Donor-Acceptor Oligomers and Polymers Composed of Benzothiadiazole and 3-Hexylthiophene: Effect of Chain Length and Regioregularity

Jintu Wang,^a Huaiying Ye,^a Hongjiao Li,^a Chongyu Mei,^{*,a} Jun Ling,^b Weishi Li,^{*,a} and Zhiquan Shen^b

 ^a Laboratory of Organic Functional Materials and Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China
 ^b Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China

A series of donor-acceptor oligomer **OBTTh**_n (n=1-7) and polymer **PBTTh**₁ and **PBTTh**₂ composed of alternative 2,1,3-benzothiadiazole and 3-hexylthiophene have been designed and synthesized for the purpose of investigation on the effect of chain length and side-chain regioregularity on their basic properties and photovoltaic performance. In the **OBTTh_n**oligomers and**PBTTh₁**polymer, all the hexyl side chains on thienyl units orient to-</sub>ward the same direction. Upon elongation of the chain length, the intramolecular charge transfer (ICT) absorption band in solution gradually redshifts from 398 nm for **OBTTh₁** to 505 nm for **OBTTh₇**, then to 512 nm for **PBTTh₁** polymer. Meanwhile, the HOMO energy level increases from -5.45 eV (OBTTh₁) to -5.08 eV (OBTTh₇) and -5.09 eV (**PBTTh**₁), and the LUMO energy level decreases from -3.11 eV (**OBTTh**₁) to -3.30 eV (**OBTTh**₇) and -3.33 eV (PBTTh₁), thus giving a smaller and smaller energy bandgap for higher oligomers and polymers. Theoretical calculation suggests straight line-like backbone geometry for this series of oligomers and polymer. On the other hand, polymer PBTTh₂ possesses a different side-chain regioregularity, in which every two neighbor hexyl side chains are arranged in different orienting direction. It is theoretically suggested to have curved line-like backbone geometry. In solution, it shows similar photophysical and electrochemical properties as PBTTh₁. However in film state, it displays a less redshift in the ICT band as refer to that in solution than PBTTh₁. In combination with [6,6]-phenyl-C₆₁-butyric acid methyl ester (**PC₆₁BM**), these oligomers and polymers were used as donor material to fabricate organic bulk heterojunction solar cells. Again, chain length-dependent device photovoltaic performance was observed. The device based on **OBTTh₄** showed a power conversion efficiency of 0.16%, while it increased to 0.36% and 0.49% for the devices based on **OBTTh**₆ and **PBTTh**₁, respectively. However, the side-chain regioregularity has less influence on the device photovoltaic output since the device based on PBTTh₂ displayed an efficiency of 0.52%, comparable to that of PBTTh₁.

Keywords conjugated polymers, organic solar cells, regioregularity, donor-acceptor, oligomers

Introduction

Conjugated polymers including donor-acceptor (D-A) copolymers have attracted significant attention due to their one-dimensional π -extended backbones, which endow them outstanding photophysical and photochemical properties and a wide range of applications in opto- and electronic devices.^[1] The backbone of D-A copolymers is composed of alternative electron-rich and electron-deficient π -conjugated moieties. This specific structural feature generally narrows the polymer bandgap, enables a wide light absorption spectrum extending into far visible and even near infrared region, and thus affords a better solar spectral coverage than homopoly-

mers, such as polythiophenes and poly(phenylenevinylene)s. In addition, the combination of D and A units benefits to tune energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These advantages have raised extensive investigations on D-A copolymers for organic photovoltaics (OPVs) in the past decades. So far, a huge number of D-A copolymers have been designed and developed,^[2] some of which show promising photovoltaic properties with a power conversion efficiency (PCE) over 7%.^[3] However, the most reported works focused only on polymer systems, which are generally a mixture of homologues and have issues of batchdependent average molecular weight and polydispersity

^{*} E-mail: meichy@sioc.ac.cn (C.Y.M.), liws@mail.sioc.ac.cn (W.S.L.); Tel. & Fax: 0086-021-54925381 Received July 4, 2013; accepted August 13, 2013; published online XXXX, 2013. Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201300519 or from the author.

(PDI). Therefore, the basic structure-property relationship for most D-A copolymers remains unclear, which hampers the fundamental understanding of the origination and influence factors for their photovoltaic performance. Since oligomers have a definite chemical structure and chain length, thus enabling an easy correlation with their properties, oligomer approaching is a good way to address the above issue. With this in mind, we are motivated recently to explore D-A oligomers and to systematically study their chain length-dependent photovoltaic properties.

In this work, we are focusing on a family of D-A oligomers (**OBTTh**_{*n*}, n=1-7) composed of 2,1,3-benzothiadiazole (BT) and 3-hexylthiophene (Th), as shown in Figure 1. BT is a famous electron-deficient unit and has been applied in the synthesis of a variety of D-A copolymers.^[2c,4] For example, the first D-A copolymer for OPVs reported by Janssen et al. in 2001 is composed of pyrrole, thiophene and BT.^[5] In 2003, Anderson and coworkers developed PFDTBT copolymer based on fluorene, thiophene and BT, and demonstrated an impressing large open-circuit voltage (V_{OC}) around 1 V.^[6] Getting clues from **PFDTBT**, several analogue D-A copolymers have been designed by using other similar units, like carbazole,^[7] dibenzosilole,^[8] germa-fluorene,^[9] and dithienopyrrole,^[10] to replace fluorene unit, some of which have shown outstanding photovoltaic properties. In addition to PFDTBT and its analogues, other famous BT-containing D-A copolymers

include those copolymerized with C-^[11] or Si-bridged dithiophenes,^[12] or ladder-type electron-donating units.^[13] For oligothiophenes, dimer to octamer have been reported to pair with **BT** for construction of D-A copolymers.^[14] An outstanding work was done by Chen and coworkers, who synthesized BT-quaterthiophene copolymers and achieved a PCE of 6.26%.^[15] In our work, we chose a very simple donor unit, 3-hexylthiophene, to cooperate with **BT**. Either polymer or oligomer with such simple alternative **BT** and thiophene structure has not yet been reported.

In addition to π -conjugated skeleton, we also pay special attention to the orientation of the side chain of the thiophene units in this work. Since just one hexyl chain is attached to the 3-position of the thiophene ring, the different orientation of these alkyl tails in the polymer/oligomer backbone will produce different regioregularity. It was reported by Kim et al. in 2006 that the side-chain regioregularity has great impact on photovoltaic performance of poly(3-hexylthiophene) (P3HT).^[16] They found the devices based on P3HT having regioregularity of 95.2% exhibited a PCE of 2.4%, which was further increased to 4.4% after optimization. In contrast, the devices based on P3HT having a slightly smaller regioregularity (93%) showed a PCE of 1.8%. The PCE further decreased to 0.7% when the regioregularity was 90.7%. They believed that **P3HT** with high regioregularity can easily form regular and tight π - π stacking structure in film, which could



Figure 1 Chemical structures of $OBTTh_n$ (n=1-7) D-A oligomers and $PBTTh_1$ and $PBTTh_2$ polymers. $OBTTh_7$ is shown as an example for regionegular oligomers.

afford good hole mobility.^[17] However, Fréchet *et al.* proved later that the devices based on three **P3HT**s having regioregularity of 96%, 90% and 86% respectively, outputted similar PCE values (3.8% - 3.9%) after device optimization individually.^[18] They further demonstrated that the devices using lower regioregular **P3HT** had better thermal stability. These conflict results indicate that the real impact of side-chain regioregularity on OPV performance is still ambiguous even for well-studied **P3HT**. As for D-A copolymers, to the best of our knowledge, there is no precedent example to study the effect of side-chain regioregularity.

In combination of the above two aspects, we report here the synthesis, characterization and properties of D-A oligomers (**OBTTh**_{*n*}, n=1-7) and two polymers (PBTTh₁ and PBTTh₂) having different side-chain regioregularity (Figure 1). In $OBTTh_n$ and $PBTTh_1$, all neighboring **BT-Th** units are linked by a head-to-tail style, thus making all the hexyl side chains orienting toward the same direction. While, **PBTTh₂** is another regioregular polymer but having completely different linkage patterns between the neighboring **BT-Th** units (head-to-head or tail-to-tail styles). Thus, in **PBTTh**₂, every two neighbor hexyl side chains are arranged in different orientation direction. Studies revealed that their optical, electrochemical, and photovoltaic properties are highly dependent on their chain length, but not on the side-chain regioregularity.

