Sensitivity of Molecular Packing and Photovoltaic Performance to Subtle Fluctuation of Steric Distortions within D–A Copolymer Backbones

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ABSTRACT: How molecular conformation variation due to the existence of steric torsions within the conjugated backbones plays a role in molecular packing and resultant polymer solar cell (PSC) performance was investigated by synthesizing two isomeric alternating D–A copolymers. In these copolymers, poly[3′,4′-dihexyl-(2,2′:5′,2″-terthiophene)-5,5″-diyl-alt-[4′,7″-di-2-(4′-ethylhexyl)thienyl-(5′,6″-difluorobenzo[6][1′,2′,5′]thiadiazole)]-5,5-diyl] (PTDTffBT(C6/EH)) and poly[3′,4′-di(2′-ethylhexyl)-(2,2′:5′,2″-terthiophene)-5,5″-diyl-alt-[4′,7″-di-2-(4-hexyl)thienyl-(5′,6″-difluorobenzo[6][1′,2′,5′]thiadiazole)]-5,5-diyl] (PTDTffBT(EH/C6)), which had comparable molecular weight, the linear hexyl and branched 2-ethylhexyl chains are interchanged between the donor and the acceptor units. Such molecular design could offer two isomeric donors with limited conformational steric distortions by positioning the given alkyl chains with fine steric disparity in the same conjugated backbone. The interchange of the side chains caused a fluctuation of ∼5° of the dihedral angles between the thiophenes within the donor units and between the ending thiophenes from the adjacent donor and acceptor units. The subtle transform on backbone steric distortions of the two copolymers leads to a negligible impact on electronic structures but a distinct one on molecular packing in film. The copolymers both embody polymorph molecular packing with preferential edge-on orientation in neat films. The (100) and (010) distance, corresponding to the lamellar stacking between the alkyl chains and the π–π stacking between the conjugated backbones, are both improved in the PTDTffBT(C6/EH) film with enhanced crystallinity than that in the PEDTffBT(EH/C6) film. Similar molecular packing feature remains for the BHJ blends of the two copolymers with the acceptor of PC71BM. Moreover, PTDTffBT(C6/EH) exhibits the apparent coexistence of face-on orientation with improved crystallinity. The PTDTffBT(C6/EH): PC71BM PSC devices offer a much improved maximum power conversion efficiency (PCE) of 8.24% over 6.13% of the PTDTffBT(EH/C6) device, mainly due to more efficient charge generation and balanced charge transport resulted from the optimized film microstructure. The investigation clearly shows the sensitivity of molecular packing and corresponding PSC device performance to subtle steric distortions within conjugated backbones.

KEYWORDS: polymer solar cell, D–A copolymer, side-chain engineering, molecular conformation, morphology

1. INTRODUCTION

As a prospective technology for green and sustainable energy by photovoltaic effect, bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted considerable attention in recent years because of their advantages of low cost, light weight, large-area fabrication capability, and flexibility.1,2 It has been well-demonstrated that each single step within a photovoltaic conversion process is strongly correlated with both the electronic structures of the materials employed and the morphological structure of the BHJ film for a specific PSC device.5–5 The superposed efforts, both from molecular engineering on optimizing the electronic and morphological structure of active materials and from interfacial engineering on devices, have become popular and indispensable plots in PSC research to push performance up forward.5–10 Owing to chemists by continuously feeding the area with remarkable active materials, the maximum power conversion efficiencies (PCE) of PSCs in a single junction have

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been achieved up to 12% for polymer:fullerene blends, 9% for all-polymer blends, and 14% for polymer:nonfullerene small molecular acceptor blends.17–22

