(BO). 5,10-bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.94 (s, 2H), 7.92 (s, 2H), 2.60 (d, 4H), 1.80 (m, 2H), 1.2-1.5 (m, 48H), 0.80-0.90 (m, 12H). NTz(BO). 5,10-bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.94 (s, 2H), 7.92 (s, 2H), 2.60 (d, 4H), 1.80 (m, 2H), 1.2-1.5 (m, 32H), 0.80-0.90 (m, 12H). **Polymer synthesis.** Stille cross-coupling polymerization reactions were conducted in an Anton Paar Monowave 300 microwave reactor. Stannylated BBT (0.10 mmol), dibrominated NTz (0.10 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (0.002 mmol), anhydrous chlorobenzene (CB, 4 mL), and dimethylformamide (DMF, 0.2 mL) were added to a reaction vial equipped with a stirrer bar under a flow of argon. The reaction tube was sealed and transferred to the reactor. Polymerization was performed at 180 °C with stirring at 800 rpm for 30 min. The reaction mixture was poured into methanol and the precipitate was then purified by Soxhlet extraction in methanol, hexane, chloroform, and chlorobenzene. The residue was reprecipitated from methanol to afford a dark green solid.

C12-DT. This polymer was synthesized from 2,6-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (30 mg, 0.03 mmol), 5,10-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (36.5 mg, 0.03 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.78 mg, 0.68 µmol) in a mixture of N<sub>2</sub>-bubbled anhydrous CB (4 mL) and DMF (0.2 mL). (Yield: 77%, 40 mg).

**C12-OD.** This polymer was synthesized from 2,6-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (57 mg, 0.057 mmol), 5,10-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (67 mg, 0.057 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.57 mg, 1.36  $\mu$ mol) in a mixture of N<sub>2</sub>-bubbled anhydrous CB (4 mL) and DMF (0.2 mL). (Yield: 26%, 25 mg).

C12-HD. This polymer was synthesized from 2,6-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (30 mg, 0.03 mmol), 5,10-bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (30 mg, 0.03 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.77 mg, 0.68  $\mu$ mol) in a mixture of N<sub>2</sub>-bubbled anhydrous CB (4 mL) and DMF (0.2 mL). (Yield: 6%, 5 mg).

**HD-HD.** This polymer was synthesized from 2,6-bis(3-(2-hexyldecyl)-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (108 mg, 0.095 mmol), 5,10-bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (97 mg, 0.095 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (2.54 mg, 2.2  $\mu$ mol) in a mixture of N<sub>2</sub>-bubbled anhydrous CB (5 mL) and DMF (0.2 mL). (Yield: 74%, 119 mg).

**HD-BO.** This polymer was synthesized from 2,6-bis(3-(2-hexyldecyl)-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (94 mg, 0.083 mmol), 5,10-bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (75 mg, 0.083 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (2.21 mg, 1.9  $\mu$ mol) in a mixture of N<sub>2</sub>-bubbled anhydrous CB (5 mL) and DMF (0.2 mL). (Yield: 34%, 45 mg).

**BO-BO.** This polymer was synthesized from 2,6-bis(3-(2-butyloctyl)-5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) (131 mg, 0.128 mmol), 5,10-bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (116 mg, 0.128 mmol), and  $(Pd(PPh_3)_4$  (3.42 mg, 2.9 µmol) in a mixture of N<sub>2</sub>-bubbled anhydrous CB (6 mL) and DMF (0.2 mL). (Yield: 44%, 83 mg).