Experimental

Tetrahydrofuran (THF) and ethyl ether were distilled over sodium/benzophenone. *N*,*N*-Dimethylformamide (DMF) was distilled over CaH₂ under reduced pressure. Other reagents were used as received without further purification unless stated otherwise. Sodium 4-hexyl-2-thienylboronate,^[19] 4-bromo-2,1,3-benzothiadiazole,^[20] and 4,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2,1,3-benzothiadiazole (**B-BT-B**)^[21] were prepared via literature methods.

¹H NMR spectra were recorded on a Varian Mercury spectrometer operated at 300 MHz using deuterated solvents and tetramethyl silane (TMS) as an internal reference. Matrix-assisted laser deionization time-offlight (MALDI-TOF) mass spectroscopy was carried out on a Shimadzu Biotech Axima Performance mass spectrometer using dithranol or α -cyano-4-hydroxycinnamic acid (CHCA) as a matrix. Gel permeation chromatography (GPC) was carried out on a Waters 1515 HPLC instrument equipped with a Waters 2489 UV detector, using THF as an eluent. The molecular weight and PDI were calculated based on polystyrene standards. Recycling preparative size-exclusion chromatography (SEC) was performed with CHCl₃ as an eluent using JAIGEL 1H and 2.5H on a JAI model LC-9201 recycling HPLC system equipped with a JASCO model MD-2010 variable-wavelength UV-vis detector. UV-vis absorption spectroscopy was performed on a Hitachi U-3310 spectrophotometer at room temperature. Cyclic voltammetric (CV) measurements were performed in CH₂Cl₂ with a sample concentration of 0.1 mmol•L⁻¹ on a CHI 660C instrument using a three-electrode cell with a glassy carbon as working electrode, a platinum wire as counter electrode, and Hg/Hg₂Cl₂ (SCE) as reference electrode. 0.1 mol•L⁻¹ Bu₄NPF₆ was used as electrolyte and the scan rate was 100 mV•min⁻¹. Atomic force microscopy (AFM) was performed on a Veeco Nanoscope IIIa Multimode apparatus by tapping mode with a silicon tip.

Synthesis of 4-bromo-7-(4-hexylthiophen-2-yl)-2,1,3benzothiadiazole (Br-BTTh)

A mixture of sodium 4-hexyl-2-thienylboronate (1.00 g, 4.0 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (4.50 g, 15.3 mmol), Na₂CO₃ aqueous solution (2 mol• L^{-1} , 6 mL), and THF (75 mL) was subjected to thoroughly degassing by freeze-pump-thaw cycle three times, and then added with $Pd(PPh_3)_4$ (0.136 g, 0.12 mmol). After degas again by freeze-pump-thaw cycle three times, the reaction mixture was stirred and refluxed overnight, followed by extraction with CH₂Cl₂ several times. The organic phases were combined, washed with water, and dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was subjected to silica columnar chromatography using CH₂Cl₂/petroleum ether (1/3, V/V) as an eluent, affording 0.582 g **Br-BTTh** as yellow solid in a yield of 38%. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta$: 7.96 (s, 1H), 7.84 (d, J=7.8 Hz, 1H), 7.70 (d, J=7.8 Hz, 1H), 7.07 (s, 1H), 2.69 (t, J=7.8 Hz, 2H), 1.75-1.63 (m, 2H), 1.45-1.28 (m, 6H), 0.90 (t. J = 6.9 Hz. 3H).

Synthesis of 4-(4-hexylthiophen-2-yl)-7-(boronic acid)-2,1,3-benzothiadiazole (B-BTTh)

A mixture of **Br-BTTh** (0.525 g, 1.38 mmol), bis(pinacolato) diboron (0.412 g, 1.62 mmol), PdCl₂(dppf)•CH₂Cl₂ (0.118 g, 0.138 mmol), and KOAc (0.387 g, 3.94 mmol) in 1,4-dioxane (15 mL) was thoroughly degased by freeze-pump-thaw cycle several times. After stirring at 80 °C for 2 h, the reaction mixture was extracted with CH₂Cl₂ several times. The combined organic phases were washed with water and dried over anhydrous MgSO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was subjected to silica columnar chromatography using CH_2Cl_2 /petroleum ether (1/3, V/V) as an eluent, affording 0.366 g product as a form of **B-BTTh** in a yield of 77% due to the hydrolysis by the acidic silica gel during the column chromatography. ¹H NMR (300 MHz, $CDCl_3$) δ : 8.22 (d, J=6.0 Hz, 1H), 8.06 (s, 1H), 7.90 (d, J=6.0 Hz, 1H), 7.10 (s, 1H), 6.35 (s, 2H), 2.75-2.64 (m, 2H), 1.71–1.67 (m, 2H), 1.40–1.30 (m, 6H), 0.90 (t, J = 6.0 Hz, 3 H).

Synthesis of 4-(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (OBTTh₁)

A mixture of 4-bromo-2,1,3-benzothiadiazole (1.09 g, 5.07 mmol), sodium 4-hexyl-2-thienylboronate (2.31 g, 9.16 mmol), Pd(PPh₃)₄ (0.184 g, 0.15 mmol), aqueous Na_2CO_3 solution (2 mol·L⁻¹, 7.7 mL, 15.4 mmol) and THF (25 mL) was degased thoroughly by freeze-pumpthaw cycle several times. After refluxing overnight, the reaction mixture was extracted with CH₂Cl₂ several times. The combined organic phases were washed with water and dried over anhydrous MgSO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was subjected to silica columnar chromatography using CH_2Cl_2 /petroleum ether (1/5, V/V) as an eluent, affording 1.16 g OBTTh₁ as oil in a yield of 76%. ¹H NMR (300 MHz, CDCl₃) δ: 7.97 (s, 1H), 7.89 (d, J=9.0 Hz, 1H), 7.80 (d, J=6.9 Hz, 1H), 7.61-7.56(m, 1H), 7.04 (s, 1H), 2.69 (t, J=7.7 Hz, 2H), 1.72-1.64 (m, 2H), 1.48 - 1.27 (m, 6H), 0.90 (t, J = 6.4 Hz, 3H).

General procedure for synthesis of $OBTTh_{n-1}$ -Br $(n \ge 2)$

The THF solution of *N*-bromosuccinimide (NBS) was dropwise added into a solution of **OBTTh**_{*n*-1} ($n \ge 2$) in anhydrous THF under ice/water bath within 10 min. After stirring overnight, the reaction mixture was concentrated under reduced pressure. The residue was subjected to silica columnar chromatography to separate the corresponding **OBTTh**_{*n*-1}-**Br** ($n \ge 2$) product.

General procedure for synthesis of OBTTh_n $(n \ge 2)$

A mixture of **OBTTh**_{*n*-1}-**Br** $(n \ge 2)$, **B-BTTh**, Pd(PPh₃)₄, aqueous Na₂CO₃ solution and THF was degased thoroughly by freeze-pump-thaw cycle several times. After refluxing overnight, the reaction mixture was extracted with CH₂Cl₂ several times. The combined organic phases were washed with water and dried over anhydrous MgSO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was subjected to silica columnar chromatography to separate the corresponding **OBTTh**_{*n*} $(n \ge 2)$ product.

Synthesis of OBTTh₁-Br

OBTTh₁-Br was prepared with **OBTTh₁** (0.53 g, 1.76 mmol), NBS (0.31 g, 1.72 mmol) in anhydrous THF (25 mL) following the general procedure to afford 0.59 g in a yield of 88%. ¹H NMR (300 MHz, CDCl₃) δ : 7.96 (s, 1H), 7.84 (d, *J*=7.7 Hz, 1H), 7.69 (d, *J*=7.7 Hz, 1H), 7.07 (s, 1H), 2.69 (t, *J*=7.5 Hz, 2H), 1.73-1.68 (m, 2H), 1.45-1.28 (m, 6H), 0.90 (t, *J*=6.9 Hz, 3H).