Polymer donors consisting alternating electron-donating (D) and electron-accepting (A) building blocks with variable strength represents one of the most powerful material sources because of its facile tunability on electronic structures.23 Molecular engineering on D–A copolymers for efficient solution-processed BHJ solar cells have been unexceptionally carried out on constituting components of conjugated backbones, electron donating or withdrawing substituents and side chains, which often synergistically exert functions and cannot be solely explained by their own influences. Linear- and angular-shaped heterocenes as well as ladder-type donor units have been widely explored as conjugated backbones as the primary factor in dictating the intrinsic electronic properties of resulted copolymers. The introduction of oligo thiophenes and/or π-extended heterocenes with ending thiophenes as building blocks has been noticeably proved to offer efficient photovoltaic properties.24–27 Properly decorated side chains of a given D–A copolymer donor, such as alkyl, alkoxy, oligo(ethylene glycol), and even fluorinated chains, have been found to not only serve as solubilizing groups for easy processing but also play a critical role on its electronic and morphological features within the corresponding BHJ blend.28–34 Tremendous efforts on side chain engineering, for example, modifying the polarity, length, branch point, and position linked to the D and/or A units, have been paved out toward understanding their influence on photovoltaic properties and achieving high performance.33–41 The main argument is that structural rearrangement and intramolecular interactions occur by varying the position and nature of the side chains in D–A copolymers with a specific conjugated backbone; the corresponding optoelectronic, morphological, and photovoltaic properties of the copolymers also vary with these changes. Given the premise that the solubility issue can be guaranteed, it is essential whether the electronic and morphological features of a D–A copolymer perturbed by structure variation satisfy the requirement for highly efficient photoelectric conversion procedures within the PSC device through molecular engineering on constituting conjugated backbones, substituents, and side chains. When engineering D–A copolymers on these structural components, no matter what constitution is introduced as mentioned above, the molecular conformation of the final polymers varies accordingly. Assuming the structural perturbation resulted from molecular engineering mainly by tuning both the intrachain conformational structure and interchain interactions, we envision that the molecular conformational variation could be responsible as well for morphological evolution of D–A copolymers and their corresponding PSC device performance. Despite above-mentioned ongoing progress, the impact of molecular conformational variation on both the morphological features and thereafter the performance of corresponding PSC device is not yet fully realized and understood in the case that the position and nature of the side chains are all set beforehand within a specific D–A copolymer. The most effective way to obtain such D–A copolymers with varied stable molecular conformations would most likely have to be achieved through isomers bearing different steric torsions within their conjugated backbones.

The D–A copolymers with a A unit of 4,7-dithienyl-5,7-difluorobenzo[c][1,2,5]thiadiazole (DTrfBT) and a D unit of oligothiophene (T) have emerged as the most successful polymer donors enabling highly efficient PSCs.26 The PSC device performance has been found to be very sensitive to the size and the position of alkyl chains for blends of DTrfBT based polymers and fullerene acceptors.17,42–44 To investigate how the molecular conformation variation due to the existence of steric torsions within the conjugated backbones plays the role on affecting molecular packing and corresponding PSC performance, herein, we well-designed two isomeric D–A copolymers via interchanging the alkyl side chains positioned on the donor and acceptor units using the platform of D–A copolymers with the D unit of 3′,4′-dialkyl-2,2′-2′-terthiophene (T) and the acceptor unit of 4,7-bis(4-(2-alkyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (DTrfBT). The alkyl chains of hexyl and 2-ethylhexyl were incorporated at the positions as indicated in T and DTrfBT units, respectively, affording two isomeric D–A copolymers of poly[3′,4′-dihexyl-(2,2′:5′:2″-terthiophene)-5,5″-diyl-alt-[4′,7′-di-2-(4-(2-ethylhexyl)thienyl)-(5′,6′-difluorobenzo[c]-[1′,2′,5′]thiadiazole)]-5,5-diyl] (PTDTfBT(C6/EH)) and poly[3′,4′-di(2-ethylhexyl)-(2,2′:5′:2″-terthiophene)-5,5″-diyl-alt-[4′,7′-di-2-(4-hexyl)thienyl-(5′,6′-difluorobenzo[c]-[1′,2′,5′]thiadiazole)]-5,5-diyl] (PTDTfBT(EH/C6)). Taking advantage of the fine disparity of the steric effect between the linear hexyl and the branched 2-ethylhexyl chains in conjugation with their fixed anchor position on the donor and acceptor units, we can create a subtle steric distortion variation along the whole conjugated backbone between the two copolymers. A fluctuation around 5° of dihedral angles are obtained between the thiophenes within the donor units and between the ending thiophenes from the adjacent donor and acceptor units by DFT calculations. This gentle molecular conformation variation of the two copolymers impacts barely on their electronic structures but distinctively on molecular packing both in neat films and in the BHJ blends with the acceptor of PC71BM. The PTDTfBT(C6/EH):PC71BM polymer solar cell (PSC) device enables a much improved maximum PCE of 8.24% over 6.13% from the PTDTfBT(EH/C6) device.