**General measurements.** Steady-state photoabsorption and fluorescence spectroscopies were performed using a Jasco V-570 UV-vis and a Jasco FP-8300 spectrophotometers, respectively. Molecular weights and polydispersity indices of the polymers were determined using the gel permeation chromatography (GPC) method with polystyrene standards. GPC analyses were performed with chloroform as the eluent at a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup> at 40 °C, on a SHIMADZU LC-20AT, CBM-20A, CTO-20A chromatograph connected to a SHIMADZU SPD-M20A UV-vis detector. Photoelectron yield spectroscopy (PYS) of the polymer films on indium-tin-oxide (ITO) glass was performed on a Bunko Keike BIP-KV2016K instrument. Differential scanning calorimetry (DSC) was conducted on a NETZSCH DSC204F1 Phoenix. Atomic force microscopy (AFM) was carried out on a Bruker Innova AFM microscope. Domain size in AFM images were determined using a Nanoscope Analysis ver. 1.5 software (Bruker). Film thicknesses were measured using a Bruker Dektak XT surface profiler. Xe-flash time-resolved microwave conductivity (Xe-TRMC at ~9.1 GHz) experiments were conducted with a pseudo-sunlight white-light pulse  $(0.3 \text{ mJ cm}^{-2} \text{ pulse}^{-1})$  as the excitation source. The photoconductivity  $\Delta \sigma$  was obtained by applying the formula  $\Delta P_r / A P_r$ , where  $\Delta P_r$ , A, and  $P_r$  are the transient power change of the reflected microwave power, the sensitivity factor, and the reflected microwave power, respectively. Laser-flash TRMC experiments were conducted for the optimum OPV blends (drop cast on quartz plates) using the third harmonic generator (THG; 355 nm) of a Nd:YAG laser (Continuum Inc., Surelite II, 5– 8 ns pulse duration, 10 Hz) as the excitation source  $(4.6 \times 10^{15} \text{ photons cm}^{-2})$ pulse<sup>-1</sup>). The photoconductivity transient  $\Delta \sigma$  was converted to the product of the quantum yield ( $\varphi$ ) and the sum of charge carrier mobilities  $\sum \mu (= \mu_{+} + \mu_{-})$ by the formula  $\phi \sum \mu = \Delta o (eI_0 F_{\text{light}})^{-1}$ , where *e* and  $F_{\text{light}}$  are the unit charge of a single electron and a correction (or filling) factor, respectively. Twodimensional grazing-incidence X-ray diffraction (2D-GIXRD) experiments were conducted on the BL46XU beamline at SPring-8 (Japan Synchrotron Radiation Research Institute, JASRI), using 12.39 keV ( $\lambda$  = 1 Å) X-rays. The GIXRD patterns were recorded with a 2-D image detector (Pilatus 300K). Time-dependent density functional theory (DFT) calculations were performed using Gaussian 09, Revision D.01.

**OPV device fabrication.** The device configuration was: ITO (120-160 nm)/ZnO (30 nm)/BHJ active layer/MoO<sub>3</sub> (10 nm)/Ag (100 nm) with an active area of 7.1 mm<sup>2</sup>. PC<sub>61(71)</sub>BM was purchased from Frontier Carbon Inc. and used as the n-type material. Current-voltage (*J-V*) curves were measured using a ADCMT Corp., 6241A source/monitor under AM1.5G solar illumination at 100 mW cm<sup>-2</sup> (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250KD) using a 300 W solar simulator (SAN-EI Corp., XES-301S). The external quantum efficiency (EQE) spectra were measured on a Bunko Keiki model BS-520BK instrument equipped with a Keithley model 2401 source

meter. The monochromatic light power was calibrated using a silicon photovoltaic cell (Bunko Keiki model S1337-1010BQ).

# Optimization of OPV performance HD-HD polymer

Table 11. Optimization trails for HD-HD OPV devices using  $PC_{61}BM$ .

Solvent	Blend ratio	conc. /mg.ml <sup>-1</sup>	DIO /vol. %	<i>L</i> /nm	J <sub>SC</sub> /mA.cm <sup>-2</sup>	Voc/V	FF	PCE/ %
			-	57	4.06	0.38	0.40	0.56
	1:07		1	67	3.83	0.44	0.43	0.73
	1. 0.7	11	9	66	4.25	0.27	0.39	0.44
		11	ð	120	4.33	0.39	0.41	0.70
	1.1 5		1	148	2.18	0.88	0.44	0.86
CP	1.1.0		T	129	2.23	0.92	0.51	1.04
СБ		10		197	2.77	0.94	0.62	1.61
		10		192	2.84	0.93	0.60	1.57
	1.0	1.0		280	2.36	0.96	0.59	1.34
	1.2	13	3	258	2.56	0.96	0.59	1.46
		15		261	3.24	0.95	0.53	1.64
				264	3.23	0.95	0.53	1.61
		12		196	3.84	0.94	0.67	2.41
				167	4.32	0.93	0.63	2.53
	1: 2	15		151	3.79	0.85	0.59	1.88
				235	3.71	0.88	0.60	1.94
			0	169	2.70	0.81	0.60	1.32
0-000				144	2.71	0.86	0.62	1.45
				142	4.51	0.92	0.56	2.33
		10	9	149	4.09	0.75	0.57	1.75
	1.0	10	చ	199	3.72	0.92	0.56	1.93
	1.3			147	3.85	0.91	0.60	2.11
			1	133	2.45	0.96	0.70	1.64
	1:2		T	101	2.62	0.94	0.64	1.57
(4:1)		12	3	175	3.72	0.90	0.52	1.73



**Figure 45.** Microscopic images of HD-HD device film showing deep cracks and deficient film morphology.



**Figure 46.** AFM phase (top) and height (bottom) images of HD-HD OPV devices using different processing solvents.  $2 \times 2 \mu m$  scale.