Synthesis of OBTTh₂

OBTTh₂ was prepared with **OBTTh**₁-**Br** (1.02 g, 2.69 mmol), **B-BTTh** (1.22 g, 3.52 mmol), Pd(PPh₃)₄ (0.157 g, 0.134 mmol), aqueous Na₂CO₃ solution (2 mol·L⁻¹, 4.1 mL, 8.20 mmol) and THF (20 mL) following the general procedure to afford 1.24 g in a yield

of 76%. ¹H NMR (300 MHz, CDCl₃) δ : 8.13 (s, 1H), 8.04 (s, 1H), 7.95–7.91 (m, 3H), 7.71 (d, *J*=9 Hz, 1H), 7.64–7.61 (m, 1H), 7.08 (s, 1H), 2.75–2.67 (m, 4H), 1.76–1.69 (m, 4H), 1.35–1.23 (m, 12H), 0.91 (t, *J*=6 Hz, 3H), 0.82 (t, *J*=6 Hz, 3H); MS (MALDI-TOF) *m/z* (%): 602.0 (M⁺, 100). Anal. calcd for C₃₂H₃₄N₄S₄: C 63.75, H 5.68, N 9.29, S 21.27; found C 64.40, H 6.36, N 7.98, S 18.10.

Synthesis of OBTTh₂-Br

OBTTh₂-Br was prepared with **OBTTh₂** (1.08 g, 1.79 mmol), NBS (0.33 g, 1.83 mmol) in anhydrous THF (25 mL) following the general procedure to afford 1.21 g in a yield of 99%. ¹H NMR (300 MHz, CDCl₃) δ : 8.12 (s, 1H), 7.97–7.81 (m, 4H), 7.74–7.59 (m, 2H), 2.73 (d, *J*=7.5 Hz, 2H), 2.66 (d, *J*=7.5 Hz, 2H), 1.71 –1.69 (m, 4H), 1.43–1.29 (m, 12H), 0.91 (t, *J*=7.5 Hz, 3H), 0.85 (t, *J*=7.5 Hz, 3H).

Synthesis of OBTTh₃

OBTTh₃ was prepared with **OBTTh₂-Br** (1.21 g, 1.77 mmol), **B-BTTh** (0.84 g, 2.43 mmol), Pd(PPh₃)₄ (0.10 g, 0.086 mmol), Na₂CO₃ aqueous solution (2 mol•L⁻¹, 2.7 mL, 5.40 mmol) and THF (11 mL) following the general procedure to afford 1.22 g in a yield of 79%. ¹H NMR (300 MHz, CDCl₃) δ : 8.18 (s, 1H), 8.14 (s, 1H), 8.05 (s, 1H), 8.00 (d, *J*=7.2 Hz, 1H), 7.95–7.92 (m, 3H), 7.73 (dd, *J*=7.5, 2.2 Hz, 2H), 7.67–7.62 (m, 1H), 7.09 (s, 1H), 2.80–2.71 (m, 6H), 1.73–1.60 (m, 6H), 1.40–1.18 (m, 18H), 0.92–0.83 (m, 9H); MS (MALDI-TOF) *m/z* (%): 902.1 (M⁺, 100). Anal. calcd for C₄₈H₅₀N₆S₆: C 63.82, H 5.58, N 9.30, S 21.30; found C 64.15, H 5.76, N 9.05, S 20.92.

Synthesis of OBTTh₃-Br

OBTTh₃-Br was prepared with **OBTTh₃** (1.08 g, 1.20 mmol), NBS (0.23 g, 1.28 mmol) in anhydrous THF (25 mL) following the general procedure to afford 1.03 g in a yield of 88%. ¹H NMR (300 MHz, CDCl₃) δ : 8.18 (s, 1H), 8.14 (s, 1H), 8.01 (d, *J*=7.5 Hz, 1H), 7.96 -7.90 (m, 2H), 7.89-7.83 (m, 2H), 7.73 (dd, *J*=7.6, 3.5 Hz, 2H), 7.67-7.62 (m, 1H), 2.76 (t, *J*=7.5 Hz, 4H), 2.68 (t, *J*=7.5 Hz, 2H), 1.76-1.67 (m, 6H), 1.41 -1.19 (m, 18H), 0.94-0.81(m, 9H).

Synthesis of OBTTh₄

OBTTh₄ was prepared with **OBTTh**₃-**Br** (1.25 g, 1.27 mmol), **B-BTTh** (0.60 g, 1.73 mmol), Pd(PPh₃)₄ (0.068 g, 0.059 mmol), aqueous Na₂CO₃ solution (2 mol·L⁻¹, 2.0 mL, 4.0 mmol) and THF (8 mL) following the general procedure to afford 1.16 g in a yield of 76%. ¹H NMR (300 MHz, CDCl₃) δ : 8.20 (s, 2H), 8.14 (s, 1H), 8.05 (s, 1H), 8.03 (s, 1H), 8.01 (s, 1H), 7.94–7.92 (m, 3H), 7.77–7.73 (m, 3H), 7.76–7.62 (m, 1H), 7.09 (s, 1H), 2.80–2.72 (m, 8H), 1.73–1.69 (m, 8H), 1.35–1.23 (m, 24H), 0.92 (t, J=6 Hz, 3H), 0.86–0.82 (m, 9H); MS (MALDI-TOF) *m*/*z* (%): 1202.3 (M⁺, 100). Anal. calcd for C₆₄H₆₆N₈S₈: C 63.86, H 5.53, N 9.31, S

Donor-Acceptor Oligomers and Polymers Composed of Benzothiadiazole and 3-Hexylthiophene

21.31; found C 63.97, H 5.49, N 9.29, S 21.90.

Synthesis of OBTTh₄-Br

OBTTh₄-Br was prepared with **OBTTh₄** (1.08 g, 0.90 mmol), NBS (0.18 g, 1.00 mmol) in anhydrous THF (25 mL) following the general procedure to afford 1.03 g in a yield of 89%. ¹H NMR (300 MHz, CDCl₃) δ : 8.19 (s, 2H), 8.14 (s, 1H), 8.04 (s, 1H), 8.02 (s, 1H), 7.95-7.84 (m, 4H), 7.77-7.71 (m, 3H), 7.64-7.62 (m, 1H), 2.80-2.75 (m, 6H), 2.67 (t, *J*=7.2 Hz, 2H), 1.76 -1.68 (m, 8H), 1.35-1.24 (m, 24H), 0.92 (t, *J*=6.9 Hz, 3H), 0.86-0.82 (m, 9H).

Synthesis of OBTTh₅

OBTTh₅ was prepared with **OBTTh**₄-**Br** (1.03 g, 0.80 mmol), **B-BTTh** (0.36 g, 1.04 mmol), Pd(PPh₃)₄ (0.047 g, 0.041 mmol), aqueous Na₂CO₃ solution (2 mol•L⁻¹, 1.2 mL, 2.4 mmol) and THF (8 mL) following the general procedure to afford 0.99 g in a yield of 82%. ¹H NMR (300 MHz, CDCl₃) δ : 8.20 (s, 3H), 8.14 (s, 1H), 8.07–7.98 (m, 4H), 7.97–7.88 (m, 3H), 7.78–7.72 (m, 4H), 7.67–7.62 (m, 1H), 7.09 (s, 1H), 2.87–2.70 (m, 10H), 1.78–1.68 (m, 10H), 1.37–1.19 (m, 30H), 0.90–0.80 (m, 15H); MS (MALDI-TOF) *m/z* (%): 1503.6 (M⁺, 100). Anal. calcd for C₈₀H₈₂N₁₀S₁₀: C 63.88, H 5.49, N 9.31, S 21.32; found C 64.03, H 5.49, N 9.18, S 21.20.

Synthesis of OBTTh₅-Br

OBTTh₅-Br was prepared with **OBTTh**₅ (0.99 g, 0.66 mmol), NBS (0.13 g, 0.72 mmol) in anhydrous THF (15 mL) following the general procedure to afford 0.96 g in a yield of 92%. ¹H NMR (300 MHz, CDCl₃) δ : 8.19 (s, 3H), 8.14 (s, 1H), 8.03–8.00 (m, 3H), 7.95–7.91 (m, 2H), 7.88–7.84 (m, 2H), 7.77–7.71 (m, 4H), 7.67–7.62 (m, 1H), 2.81–2.74 (m, 8H), 2.67 (t, *J*=7.5 Hz, 2H), 1.77–1.67 (m, 10H), 1.38–1.18 (m, 30H), 0.92–0.81 (m, 15H).