2. EXPERIMENTAL SECTION

General information on materials, device fabrication, and characterization can be found in the Supporting Information.

**Synthesis of Poly[3′,4′-dihexyl-(2,2′:5′:2″-terthiophene)-5,5″-diyl-alt-[4′,7′-di-2-(4-(2-ethylhexyl)thienyl)-(5′,6′-difluorobenzo[c]-[1′,2′,5′]thiadiazole)]-5,5-diyl]** (PTDTfBT(C6/EH)). Into a 50 mL round-bottom flask was added 4,7-bis(5-bromo-4-(2-ethylhexyl)thienophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (0.22 g, 0.30 mmol), 3′,4′-dihexyl-(2,2′:5′:2″-terthiophene)-5,5″-diyl bis(trimethylsilyl) (0.02 g, 0.30 mmol). The flask was then transferred to a glovebox where Ph3P (0.02 g, 0.24 mmol), Pd2dba3 (8.24 mg, 0.009 mmol), tris(o-toly)phosphine (16.42 mg, 0.054 mmol) and 8.0 mL of anhydrous chlorobenzene were added under nitrogen. After being transferred out of the glovebox, the round-bottom flask was heated at reflux for 48 h under the protection of N2. The reaction mixture was then droppedwise into 100 mL of methanol at room temperature. The precipitate was collected by filtration and extracted by a Soxhlet apparatus with acetone, hexane, dichloromethane and chloroform sequentially. The chloroform fraction was then concentrated via rotavap evaporation and precipitated in methanol. The solid was filtered and dried under vacuum to offer the final product (135 mg, yield 46.5%). Resolvable 1H NMR spectrum of PTDTfBT(C6/EH) was unable to be obtained due to its strong aggregation in CDCl3.
The polymer was synthesized according to the similar procedure for PTDTffBT(C6/EH) from 4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenz[c][1,2,5]thiadazole (0.20 g, 0.30 mmol) and (3′,4′-bis(2-ethylhexyl)-(2,2′:5′,2″-terthiophene)-5,5″-diyl)-bis-(trimethylstannane) (0.24 g, 0.30 mmol) and 115 mg of the final product was obtained from the chloroform fraction after Soxhlet extraction with a yield of 40.5%. Resolvable 1H NMR spectrum of PTDTffBT(EH/C6) was unable to be obtained in CDCl3, as similarly happened for PTDTffBT(C6/EH).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The synthesis of the target D–A copolymers are presented in Scheme 1. The corresponding monomers of (3′,4′-dialkyl-(2,2′:5′,2″-terthiophene)-5,5″-diyl)-bis-(trimethylstannane) (T) and 4,7-di(5-bromo-4-alkylthiophen-2-yl)-5,6-difluoro-benzo[c][1,2,5]-thiadazole (DTffBT) were prepared as described in the Supporting Information. The copolymers were then synthesized via Stille cross-coupling reaction using chlorobenzene as the solvent and tri(dibenzylideneacetone)dipalladium (Pd2(dba)3) and tri(o-tolyl)-phosphine (P(o-Tol)3) as the catalyst. Both copolymers showed good solubility in common organic solvents such as chloroform and o-dichlorobenzene (o-DCB). The number-average molecular weights of PTDTffBT(EH/C6) and PTDTffBT(C6/EH) are 14.1 and 12.2 kDa, with the polydispersity index (PDI) of 1.8 and 1.6, respectively, as measured by gel permeation chromatography (GPC) in trichlorobenzene at 150 °C against polystyrene standards. It is worth noting that the number-average molecular weights of two copolymers are comparable, which minimizes the effects of molecular weight on the various properties of resulted polymers. The thermal properties of the copolymers were investigated using thermogravimetric analysis (TGA) under nitrogen. Both of the copolymers exhibited good thermal stability with the decomposition temperature (defined as the 5% weight-loss temperature, Td) over 430 °C (Figure S25).