#### HD-BO polymer

Three molecular weight ranges of HD-BO polymer were synthesized and categorized by soxhlet extraction according to their solubility to chloroform (CF), cholorobenzene (CB) and hot CB (H-CB) soluble fractions. The molecular weights and OPV performance are shown in Tables 9 and 10, respectively.

Polymers	Solubility	<i>M</i> <sub>n</sub> /Da	<i>M</i> <sub>₩</sub> /Da	$PDI = M_w / M_n$
HD – BO (CF)	CF, CB	43363	57853	1.33
HD – BO (CB)	СВ	39845	72903	1.83
HD – BO (H-CB)	Hot CB	43794	236494	5.4

Table 12. Molecular weights of three fractions of HD-BO polymer.

**Table 13.** OPV devices performances for different Mwts of HD-BO polymer using PC<sub>61</sub>BM. Concentration of 10 mg.ml<sup>-1</sup> were used with 1 vol.% DIO.

Polymer	Solvent	Blend ratio	<i>L</i> /nm	$J_{\rm SC}$ /mA.cm <sup>-2</sup>	V <sub>oc</sub> / V	$\mathbf{FF}$	PCE/ %
<b>CE</b> soluble		1: 1.5	134	2.78	0.86	0.46	1.11
CF-soluble			87	3.09	0.89	0.53	1.45
CB-soluble	oluble CB		105	4.20	0.66	0.35	0.97
			102	4.46	0.89	0.50	1.98
			213	6.59	0.85	0.47	2.61
Hot CB-			131.5	5.84	0.84	0.46	2.23
soluble			109	9.70	0.80	0.46	3.56
	o-DCB		64	9.32	0.81	0.49	3.71



**Figure 47.** JV curve and EQE spectra of HD-BO OPV devices using different processing solvents.



**Figure 48.** AFM phase (top) and height (bottom) images of HD-BO OPV devices using CB as processing solvents.  $2 \times 2 \mu m$  scale.



**Figure 49.** Photoconductivity from Xe lamp TRMC for CF, CB and H-CB soluble fractions of HD-BO polymer.

### **BO-BO** polymer

Solvent	Blend ratio	DIO/ vol. %	<i>L</i> /nm	$J_{ m SC}$ /mA cm $^{-2}$	V <sub>OC</sub> / V	FF	PCE/ %
			211	5.19	0.74	0.40	1.54
		3	220	4.96	0.7	0.44	1.55
o-DCB	1.0	1	171	6.53	0.79	0.43	2.23
	1. 2		142	7.21	0.78	0.42	2.40
		0	179	6.43	0.58	0.41	1.53
			211	6.61	0.58	0.42	1.64
СВ		3	190	6.63	0.81	0.42	2.26
	1.0		116	8.20	0.81	0.41	2.73
	1.2	1	311	4.99	0.89	0.43	1.89
			167	7.15	0.85	0.40	2.37
	1:3		511	3.21	0.87	0.47	1.31

Table 14. Optimization trails for BO-BO OPV devices using  $PC_{61}BM$ .

			285	5.16	0.82	0.42	1.76
		342	5.68	0.85	0.37	1.80	
			150	7.96	0.84	0.43	2.87
			108	8.94	0.78	0.43	3.00
1: 1.5	1.1.5		115	8.61	0.83	0.43	3.09
o-DCB/CF	/CF		173	7.27	0.81	0.44	2.58
(4:1)			145	7.63	0.81	0.44	2.74



Figure 50. Active layer thickness effect of current density ratio.



Figure 51. AFM phase (top) and height (bottom) images of BO-BO OPV devices using different processing solvents.  $2 \times 2 \ \mu m$  scale.

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## Chapter 5 Conclusion of this Dissertation

The work presented in this thesis focused on the photovoltaic properties for different molecular designs of semiconducting polymers. The accomplished findings through this work are summarized as follows.

*Chapter 1* provided a background review of the optoelectronic effect in conjugated polymers. The basic criteria for obtaining high photovoltaic performance of low bandgap polymers were thoroughly discussed from the aspects of energy levels, the nano-scale morphology and p-/ n- materials interactions at the interfaces. A brief literature history of the electron donor and acceptor monomers benzotrithiophene, benzobisthiazole and naphthobisthiadiazole were highlighted.