Synthesis of OBTTh₆

OBTTh₆ was prepared with **OBTTh**₅-**Br** (0.96 g, 0.61 mmol), **B-BTTh** (0.37 g, 1.07 mmol), Pd(PPh₃)₄ (0.047 g, 0.041 mmol), aqueous Na₂CO₃ solution (2 mol·L⁻¹, 0.8 mL, 1.6 mmol) and THF (8 mL) following the general procedure to afford 0.94 g in a yield of 86%. ¹H NMR (300 MHz, CDCl₃) δ : 8.21 (s, 2H), 8.20 (s, 2H), 8.14 (s, 1H), 8.08-8.00 (m, 5H), 7.98-7.89 (m, 3H), 7.77-7.73 (m, 5H), 7.67-7.62 (m, 1H), 7.09 (s, 1H), 2.81-2.71 (m, 12H), 1.78-1.68 (m, 12H), 1.39-1.23 (m, 36H), 0.92-0.82 (m, 18H); MS (MALDI-TOF) *m*/*z* (%): 1804.0 (M⁺, 100). Anal. calcd for C₉₆H₉₈-N₁₂S₁₂: C 63.89, H 5.47, N 9.31, S 21.32; found C 63.83, H 5.44, N 9.28, S 20.70.

Synthesis of OBTTh₆-Br

OBTTh₆-Br was prepared with **OBTTh₆** (0.67 g, 0.37 mmol), NBS (0.07 g, 0.39 mmol) in anhydrous THF (10 mL) following the general procedure to afford 0.66 g in a yield of 94%. ¹H NMR (300 MHz, CDCl₃) δ :

8.25-8.17 (m, 4H), 8.24 (s, 1H), 8.03-8.00 (m, 4H), 7.95-7.91 (m, 2H), 7.88-7.84 (m, 2H), 7.77-7.71 (m, 5H), 7.67-7.61 (m, 1H), 2.81-2.74 (m, 10H), 2.67 (t, J=7.5 Hz, 2H), 1.77-1.68 (m, 12H), 1.40-1.15 (m, 36H), 0.90-0.82 (m, 18H).

Synthesis of OBTTh₇

OBTTh₇ was prepared with **OBTTh**₆-**Br** (0.66 g, 0.35 mmol), **B-BTTh** (0.18 g, 0.52 mmol), Pd(PPh₃)₄ (0.047 g, 0.041 mmol), aqueous Na₂CO₃ solution (2 mol·L⁻¹, 0.4 mL, 0.8 mmol) and THF (6 mL) following the general procedure to afford 0.68 g in a yield of 92%. ¹H NMR (300 MHz, CDCl₃) δ : 8.21–8.20 (m, 5H), 8.14 (s, 1H), 8.08–7.98 (m, 6H), 7.95–7.91 (m, 3H), 7.82–7.70 (m, 6H), 7.67–7.62 (m, 1H), 7.09 (s, 1H), 2.82–2.70 (m, 14H), 1.78–1.69 (m, 14H), 1.38–1.17 (m, 42H), 0.96–0.75 (m, 21H); MS (MALDI-TOF) *m/z* (%): 2105.3 (M⁺, 100). Anal. calcd for C₁₁₂H₁₁₄N₁₄S₁₄: C 63.90, H 5.46, N 9.32, S 21.32; found C 63.40, H 5.50, N 8.81, S 20.13.

Synthesis of 4-(4-hexylthiophen-5-bromo-2-yl)-7-(boronic acid)-2,1,3-benzothiadiazole (B-BTTh-Br)

To the solution of **B-BTTh** (0.32 g, 0.92 mmol) in THF (20 mL) was added the solution of NBS (0.17 g, 0.94 mmol) in THF (10 mL) under ice/water bath. After stirring at room temperature overnight in darkness, the reaction mixture was concentrated by evaporating off solvents under reduced pressure. The residue was subjected to silica columnar chromatography using CH₂Cl₂/ petroleum ether (1/4, *V*/*V*) then CH₂Cl₂/methanol (9/1, *V*/*V*) as eluents, affording 0.37 g **B-BTTh-Br** in a yield of 96%. ¹H NMR (300 MHz, CDCl₃) δ : 8.22 (d, *J*=9.0 Hz, 1H), 7.86 (s, 1H), 7.83 (d, *J*=9.0 Hz, 1H), 6.28 (s, 2H), 2.65 (t, *J*=9.0 Hz, 2H), 1.73–1.63 (m, 2H), 1.46 – 1.30 (m, 6H), 0.90 (t, *J*=7.5 Hz, 3H).

Synthesis of polymer PBTTh₁

Monomer B-BTTh-Br (374 mg, 0.88 mmol) and Pd(PPh₃)₄ (55 mg, 0.048 mmol) were added into a mixture of toluene (20 mL) and 20% aqueous Et₄NOH (6 mL). The reaction mixture was subjected to thoroughly degassing by freeze-pump-thaw cycles and then refluxed under vigorous stirring for 72 h under Ar. Afterward, the reaction mixture was added with B-BTTh (0.0427 g, 0.12 mmol) and 6 h later with OBTTh₁-Br (0.0641 g, 0.17 mmol) as monofunctional end-capping reagents. After further refluxing for 6 h, the reaction mixture was cooled down to room temperature and extracted with chloroform for three times. The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered, and evaporated off solvents to dryness. The solid residue was subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform. The chloroform fraction was evaporated to dryness and further dried in vacuum for 1 d, affording 0.21 g **PBTTh₁** product as red-brown solid with a yield of 80%.

5

Synthesis of 4,7-bis-(3-hexyl-thiophen-2-yl)-2,1,3benzothiadiazole (ThBTTh)

The mixture of 2-bromo-3-hexylthiophene (0.87g, 3.52 mmol), B-BT-B (0.70 g, 1.80 mmol), Pd(PPh₃)₄ (65 mg, 0.056 mmol), aqueous Na₂CO₃ solution (2 mol•L⁻¹, 2.6 mL, 5.2 mmol), and THF (20 mL) was degased thoroughly by freeze-pump-thaw cycles and refluxed overnight under Ar. After cooled to room temperature, the mixture was extracted with CH₂Cl₂ for three times. The combined organic phases were washed with water, dried over anhydrous Na₂SO₄, filtered and concentrated. The residue was subjected to silica columnar chromatography using dichloromethane/ petroleum ether (1/9, V/V) as an eluent. The separated crude product was further purified by preparative SEC, affording 0.39 g of ThBTTh in a yield of 32%. ¹H NMR (300 MHz, CDCl₃) δ : 7.65 (s, 2H), 7.44 (d, J=5.2Hz, 2H), 7.11 (d, J=5.2 Hz, 2H), 2.66 (t, J=7.5 Hz, 4H), 1.70–1.58 (m, 4H), 1.31–1.10 (m, 12H), 0.93– 0.70 (m, 6H).

Synthesis of 4,7-bis-(3-hexyl-thiophen-5-bromo-2-yl)-2,1,3-benzothiadiazole (Br-ThBTTh-Br)

The solution of NBS (0.39 g, 2.17 mmol) in THF (10 mL) was dropwise added into a solution of **ThBTTh** (0.39 g, 0.83 mmol) in anhydrous THF (20 mL) in darkness under ice/water bath within 10 min. After stirring overnight, the solvent was removed under reduced pressure. The residue was subjected to silica columnar chromatography using dichloromethane/petroleum ether (1/9, *V/V*) as an eluent affording 0.47 g of desired product in a yield of 90%. ¹H NMR (300 MHz, CDCl₃) δ : 7.60 (s, 2H), 7.06 (s, 2H), 2.61 (t, *J*=7.5 Hz, 4H), 2.68 –2.55 (m, 4H), 1.31–1.10 (m, 12H), 0.82 (t, *J*=7.5 Hz, 6H).