3.2. Theoretical Calculations and Optical and Electrochemical Properties. To explore the effect of side chain interchanging between the donor of 3′,4′-dialkyl-(2,2′:5′,2″-terthiophene) and the acceptor unit of (4-alkylthiophen-2-yl)-5,6-difluoro-benzo[c][1,2,5]thiadazole (DTffBT) on polymer properties, the dihedral angles between the thiophenes within the donor unit and between the ending thiophenes from the adjacent donor and acceptor units, and frontier orbital distribution of corresponding two model compounds (TDffBT(EH/C6) and TDffBT(C6/EH) as presented in Figure 1 were calculated using density functional theory (DFT). The hexyl and 2-ethylhexyl groups remained for the calculation to objectively reflect the subtle structure con-
formation deviation caused by the interchanging of alkyl side chains. As shown in Figure 1, at the minimum energy state, the dihedral angles of ∼56° between the thiophenes within the terthiophene unit and ∼41° between the ending thiophenes from the adjacent donor of terthiophene and the acceptor of DT@TB were obtained in TD@TB(EH/C6). In TD@TB(C6/EH), nevertheless, the dihedral angles of ∼52° within the terthiophene unit and ∼47° between the donor and acceptor unit were obtained. Positioning branched 2-ethylhexyl chains results in an increase around 5° of the dihedral angles either on the donor unit or the acceptor units while it is on the contrary for linear hexyls. Such subtle dihedral angle fluctuations cause little variation on electronic communication between the donor and acceptor unit for the two model compounds due to their similar electron cloud distributions at frontier molecular orbitals and very close energy levels as depicted in Figure 1. However, TD@TB(C6/EH) has a higher ground state dipole moment of 0.80 D than that of 0.20 D in TD@TB(EH/C6) (Figure S26), suggesting that PTDT@TB(C6/EH) could be expected to exhibit a more closed packing structure because higher dipole moment can help to enhance molecular interactions.55–47

The temperature-dependent UV–vis absorption spectra of the two copolymers in diluted o-DCB solution with the concentration of (1 × 10−2) g mL−1 are presented in Figure S27. As can be seen from Figure S27a, PTDT@TB(EH/C6) is well dissolved over 90 °C and a bathochromic shift of ∼12 nm can be observed for the maximum absorption wavelength (λmax,sol) at ∼526 nm when the temperature decreases from 100 °C to room temperature. PTDT@TB(EH/C6) is found to be similarly well dissolved at elevated temperature over 90 °C with the λmax,sol at ∼533 nm with a bathochromic shift of ∼7 nm to that of PTDT@TB(EH/C6), indicative of a slight impact on spectral tuning by interchanging the alkyl side chain of hexyl and 2-ethylhexyl on the terthiophene unit and the DT@TB unit. As the temperature decreases from 100 °C to room temperature, the λmax,sol moves to ∼538 nm with a slight bathochromic shift of around 5 nm. Such slight variations of the λmax,sol of the two copolymers suggest no obvious temperature dependent aggregation existed as observed from the literatures. The absorption spectra of the two copolymers in the diluted solutions at 100 °C and in thin film at room temperature are thus compiled in Figure 2. Both copolymers exhibit characteristic dual absorption bands in solution as observed for a typical D–A alternating copolymer, where the high-energy one (∼395 nm) is originated from the π–π* transition and the low-energy one (∼530 nm) is assigned to the intramolecular charge transfer transition from the donor to the acceptor units. For thin films as cast from the o-DCB solution, PTDT@TB(EH/C6) and PTDT@TB(C6/EH) exhibit an absorption maxima (λmax, film, Table 1) at 606 and 612 nm, respectively, both red-shifted by around 80 nm when compared with those of corresponding solutions. The films of the two copolymers show a vibronic shoulder peak at around 665 nm. Moreover, the shoulder peak of PTDT@TB(C6/EH) is a little bit stronger than that of PTDT@TB(EH/C6), suggesting its more prominent interchain aggregation through effective π–π stacking in film. It needs to be noted that PTDT@TB(C6/EH) shows gentler higher extinction coefficients along most of the visible region both in solution and in film, which seems to play a positive role on the absorption capability of corresponding PSC device as can be observed lately from the device characterization.

From the absorption onset, the optical band gaps (Eg,opt Table 1) of PTDT@TB(EH/C6) and PTDT@TB(C6/EH) were estimated to be 1.68 and 1.67 eV, respectively. The energy levels of both copolymers were further measured by cyclic voltammetry (CV) of thin films as depicted in Figure S28. The HOMO energy levels of PTDT@TB(EH/C6) and PTDT@TB(C6/EH) were determined to locate at −5.28 and −5.23 eV calculated from the onset oxidation potentials (Eox) and the LUMO energy levels at −3.60 and −3.56 eV respectively from the formula of ELOMO = EHOBO + Eg-opt. The gap between the HOMOs and LUMOs of the two copolymers was rather smaller than 0.05 eV, indicative of the negligible effect of switching the alkyl chains between the donor and acceptor units on the electronic structure of the resulting copolymers. All optical and electrochemical parameters of the copolymers are tabulated in Table 1.