Chapter 2 illustrated the bandgap manipulation of benzotrithiophene (BTT)-based polymers. BTT donor monomer was copolymerized with three strong acceptor monomers providing a cascade of HOMO levels. The deep HOMO levels of BTT polymers resulted in high  $V_{OC}$  when implanted in the OPV devices approaching 1.0 V. Nevertheless, BTT polymers suffered from high aggregations in the BHJ that led to low  $J_{SC}$  and overall performances (0.78 mA cm<sup>-2</sup>, 0.35% PCE for BTT-TP). Fluorine modification in the BTT-FT polymer resulted in fibrous morphology and improved  $J_{SC}$  (2.59 mA cm<sup>-2</sup>, 1.4% PCE). The best PCE of BTT polymers was the BTT-NTz (4.31 mA cm<sup>-2</sup>, 1.87% PCE) attributed to its low bandgap and higher LUMO energy offset. The results showcase the important feature of deep HOMO level with optimized LUMO offset in order to obtain high  $V_{OC}$  and  $J_{SC}$  of the OPV devices.

Chapter 3 discussed the origin of  $V_{\rm OC}$  in BTT polymers through the investigation of the low energy loss in their devices. A linear correlation of the  $V_{\rm OC}$  with the effective bandgaps of BTT polymers with a unity slope and an intercept of 0.4 eV (equal to the difference between  $V_{\rm OC}$  and effective bandgap) suggested similar factors determined the  $V_{\rm OC}$  in these devices. Thus, the current density in the absence of light was investigated for BTT polymers at low temperatures (100-300 K). The Arrhenius plot of the dark current provided the numerical evaluation of the activation energy  $\triangle E$  at each BHJ.  $\triangle E$  that accounts as the charge transfer (CT) state energy was found to

contribute mainly to the obtained  $V_{\rm OC}$ . Therefore the results provide a numerical prove of the limitation of the  $V_{\rm OC}$  by the CT state energy. Additionally, the deviation of  $V_{\rm OC}$  from  $\triangle E$  was found to be minimum for BTT-NTz suggesting the low charges recombination in its OPV device following the optimum LUMO offset and enhanced  $J_{\rm SC}$ .

Chapter 4 enlightened the systematic illustration of the morphological effects in the benzobisthiazole-naphthobisthiadiazole (BBT-NTz) polymers. As a consequence of the planarity and comprehensive alkyl chain engineering, the BBT-NTz polymers with different combinations of alkyl chain lengths showed the PCE as high as 6.6%. Morphology, crystallinity ( $\pi$ - $\pi$  staking distance), and TRMC photoconductivities were in good agreement to the device performances, which were greatly varied by the alkyl chain. The results highlight the significant impact of alkyl engineering in the polymer backbone to achieve the optimal morphology of BHJ. It is anticipated that these findings will provide the foundations for the future directions of alkyl engineering of conjugated polymers for optoelectronics.

Thereafter, the study presented here elucidates the parameters contributing to the photovoltaic performance through molecular design of the low bandgap conjugated polymers. The exploration focused on the aspects of donor-acceptor combination, polymer backbone planarity and symmetricity, and side groups influence on polymer orientation and BHJ morphology. The alkyl chain length in BBT-NTz polymers revealed a significant morphological changes from aggregated domains to high crystalline oriented fibrous structures. The author anticipates the polymer alkyl side chains to be considered as an effective optimization tool for improved optoelectronic properties of the same polymer backbone.

# List of Publications

- <u>Al-Naamani, E</u>.; Ide, M.; Gopal, A.; Saeki, A.; Osaka, I.; Seki, S. Study of Photoelectric Conversion in Benzotrithiophene-Based Conjugated Semiconducting Polymers. *J. Photopolym. Sci. Tech.* **2015**, *28*, 605–610.
- (2) <u>Al-Naamani, E</u>.; Ide, M.; Gopal, A.; Saeki, A. Insight into the Energy Loss in Organic Solar Cells Based on Benzotrithiophene Copolymers: A Dark Current Analysis at Low Temperature. *Jpn. J. Appl. Phys.* **2016**, *55*, 022303/1–4.
- (3) <u>Al-Naamani, E.</u>; Gopal, A.; Ide, M.; Osaka, I.; Saeki, A. Exploring Alkyl Chains in Benzobisthiazole-Naphthobisthiadiazole Polymers: Impact on Solar Cell Performance, Crystalline Structures, and Optoelectronics. *ACS Appl. Mater. Interfaces* **2017**, *9*, 37702-37711.

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