Synthesis of polymer PBTTh₂

Monomer Br-ThBTTh-Br (63.4 mg, 0.10 mmol), monomer **B-BT-B** (40.2 mg, 0.10 mmol), and Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) were added into a mixture of toluene (5 mL) and 20% aqueous Et₄NOH solution (0.6 mL). The reaction mixture was subjected to thoroughly degassing by freeze-pump-thaw cycles and then refluxed under vigorous stirring for 7 d under Ar. Afterward, the reaction mixture was added with **B-BTTh** (6.4 mg, 0.018 mmol) and 6 h later with 2-bromo-3-hexylthiophene (3.6 µL, 0.018 mmol) as monofunctional end-capping reagents. After further refluxing for 6 h, the reaction mixture was cooled down to room temperature and extracted with chloroform for three times. The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered, and evaporated off solvents to dryness. The solid residue was subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform. The chloroform fraction was evaporated to dryness and further dried in vacuum for 1 d, affording 34.3 mg PBTTh₂ product as red-brown solid with a vield of 57%.

Fabrication and characterization of organic photovoltaic devices

The solar cell devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/Ca/Al. A thin layer of PEDOT:PSS (Heraeus Clevios P VP. Al 4083) was spin-coated on top of well cleaned ITO glass at 4000 r/min and baked at 120 °C for 15 min, affording a thickness of 30 nm. After transfer into a N₂-filled glove box, the active layer was spin-coated from a chlorobenzene solution of a mixture of the test oligomer or polymer and PC₆₁BM (Lumitec LT-8905) at 2000 r/min. Finally, 10 nm-thick Ca layer and a 100 nm-thick Al layer were subsequently thermally deposited on the top of the active layer under high vacuum ($<10^{-5}$ mbar) through a shadow mask. The effective cell area is 7 mm². Laver thickness was measured on a Veeco Dektak 150 profilometer. Current density-voltage (J-V) curves were recorded with a Keithley 2420 source meter. Photocurrent was acquired upon irradiation using an AAA solar simulator (Oriel 94043A, 450 W) with AM 1.5G filter. The intensity was adjusted to be 100 mW•cm⁻² under the calibration with a NREL-certified standard silicon cell (Orial reference cell 91150). External quantum efficiency (EQE) was detected with a 75 W Xe lamp, Oriel monochromator 74125, optical chopper, lock-in amplifier and a NREL-calibrated crystalline silicon cell.

Results and Discussion

Synthesis and characterization

The synthesis of regionegular **OBTTh**_n oligomers followed an iterative growing approach, as shown in Scheme 1. During this approach, compound **B-BTTh** having a boron acid functionality at 7-position of **BT** serves as a growing monomer and plays an important role. For the synthesis of this growing monomer, Br-BTTh is a key precursor and was prepared in a yield of 38% by the Suzuki coupling between sodium 4-hexyl-2-thienylboronate and 4 molar equivalent of 4,7-dibromo-2,1,3-benzo-thiadiazole. After reacting with bis(pinacolato)diboron in the presence of Pd(dppf)Cl₂ in 1,4-dioxane, **Br-BTTh** was converted into a pinacol boronate compound, which was further hydrolyzed during the silica column chromatography into **B-BTTh** in a yield of 77% based on **Br-BTTh**. Meanwhile, the first oligomer (OBTTh₁) was obtained though Suzuki coupling of 4-bromo-2,1,3-benzothiadiazole with sodium 4-hexyl-2-thienylboronate. With the growing monomer (**B-BTTh**) and the first oligomer (OBTTh₁) on hand, the iterative process was started for synthesis of longer oligomers. Firstly, **OBTTh₁** was brominated with NBS, affording an intermediate compound **OBTTh₁-Br**. Subsequently, the Suzuki coupling was carried out between OBTTh₁-Br and the growing monomer B-BTTh, producing OBTTh₂. The yield of **OBTTh₂** for the above two steps was 67%. Following the same way, higher oligomers **OBTTh**_n (n=3-7)





were finally prepared from their one-repeating unit-less oligomers in a moderate to good yield (65%-85%). Here, the bromination of all **OBTTh**_n oligomers with NBS only took place on the 5-position of the end thienyl unit. This is another important point to achieve the successful iterative synthesis of **OBTTh**_n oligomers. The structure of all oligomers was unambiguously confirmed by ¹H NMR, MALDI-TOF mass spectroscopy, and elemental analysis.

Scheme 2 outlines the synthetic routes for **PBTTh₁** and **PBTTh₂** polymers. Polymer **PBTTh₁** with all side hexyl chains orienting the same direction was achieved by the Suzuki-coupling polymerization of an AB-type monomer, **B-BTTh-Br**. It was prepared in a yield of 96% by the bromination of **B-BTTh** with NBS. The polymerization of this AB-type monomer ensures the formation of the polymer with all neighboring **BT-Th** units linked by a head-to-tail style. The number-average

Scheme 2 Synthesis of PBTTh₁ and PBTTh₂ polymers

molecular weight (M_n) and PDI of the prepared **PBTTh**₁ were 89.0 kDa and 2.31, respectively, as determined by GPC using polystyrenes as standards. The synthesis of polymer **PBTTh₂** with alternative orienting side chains was a little complicated. Firstly, a diboronate-functionalized BT compound, B-BT-B, was subjected to Suzuki-coupling with 2-bromo-3-hexyl thiophene, affording **ThBTTh**. Then, it was brominated to give monomer Br-ThBTTh-Br. The final polymer PBTTh₂ was produced in a yield of 57% via Suzuki-coupling copolymerization between Br-ThBTTh-Br and B-BT-B monomers. The number-average molecular weight (M_n) and PDI were 7.5 kDa and 1.73 refer to polystyrene standards for the so-produced PBTTh₂, quite different from those of **PBTTh**₁. Since the molecular weight was reported to have great impact on polymer photovoltaic performance,^[22] it is not applicable to directly use the so-prepared polymers (**PBTTh**₁ and **PBTTh**₂) to study



7

the effect of side-chain regioregularity on their basic and photovoltaic properties. To ensure a comparison basis, the two polymers were subjected to preparative SEC and the fractions with the same elution time were collected. The final polymers used for property study and organic solar cells have M_n and PDI of 5.05 kDa and 1.86 for **PBTTh₁**, while 4.66 kDa and 1.16 for **PBTTh₂**.

Photophysical properties

The UV-vis spectroscopy of all oligomers and polymers were carried out in both CHCl₃ solution and film state (Figure 2). The data were summarized in Table 1. In CHCl₃ solution, all oligomers except **OBTTh₁** and polymers show two distinguished absorption bands in the range of 300-350 and 400-600 nm. The former band originates from the π - π * transition of their conjugated backbones, while the latter is assignable to intramolecular charge transfer (ICT) absorption between **BT** and 3-hexylthiophene units. The apex position for the both peaks displays red-shift along with the elongation of the oligomer chain length. For example, **OBTTh₂** displays π - π * transition peak around 308 nm

and ICT peak around 449 nm. The position of the π - π * transition peak shifts to 312 nm for OBTTh₃, 314 nm for **OBTTh₄**, and 316 nm for **OBTTh₅**, **OBTTh₆**, and **OBTTh₇**. Meanwhile, the ICT peak changes to around 476 nm for OBTTh₃, 489 nm for OBTTh₄, 497 nm for OBTTh₅, 501 nm for OBTTh₆, and 505 nm for **OBTTh₇**. These observations suggest that the effective conjugated length becomes longer and longer when the number of repeating unit increases. It is also valuable to point out that chain length-dependent absorption redshift for ICT bands are larger than those for π - π * transition band. This implies that the ICT band is delocalized to a more extent through the backbone than π - π * transition band. For polymers, PBTTh₁ and PBTTh₂ display absorption bands at similar positions, around 320 nm for π - π * transition band and 512 nm for ICT peak. Since both polymers have similar molecular weight and polydispersity, the above fact suggests that the side-chain regioregularity does not interfere electron delocalization in the backbone. However, compared with those of the oligomers, these two peaks of the polymers exhibit further redshift, indicating the poly-



Figure 2 Normalized UV-vis absorption spectra of $OBTTh_n$ (n=1-7) oligomers and $PBTTh_1$ and $PBTTh_2$ polymers (a) in CHCl₃ solution and (b) in film state.