3.3. Photovoltaic Properties. PSC devices with conventional device configuration of ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al were fabricated to evaluate the photovoltaic performance of the two copolymers. The energy levels of the polymer donors and the acceptor of PC71BM are presented in Figure S29 in conjugation with the other electronic materials within the devices. The active layers were spin-coated from the polymer:PC71BM solutions in o-DCB with the polymer concentration of 10 mg mL−1. The optimal weight ratio of polymer: PC71BM was found to be 1:1 (Table S1) for the two copolymers. The film thickness of optimized devices was 102 nm for the PTDT@TB(EH/C6):PC71BM blend and 106 nm for the PTDT@TB(EH/C6):PC71BM blend. Varied amounts of processing additives such as diphenyl ether (DPE), 1,8-diiodooctane (DIO) and 1-chloronaphthalene (CN) for the BHJ films were tried as well only to find that none of them worked positively (Table S2), suggesting that the solvent additives did harm to the morphology evolution of the BHJ films during casting. Figure 3a presents the typical current–voltage (J–V) characteristics of the optimized BHJ PSCs under simulated AM 1.5G solar illumination while the detailed photovoltaic parameters are listed in Table 2. The highest PCE was found to be 8.24% for the PTDT@TB(EH/C6):PC71BM blend, with an open circuit voltage (VOC) of 0.789 V, a short-circuit current density (JSC) of 17.36 mA cm−2, and an fill factor (FF) of 0.60. Lower photovoltaic performance was found for the PTDT@TB(EH/C6):PC71BM blend with the highest PCE of 6.13% due to the

![Figure 2](image-url)
Table 1. Optical and Electrochemical Parameters of the Copolymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{max}}$ film (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{\text{g,opt}}$ (eV)</th>
<th>$E_{\text{ph}}$ (V)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}^\lambda$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDTfBBT (EH/C6)</td>
<td>526</td>
<td>606, 665</td>
<td>741</td>
<td>1.68</td>
<td>0.48</td>
<td>-5.28</td>
<td>-3.60</td>
</tr>
<tr>
<td>PTDTfBBT (C6/EH)</td>
<td>533</td>
<td>612, 665</td>
<td>745</td>
<td>1.67</td>
<td>0.43</td>
<td>-5.23</td>
<td>-3.56</td>
</tr>
</tbody>
</table>

*Calculated from the onset of the electronic absorption of the polymer films ($E_{\text{g,opt}} = 1240/\lambda$ (nm)). *Estimated from the oxidation onset vs Fc/Fc*+ by the equation of $E_{\text{HOMO}} = -4.8 - E_{\text{onset}}$. *Estimated by the equation of $E_{\text{LUMO}}^\lambda = E_{\text{HOMO}} + E_{\text{g,opt}}$.

Figure 3. (a) Typical $J$–$V$ curves of the optimized PSCs with PTDTfBBT(EH/C6):PC$_{71}$BM and PTDTfBBT(C6/EH):PC$_{71}$BM blends in conventional device configuration and (b) their corresponding EQE spectra.

Table 2. Optimized Maximum Photovoltaic Parameters of the Prepared PSCs with Parenthesized Averages and Standard Deviations Derived from 20 PSCs

<table>
<thead>
<tr>
<th>donor in BHJ blend</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE$_{\text{max}}$ (%)</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDTfBBT(EH/C6)</td>
<td>0.793 (0.787 ± 0.007)</td>
<td>14.63 (14.48 ± 0.23)</td>
<td>53.4</td>
<td>6.13 (6.04 ± 0.13)</td>
<td>2.11 × 10$^{-4}$</td>
<td>1.34 × 10$^{-4}$</td>
</tr>
<tr>
<td>PTDTfBBT(C6/EH)</td>
<td>0.789 (0.786 ± 0.005)</td>
<td>17.36 (17.19 ± 0.21)</td>
<td>60.2</td>
<td>8.24 (8.10 ± 0.19)</td>
<td>6.54 × 10$^{-4}$</td>
<td>5.11 × 10$^{-4}$</td>
</tr>
</tbody>
</table>