Table 1	Summary of	optical,	electrochemical	properties	and	theoretical	calculation	results	of	OBTTh _n	(n=1-7)	oligomers	and
PBTTh ₁ a	and PBTTh₂ po	olymers											

Oligomer/	$\lambda_{\rm max}/{\rm nm}$		1 /	$E_{\rm ox, onset}/{\rm V}$	$E_{\rm red, onset}/{ m V}$	HOMO/eV		LUMO/eV		E_{g}/eV		
Polymer	Solution Film		$-\lambda_{\text{onset}}/\text{nm}$			CV^{a}	calcd	CV^b	calcd	optica	l ^c CV	calcd
OBTTh ₁	398	_	_	1.05	-1.29	-5.45	-5.97	-3.11	-2.82	_	2.34	3.15
OBTTh ₂	308, 449	316, 468	574	0.95	-1.24	-5.35	-5.53	-3.16	-3.02	2.16	2.19	2.51
OBTTh ₃	312, 476	318, 501	618	0.82	-1.27	-5.22	-5.37	-3.13	-3.11	2.01	2.09	2.26
OBTTh ₄	314, 489	320, 522	642	0.75	-1.24	-5.15	-5.28	-3.16	-3.17	1.93	1.99	2.11
OBTTh ₅	316, 497	322, 528	657	0.72	-1.12	-5.12	-5.23	-3.28	-3.20	1.89	1.84	2.03
OBTTh ₆	316, 501	322, 532	661	0.70	-1.12	-5.10	-5.20	-3.28	-3.23	1.88	1.82	1.97
OBTTh ₇	316, 505	324, 536	664	0.68	-1.10	-5.08	-5.19	-3.30	-3.24	1.87	1.78	1.95
PBTTh ₁	318, 512	328, 560	700	0.69	-1.07	-5.09	-5.19 ^{<i>d</i>}	-3.33	-3.24^{d}	1.77	1.76	1.95 ^d
PBTTh ₂	320, 512	326, 548	685	0.67	-1.15	-5.07	-5.17^{e}	-3.25	-3.24^{e}	1.81	1.82	1.93 ^e

^{*a*} Estimated from the onset of oxidation potential in the CV measurement. ^{*b*} Estimated from the onset of reduction potential in the CV measurement. ^{*c*} Estimated from the onset of the absorption spectra in film state. ^{*d*} OBTTh₇ was used to represent PBTTh₁ for theoretical calculation. ^{*e*} A BT-Th heptamer having the same side-chain regioregularity as PBTTh₂ was used to represent PBTTh₂ for theoretical calculation.

mers have a longer effective conjugated length.

The onset of the film absorption spectrum can be used for the estimation of the material optical bandgap (E_g) following the equation: $E_g = 1240/\lambda_{onset}$. The results were included in Table 1. As expected, the bandgap gradually decreases upon increment of oligomer chain length, 2.16 eV for **OBTTh**₂, 2.01 eV for **OBTTh**₃, 1.93 eV for **OBTTh**₄, 1.89 eV for **OBTTh**₅, 1.88 eV for **OBTTh**₆, and 1.87 eV for **OBTTh**₇. The energy bandgap further decreased to 1.77 and 1.81 eV for polymers **PBTTh**₁ and **PBTTh**₂ respectively.

Electrochemical properties

The material redox properties were investigated by cyclic voltammetry (CV) in CH₂Cl₂ solution at room temperature with a conventional three electrode configuration consisting of a glassy carbon working electrode, a Pt wire counter electrode and an SCE (Hg/Hg₂Cl₂) reference electrode. The measurements were carried out with a sample concentration of 0.1 mmol•L⁻¹ in the presence of 0.1 mol•L⁻¹ Bu₄NPF₆ electrolyte under a scan rate of 100 mV•min⁻¹. The measured onset oxidation and reduction potentials of oligomer **OBTTh**_n (n=1-7) and polymer **PBTTh**₁ and **PBTTh₂** are listed in Table 1. From these data, the HOMO and LUMO energy levels can be estimated following equations: HOMO= $-(4.4 + E_{ox,onset})$ and LUMO $=-(4.4+E_{\text{red. onset}})$, since the energy level of SCE is 4.4 eV below vacuum. It is reasonable to observe that HOMO level increases while the LUMO level decreases with the number increment of the repeating units in the oligomers, making the electrochemical bandgap gradually become smaller and smaller. For polymers, no significant difference was observed for the oxidation potential between PBTTh₁ and PBTTh₂, thus giving a similar HOMO level for both polymers. But for reduction potential, **PBTTh₂** exhibited a 0.08 V-lower onset potential, affording a slightly higher LUMO and larger bandgap than **PBTTh**₁. As compared with optical values, all the electrochemical bandgaps for oligomers and polymers are in good consistence.

Theoretical studies

In order to theoretically understand the effect of chain length and the side-chain regioregularity on their basic properties, quantum chemical computations were performed on oligomer **OBTTh**_n (n=1-7) and an (**BT-Th**) heptamer with the same side-chain orientation pattern as **PBTTh**₂. Here, the pendant hexyl side chains were simplified as methyl units to save computational time due to the fact that the geometries and energies negligibly depend on the pendant alkyl groups.^[23,24] Geometry optimization of oligomers was carried out by a density functional theory (DFT) method at the B3LYP/6-31G(d) level. Vibrational frequencies at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level were used to characterize stationary points as minima, *i.e.* no imaginary frequencies. Energy was evaluated at the B3LYP/

6-311+G(d,p)//B3LYP/6-31G(d,p) level. All the calculations were performed using a Gaussian 03 program.^[25] This inexpensive calculation was successfully applied in previous studies on conjugated polymers.^[23,24]

Figure 3 displays the optimized HOMO and LUMO structures and the geometrical dihedral angles of **OBTTh₇** and **PBTTh₂**-like **BT-Th** heptamer. It is clear that the different side-chain orientation pattern greatly impacts the geometry of the backbone. A straight linelike geometry was obtained for OBTTh7, while a curved line-like shape for PBTTh₂-like heptamer. Due to just one head-to-tail linkage among the BT-Th repeating units in **OBTTh₇** backbone, the local environment for all **BT** rings is same, with one adjacent thienyl unit having a far away side chain and the other adjacent thienyl unit having a nearby side chain. In optimized geometry, these two thienyl units adopt a flipped orienting direction (parallel or antiparallel) as refer to the central **BT** ring. The thienyl unit having a far away side chain is almost in planar with BT, since the estimated dihedral angle for C-C-C is 174°. But for that having a nearby side chain, the dihedral angle for C-C-C between this thienyl unit and BT ring is around 31°, indicating the side chain has imposed a large steric hindrance. In contrast, there are two different kinds of BT rings in the structure of PBTTh₂-like Th-BT heptamer, one neighboring to two thienyl units having two far away side chains, the other neighboring to two thienyl units having two nearby side chains. Because of less steric hindrance coming from the far away side chains, the former **BT** rings are almost in planar with the two neighboring thienyl units. The two dihedral angles are 173° and 177°. But for the latter kind of **BT** rings, two dihedral angles both around 30° are suggested. Furthermore, the two neighboring thienyl units cannot



Figure 3 The optimized HOMO and LUMO structures of **OBTTh7** and a (**BT-Th**) heptamer having the same side-chain regioregularity of **PBTTh2**. The bottom figures show the dihedral angles of the oligomer backbones.

9

adopt the reverse direction as refer to the central **BT** rings, thus making the geometry of the backbone curved.

We also computed the chain length-dependent HOMO and LUMO energy level (Table 1). The changing tendency is consistent very well with that observed in the electrochemical measurement. When the chain length elongates, the HOMO energy level gradually increases while the LUMO decreases, giving a smaller and smaller energy bandgap for higher oligomers. It was reported that the energy bandgap is semiempirically proportional to the reciprocal of the number of repeating units and such linear relationship can be used for prediction of the effective conjugated length.^[26] Figure 4 plots all the energy bandgaps of $OBTTh_n$ obtained from different methods against 1/n and confirms their good linear relationship. From their linear projection, the polymer having infinite number of the repeating unit would have an energy gap of 1.76 eV based on the theoretically calculated E_{g} , or 1.73 eV based on optical E_{g} , or 1.77 eV based on electrochemical $E_{\rm g}$. We noted that there is no substantial difference between the electrochemically measured energy bandgaps of **OBTTh₇** and **PBTTh₁** and the estimated value for infinite polymer, indicating OBTTh₇ and polymer PBTTh₁ have sufficient chain length to achieve a good photovoltaic performance.



Figure 4 Plot of energy bandgap versus 1/n of OBTTh_n.

Although the computation suggests big different backbone geometry for **PBTTh**₁ and **PBTTh**₂, the calculated HOMO and LUMO structures are similar and have comparable energy level (Figure 3 and Table 1). This may be understandable when considering the fact that the twisting degree and the number of twisted dihedral angles are almost the same between **OBTTh**₇ and **PBTTh**₂-like **BT-Th** heptamer. However, the different backbone geometry would influence the chain packing structure in solid state, which is reflected by the less ICT red-shifts observed for the film absorption spectrum of **PBTTh**₂, as compared with that of **PBTTh**₁.

Photovoltaic properties

Organic solar cells (OSCs) with a structure of ITO/PEDOT:PSS/active layer/Ca/Al were used to in-

vestigate the photovoltaic properties of **OBTTh**_{*n*} (n=4 -7) oligomers and **PBTTh**₁ and **PBTTh**₂ polymers. The active layer was a bulk heterojunction film composed of the checked oligomer or polymer as donor and **PC**₆₁**BM** as acceptor. **OBTTh**₅ was first chosen to optimize device fabrication conditions. After checking the weight ratio of **OBTTh**₅ to **PC**₆₁**BM**, spin-coating rate, and the thermal anneal treatment, it was concluded that the film prepared by spin-coating a chlorobenzene solution containing a mixture of **OBTTh**₅ and **PC**₆₁**BM** in a weight ratio of 1/2 with a total concentration of 20 mg•mL⁻¹ at a rate of 2000 r/min was good for OSCs. Under such conditions, the thickness of the active layer was around 80 nm.

With the above optimized conditions, we fabricated the solar cells based on the blend of **OBTTh**_n (n=4-7), **PBTTh**₁, or **PBTTh**₂ with **PC**₆₁**BM** and characterized their current-voltage performance under the illustration of AM 1.5 G with a light density of 100 mW•cm⁻² (Figure 5a). Their device parameters, such as V_{OC} , short-circuit current (J_{SC}), fill factor (FF) and PCE were summarized in Table 2. The data clearly show that both V_{OC} and J_{SC} increased when the donor material was changed from **OBTTh**₄ to **OBTTh**₅, and then to **OBTTh**₆. Together with their comparable fill factors, these increments finally resulted in the improvement in the device efficiency from 0.16% for the **OBTTh**₄based cell to 0.36% for that based on **OBTTh**₆. How-



Figure 5 (a) *J-V* curves and (b) EQE spectra of the solar cells based on the blend of $OBTTh_n$ (n=4-7), $PBTTh_1$ or $PBTTh_2$ with $PC_{61}BM$.

Table 2 Photovoltaic properties of the OSCs based on **OBTTh**_n (n=4-7) and **PBTTh**₁ and **PBTTh**₂ as donor and **PC**₆₁**BM** as acceptor under the illumination of AM1.5G, 100 mW•cm⁻²

Material	$V_{\rm OC}/{ m V}$	$J_{\rm SC}/$ (mA•cm ⁻²)	FF/%	PCE ^{<i>a</i>} /%	$J_{\rm SC}^{b/}$ (mA•cm ⁻²)
OBTTh ₄	0.59	0.93	28.7	0.16 (0.15)	0.78
OBTTh ₅	0.78	1.27	31.0	0.31 (0.26)	1.14
OBTTh ₆	0.89	1.45	27.8	0.36 (0.31)	1.35
OBTTh ₇	0.85	1.33	29.4	0.33 (0.32)	1.19
PBTTh ₁	0.80	1.94	31.8	0.49 (0.46)	1.81
PBTTh ₂	0.79	1.95	34.0	0.52 (0.49)	1.79

^{*a*} Data in parentheses are the average values. ^{*b*} Calculated from EQE spectrum.

ever, when the donor material was further changed to **OBTTh**₇, no further improvement but comparable performance was observed. The situation was changed again when polymer **PBTTh**₁ was used as donor material. Its devices displayed a larger J_{SC} while maintained comparable V_{OC} and FF, finally resulting in an improved efficiency (0.49%).

In general, the open circuit voltage of OSCs is semi-empirically proportional to the energy level difference between the HOMO of donor and the LUMO of the acceptor materials.^[27] However in this work, the devices showed an increasing tendency on V_{OC} along the chain length of **OBTTh**_n (n=4-6), obviously not obeying the above general correlation. This implies that some other factors besides the material energy levels affect the device $V_{\rm OC}$. Actually, the origin of $V_{\rm OC}$ is still under intense debate in the field, and some works have already pointed out that a couple of factors including the size of side chains, interchain interactions, ground state charge transfer interactions between donor and fullerene acceptors, and the morphology of the active layer have noticeable influence on $V_{\rm OC}$.^[28] In this work, the different chain length would endow the oligomer a different interchain interactions and the ground state charge transfer interactions with $PC_{61}BM$, thus affording an unusual increasing tendency for $V_{\rm OC}$.

On the other hand, the device photocurrent (J_{SC}) enhanced along with the increment in the chain length, from **OBTTh**₄, to **OBTTh**₆, then to **PBTTh**₁ polymerbased cells. The increasing tendency was further coincided with external quantum efficiency (EQE) spectral measurement. As shown in Figure 5b, all the checked devices exhibited photocurrent response in the range of 300-700 nm. The photocurrent generation efficiency was gradually improved from shorter oligomer (**OBTTh**₄) to longer one (**OBTTh**₆), then to **PBTTh**₁ polymer. All the above observations indicate that the chain length of the material has great impact on its photovoltaic performance.

Unlike the chain-length effect, the side-chain regioregularity was found to have less influence on the device performance. The devices based on **PBTTh₂** outputted similar V_{OC} , J_{SC} , and FF values as those based on **PBTTh**₁. In EQE spectroscopy, the **PBTTh**₂-based device displayed smaller photocurrent in the UV region, but a slightly larger photocurrent in the visible light region, finally giving a comparable total value. For these two polymers, they have comparable molecular weight and polydispersity, and exhibit similar optical and electrochemical properties in solution. But they possess quite different backbone geometry, and show some differences in the film absorption spectroscopy. However, these differences are small and not able to modify the final device photovoltaic performance.



Figure 6 AFM topographical height images $(2 \times 2 \ \mu m^2)$ of the blend films of (a) **OBTTh**₄, (b) **OBTTh**₅, (c) **OBTTh**₆, (d) **OBTTh**₇, (e) **PBTTh**₁, and (f) **PBTTh**₂ with **PC**₆₁**BM** in weight ratio of 1 : 2.

Atomic force microscopy (AFM) was applied to study the effect of the chain length and the side-chain regioregularity on the morphology of the bulk heterojunction active films. As shown in Figure 6, the blend films based on **OBTTh**_n (n=4-7) with **PC**₆₁**BM** showed AFM images with very smooth and uniform appearance, suggesting that all the checked oligomers are phase-compatible with **PC**₆₁**BM**. However, in the case of polymer blend films, obvious phase separation was observed. The domain size grew bigger from **PBTTh**₁ to **PBTTh**₂. These observations indicate the

occurrence of phase separation in the blend films requires a sufficient chain length of **BT-Th** backbone and is also affected by the side-chain regioregularity. Although it is not clear at present that the observed phase separation scale would benefit their photovoltaic performance, appropriate phase separation between donor material and fullerene acceptor components in the bulk heterojunction is one of the prerequisites for high performance OSCs.^[2] This may be one of the reasons for the performance improvement for polymer-based OSC devices as compared with the oligomer-based ones.