3.4. Exciton Generation, Dissociation, Charge Transport, and Recombination. The superior performance of the PTDTfBBT(C6/EH):PC$_{71}$BM blend over that of PTDTfBBT-(C6/EH):PC$_{71}$BM predominantly benefits from the greater contribution of the higher $J_{\text{sc}}$ (18% increase) and FF (13% increase). Practically, each step within a light-to-electricity conversion process from photon absorption to charge collection in a PSC device conceals potential energy loss mechanisms to deteriorate the overall PCE. The excitons initially generated by light absorption have to diffuse to the donor/acceptor interfaces and dissociate further to form free charge carriers as akin as to photoluminescence quenching. To evaluate the efficiency of exciton generation and dissociation, static fluorescence spectroscopy testing was thus carried out on both the neat polymer and the BHJ blend films as shown in Figure 4a. The excitation wavelength of 650 nm was chosen for both copolymers according to their absorption spectra.

Figure 4b are the plots of the photocurrent density ($J_{\text{ph}}$) as a function of the internal voltage ($V_{\text{int}}$) of the two devices, which reveal how the $J_{\text{ph}}$ responded to the $V_{\text{int}}$ of the devices composed of the two copolymers. In this case, $J_{\text{ph}} = J_{\text{L}} - J_{\text{bi}}$, where $J_{\text{L}}$ and $J_{\text{bi}}$ are the current density under incident light and in dark, respectively, and $V_{\text{int}} = V_{\text{bi}} - V_{\text{app}}$, where $V_{\text{bi}}$ is the built-in voltage when $J_{\text{ph}} = 0$ and $V_{\text{app}}$ is the applied voltage. It is observed that the $J_{\text{ph}}$ tends to saturate (defined as
the saturated photocurrent density, $J_{ph,sat}$ as $V_{oc}$ is close to 1 V and thus the maximum photoinduced charge carrier generation rate ($G_{max}$) of the devices can be calculated using the equation $J_{ph,sat} = qLG_{max}$ where $q$ is the elementary charge and $L$ is the thickness of the BHJ layer. The $J_{ph,sat}$ value is determined to be 16.5 mA cm$^{-2}$ for the PTDT$m$BT(EH/C6):PC$_{71}$BM blend and 19.1 mA cm$^{-2}$ for the PTDT$m$BT(EH/C6):PC$_{71}$BM blend, whereas the value of $G_{max}$ is accordingly calculated to be $1.01 \times 10^{28}$ m$^{-3}$ s$^{-1}$ and $1.12 \times 10^{28}$ m$^{-3}$ s$^{-1}$, respectively. The $G_{max}$ of the device with PTDT$m$BT(EH/C6) increases nearly 12%, indicating more photogenerated excitons and dissociated charge carriers offered in accordance with the photoluminescence quenching results.

Space-charge-limited current (SCLC) measurements were performed to investigate the vertical hole ($\mu_h$) and electron ($\mu_e$) mobility of the two BHJ blend films (Figure S31). The hole- and electron-only devices were fabricated in the configuration of ITO/PEDOT:PSS(40 nm)/polymers:PC$_{71}$BM/MoO$_3$/Ag and ITO/ZnO(30 nm)/polymers:PC$_{71}$BM/Ca/Al, respectively. The measured $\mu_h$ and $\mu_e$ value of the PTDT$m$BT(EH/C6):PC$_{71}$BM blend is determined to be $2.11 \times 10^{-4}$ and $1.34 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, with a $\mu_h/\mu_e$ value of 1.57. Nevertheless, the PTDT$m$BT(EH/C6):PC$_{71}$BM blend exhibits a $\mu_h$ of 6.54 $\times$ $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and a $\mu_e$ of 5.11 $\times$ $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, both increased by more than three times leading to a $\mu_h/\mu_e$ value of 1.28. The charge transport balance ($\mu_h/\mu_e$) between the hole and electron mobility within a BHJ blend is important for improving the value of $J_{ph}$ and FF for a PSC. The higher and more balanced hole and electron mobility in the PTDT$m$BT(EH/C6):PC$_{71}$BM blend would help to reduce the steady state carrier density and suppressing photocurrent loss from charge recombination to enhance the $J_{sc}$ and FF.

The dependency of the device performances such as $J_{ph}$ and $V_{oc}$ on the incident light intensity were investigated as well to identify the charge recombination state within the optimized devices. According to the equation of $J_{sc} \propto P_{light}^\alpha$, where $P_{light}$ is the light intensity, $\alpha$ should approach to the unity when the bimolecular recombination is negligible. As shown in Figure 4c, the fitted slopes ($\alpha$) of the optimized devices are calculated to be 0.96 and 0.98 for the BHJ blend with PTDT$m$BT(EH/C6) and PTDT$m$BT(EH/C6), respectively. This indicates that the bimolecular recombination was suppressed more efficiently at short-circuit condition in the PTDT$m$BT(EH/C6):PC$_{71}$BM blend. The state of the monomolecular recombination at the open circuit condition of a PSC device can be illustrated through the equation of $V_{oc} \propto (nk_B T/q) \ln(P_{light})$, where $k_B$ is the Boltzmann constant, $T$ is temperature in Kelvin, and $q$ is the elementary charge. Generally, the involvement of the monomolecular recombination and its competition with the bimolecular recombination would lead to an increased $n$ beyond 1. Relevant curves of $V_{oc}$ versus $P_{light}$ are therefore examined and presented in Figure 4d. The strongest dependence of $V_{oc}$ on the light intensity within the two devices provides a slope of 1.21 $k_B T/q$ for the PTDT$m$BT(EH/C6):PC$_{71}$BM blend with an $n$ value of 1.21 and 1.03 $k_B T/q$ for the PTDT$m$BT(EH/C6):PC$_{71}$BM blend with an $n$ value of 1.03, suggesting the least involvement of the monomolecular recombination under the open-circuit condition for the latter. The lower bimolecular recombination and significantly suppressed monomolecular recombination is consistent with the more efficient charge transport estimated.
from the SCLC method and partially accounts for the higher $J_{sc}$, FF, and EQE response of the PTDTfBBT(C6/EH):PC$_{71}$BM device.

### 3.5. Film Morphology Characterization

Given the negligible effect of alkyl side chain interchanging between the donor and acceptor units along the conjugated backbone on the electronic structure of the resulting copolymers, the improved performance on exciton generation and dissociation, charge transport and recombination of the PTDTfBBT(C6/EH):PC$_{71}$BM device could most likely be ascribed to the more optimized molecular packing and phase separation in the BHJ blend. Tapping-mode atomic force microscopy (AFM) was employed to investigate the surface morphology of the BHJ blend films as presented in Figure 5S2. The BHJ blend with PTDTfBBT(EH/C6) shows a featureless and smooth surface with a root-mean-square (RMS) roughness of 2.38 nm. In contrast, the BHJ film of PTDTfBBT(C6/EH) develops fibril structures with a RMS roughness of 9.15 nm, indicating improved ordering of the components which is beneficial for charge transport. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement was carried out as well to further disclose the intermolecular stacking distance, crystallite orientation, and crystallinity of the two copolymers in both the pure and the BHJ blend films. Figure 5a–d are GIWAXS patterns of the pristine polymer films and the corresponding BHJ blend films. As shown in Figure 5e, the diffraction scans for the neat PTDTfBBT(C6/EH) show a strong out-of-plane (OOP) (100) reflection at $q_z$ of 0.42 Å$^{-1}$ corresponding to a lamellar $d$-spacing of 14.95 Å and an in-plane (IP) (010) reflection at $q_y$ of 1.78 Å$^{-1}$ corresponding to a $\pi$–$\pi$ stacking $d$-spacing of 3.53 Å, indicating a typical edge-on orientation of the polymer crystals. A much weaker in-plane (IP) (100) reflection at $q_y$ of 0.36 Å$^{-1}$ ($d = 17.44$ Å) can also be observed without an obviously detectable OOP (010) feature, suggesting the existence of a part of face-on orientation. For the neat PTDTfBBT(EH/C6) film, the OOP (100) reflection at $q_z$ of 0.40 Å$^{-1}$ corresponds to a $d$-spacing of 15.70 Å and the IP (010) reflection at $q_y$ of 1.72 Å$^{-1}$ corresponds to the $d$-spacing value of 3.65 Å. Additionally, a blunt IP (100) reflection at $\sim0.34$ Å$^{-1}$ ($d = 18.47$ Å) can also be observed with a negligible OOP (010) feature. Briefly, the neat films of both copolymers present bimodal molecular packing with preferential edge-on orientations. The stacking space distances between the alkyl chains and between the conjugated backbones ($\pi$–$\pi$ stacking) are improved in the PTDTfBBT(C6/EH) film with enhanced crystallinity. Such stronger aggregation tendency of PTDTfBBT(C6/EH) in the film can be attributed to side chain tuning on the molecular conformation and larger dipole moment as demonstrated above. When blended with PC$_{71}$BM to form a BHJ film, the bimodal molecular packing of the polymers with preferential edge-on orientation remains in the PTDTfBBT(C6/EH):PC$_{71}$BM blend as shown in Figure 5f. The typical reflection at $\sim1.34$ Å$^{-1}$ ($d = 4.67$ Å) both along the IP and OOP direction refers to PC$_{71}$BM aggregation. The OOP (100) reflection at 0.40 Å$^{-1}$ ($d = 15.70$ Å) and the IP (010) reflection at 1.82 Å$^{-1}$ ($d = 3.45$ Å) can be observed with increased lamellar and compressed $\pi$–$\pi$ stacking distance compared to that of the neat polymer film. It is interesting that the IP (100) reflection of PTDTfBBT(C6/EH) remains almost at the same $q_y$ ($\sim0.36$, $d = 17.44$ Å) both in the neat and BHJ blend films. In the case of the PTDTfBBT(EH/C6):PC$_{71}$BM blend, an obvious OOP (100) reflection of PTDTfBBT(EH/C6) at 0.38 Å$^{-1}$ ($d = 16.53$ Å) can be observed besides the reflections of PC$_{71}$BM aggregation, suggesting a dominating edge-on orientation of the polymer crystals in spite of no corresponding evident IP (010) diffraction observed. The most distinctive feature on molecular packing within the PTDTfBBT(C6/EH):PC$_{71}$BM blend compared with the PTDTfBBT(EH/C6):PC$_{71}$BM blend is the obvious coexistence of a certain amount of face-on oriented packing besides the obvious edge-on orientation with
pressed charge recombination, leading to improved noticeable enhancement of the charge transport with pronounced molecular packing most likely accounts for the in comparison with the PTDT*