Conclusions

A series of oligomer **OBTTh**_n (n=1-7) and polymer **PBTTh₁** and **PBTTh₂** composed of alternating 3-hexylthiophene and 2,1,3-benzothiadiazole units were designed and synthesized. The structural feature of the oligomers and PBTTh₁ polymer is that all the hexyl side chains orienting toward the same direction. Whereas in polymer **PBTTh₂**, every neighboring hexyl side chain changes its orientation direction one another, thus endows it a different side-chain regioregularity. It was found that the chain length has great impact on the photophysical, electrochemical, and photovoltaic properties of the oligomers and polymers. The elongation of the chain length enables the material red-shifted absorption bands, an enhanced HOMO energy level, a decreased LUMO, a smaller energy bandgap, and finally a better photovoltaic performance. The change of side chain regioregularity makes polymer **PBTTh₂** adopt different backbone geometry, and influences its packing structure in solid state. However, it has been proved to have less influence on the UV-vis absorption spectroscopy and electrochemical properties in solution, and the final device photovoltaic outputs.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Nos. 20974119, 90922019, and 21074147), Chinese Academy of Sciences, and Shanghai Science and Technology Commission (No. 13JC1407000).

References

- (a) Roncali, J. Chem. Rev. **1997**, *97*, 173; (b) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. Mater. Sci. Eng., R **2001**, *32*, 1.
- [2] (a) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. Chem. Rev. 2007, 107, 13248; (b) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. Chem. Rev. 2009, 109, 5868; (c) Chen, J.; Cao, Y. Acc. Chem. Res. 2009, 42, 17098; (d) Li, G.; Zhu, R.; Yang, Y. Nat. Photonics 2012, 6, 153; (e) Chen, L.; Shen, X.; Chen, Y. Chin. J. Chem. 2012, 30, 2219; (f) Qian, D.; Ma, W.; Li, Z.; Guo, X.; Zhang, S.; Ye, L.; Ade, H.; Tan, Z.; Hou, J. J. Am. Chem. Soc. 2013, 135, 8464; (g) Chen, C.-P.; Chen, Y.-C.; Yu, C.-Y. Polym. Chem. 2013, 4, 1161.
- [3] (a) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.;
 Yu, L. Adv. Mater. 2010, 22, E135; (b) Huo, L.; Zhang, S.; Guo, X.;
 Xu, F.; Li, Y.; Hou, J. Angew. Chem., Int. Ed. 2011, 50, 9697; (c)

Chu, T.-Y.; Lu, J.; Beaupré, S.; Zhang, Y.; Pouliot, J.-R.; Wakim, S.;
Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. J. Am. Chem. Soc.
2011, 133, 4250; (d) Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.;
Liu, S.; You, W. Angew. Chem., Int. Ed. 2011, 50, 2995; (e) Amb, C.
M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. J. Am. Chem. Soc. 2011, 133, 10062; (f) He, Z.; Zhong,
C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Nat. Photonics 2012, 6, 591; (g)
You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.;
Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. Nat. Commun.
2013, 4, 1446.

- [4] (a) Ye, H.; Li, W.; Li, W. Chin. J. Org. Chem. 2012, 32, 266 (in Chinese); (b) He, P.; Li, Z.; Hou, Q.; Wang, Y. Chin. J. Org. Chem. 2013, 33, 288 (in Chinese).
- [5] (a) van Duren, J. K. J.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Synth. Met.* **2001**, *121*, 1587; (b) Brabec, C. J.; Winder, C.; Sariciftci, N. S.; Hummelen, J. C.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. I. *Adv. Funct. Mat.* **2002**, *12*, 709.
- [6] Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inaganäs, O.; Andersson, M. R. Adv. Mater. 2003, 15, 988.
- [7] (a) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* 2007, *19*, 2295;
 (b) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* 2009, *3*, 297.
- [8] (a) Wang, E.; Wang, L.; Lan, L.; Luo, C.; Zhuang, W.; Peng, J.; Cao,
 Y. *Appl. Phys. Lett.* **2008**, *92*, 033307; (b) Boudreault, P.-L. T.;
 Michaud, A.; Leclerc, M. *Macromol. Rapid Commun.* **2007**, *28*, 2176.
- [9] Allard, N.; Ach, R. B.; Gendron, D.; Boudreault, P.-L. T.; Tessier, C.; Alem, S.; Tse, S.-C.; Tao, Y.; Leclerc, M. *Macromolecules* **2010**, *43*, 2328.
- [10] Zhou, E.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q.; Tajima, K.; Yang, C.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302.
- [11] (a) Zhu, Z.; Waller, D.; Gaudiana, R.; Morana, M.; Mühlbacher, D.; Scharber, M.; Brabec, C. *Macromolecules* 2007, *40*, 1981; (b) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* 2007, *6*, 497.
- [12] (a) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. J. Am. Chem. Soc. 2008, 130, 16144; (b) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. Nat. Chem. 2009, 1, 657.
- [13] (a) Lu, J.; Liang, F.; Drolet, N.; Ding, J.; Tao, Y.; Movileanua, R. *Chem. Commun.* 2008, 42, 5315; (b) Zheng, Q.; Jung, B. J.; Sun, J.; Katz, H. E. *J. Am. Chem. Soc.* 2010, *132*, 5394; (b) Chen, Y.-C.; Yu, C.-Y.; Fan, Y.-L.; Hung, L.-I.; Chen, C.-P.; Ting, C. *Chem. Commun.* 2010, 46, 6503; (c) Chang, C. Y.; Cheng, Y. J.; Hung, S. H.; Wu, J. S.; Kao, W. S.; Lee, C. H.; Hsu, C. S. *Adv. Mater.* 2012, *24*, 549.
- [14] (a) Yue, W.; Zhao, Y.; Tian, H.; Song, D.; Xie, Z.; Yan, D.; Geng,
 Y.; Wang, F. *Macromolecules* 2009, *42*, 6510; (b) Liang, F.; Lu, J.;
 Ding, J.; Movileanu, R.; Tao, Y. *Macromolecules* 2009, *42*, 6107.
- [15] Ong, K.-H.; Lim, S.-L.; Tan, H.-S.; Wong, H.-K.; Li, J.; Ma, Z.; Moh, L. C. H.; Lim, S.-H.; de Mello, J. C.; Chen, Z.-K. *Adv. Mater.* 2011, 23, 1409.
- [16] Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; Mcculloch, I.; Ha, C.-S.; Ree, M. Nat. Mater. 2006, 5, 197.
- [17] Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* 1999, 401, 685.
- [18] Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. J. Am. Chem. Soc. 2008, 130, 16324.
- [19] Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. J. Org. Chem. 2002, 67, 4924.
- [20] Pilgram, K.; Zupan, M.; Skiles, R. J. Heterocyclic Chem. 1970, 7, 629.

- [21] Zhang, M.; Tsao, H. N.; Pisula, W.; Yang, C.; Mishra, A. K.; Müllen, K. J. Am. Chem. Soc. 2007, 129, 3472.
- [22] Zhao, X.; Tang, H.; Yang, D.; Li, H.; Xu, W.; Yin, L.; Yang, X. *Chin. J. Chem.* **2012**, *30*, 2052.
- [23] Ling, J.; Fomina, N.; Rasul, G.; Hogen-Esch, T. E. J. Phys. Chem. B 2008, 112, 10116.
- [24] Sriwichitkamol, K.; Suramitr, S.; Poolmee, P.; Hannongbua, S. J. Theor. Comput. Chem. 2006, 5, 595.
- [25] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hase-gawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P.

Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;
Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.;
Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.;
Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.;
Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.;
Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*,
Gaussian, Inc., Wallingford CT, **2004**.

- [26] Zade, S. S.; Zamoshchik, N.; Bendikov, M. Acc. Chem. Res. 2011, 44, 14.
- [27] Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Adv. Mater. 2006, 18, 789.
- [28] (a) Perez, M. D.; Borek, C.; Forrest, S. R.; Thompson, M. E. J. Am. Chem. Soc. 2009, 131, 9281; (b) Vandewal, K.; Tvingstedt, K.; Gadisa, A.; Inganäs, O.; Manca, J. V. Nat. Mater. 2009, 8, 904; (c) Yang, L.; Zhou, H.; You, W. J. Phys. Chem. C 2010, 114, 16793.

(Cheng, F.)