acle for the IP (100) peak than that of PTDTfBBT(C6/EH) in its BHJ blend. Such pronounced molecular packing most likely accounts for the noticeable enhancement of the charge transport with pronounced molecular packing most likely accounts for the in comparison with the PTDT*

conformation, impact of backbone steric distortions on the molecular device performance. This complementary insight on the structure optimization of polymer donors toward highly efficient PSCs.

4. CONCLUSION

In conclusion, two isomeric D-A alternating copolymers consisting the donor unit of 3',4',5',2',5'-terthiophene and the acceptor unit of 5,6-difluoro-4,7-di(4-alkylthiophen-2-yl)benzo[c][1,2,5]thiadiazole were synthesized and characterized by exchanging alkyl side chain of hexyl and branched 2-ethylhexyl between the donor and acceptor units. Positioning the alkyl chains of 2-ethylhexyl on the acceptor units and hexyl on the donor units resulted in slightly decreased dihedral angles within the donor unit and slightly increased dihedral angles between the donor and the acceptor units. Such subtle structure perturbation by the backbone steric distortions from the dihedral angles is found to show negligible impact on polymer electronic structures but lead to distinctive film microstructure. GIWAXS results reveal that the copolymer with such positioned alkyl side chains (PTDTfBBT(C6/EH)) shows higher quality of molecular packing with enhanced \(\pi-\pi\) stacking, crystallite orientation, and crystallinity while ensuring comparable solubility to its counterpart polymer (PTDTfBBT(EH/C6)), which were accordingly translated into much improved polymer solar cell device performance. This complementary insight on the impact of backbone steric distortions on the molecular conformation, film morphology, and the PSC device performance could provide meaningful guidance for the chemical structure optimization of polymer donors toward highly efficient PSCs.

ASSOCIATED CONTENT

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b00948.

General information on materials, TGA, ground-state dipole moment of TDTfBBT(EH/C6) and TDTfBBT-(C6/EH), temperature-dependent UV-vis absorption spectra of the two copolymers in diluted dichlorobenzene solution, cyclic voltammogram curves of the copolymers, detailed photovoltaic performance optimization, \(J-V\) curves of electron- and hole-only devices under dark, and tapping mode AFM images (PDF).

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Notes

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