Important of 2D Conjugated Side Chains of Benzodithiophene-Based Polymers in Controlling Polymer Packing, Interfacial Ordering, and Composition Variations of All-Polymer Solar Cells

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Supporting Information

ABSTRACT: We delineate the important role of 2D conjugated alkylthiophene side chains of polymers in manipulating the molecular orientation and ordering at the polymer donor/polymer acceptor (P_D/P_A) interface as well as the composition variations in the blend active layer of all-polymer solar cells (all-PSCs). To systematically investigate the impact of 2D conjugated side chains on the performance of all-PSCs, we synthesized a series of poly(benzo[1,2-b:4,5-b]-dithiophene-thieno[3,4-c]pyrrole-4,6-dione) (PBDTTTPD) polymer donors with different contents of alkyl and alkylthiophene side chains, from 0 to 100% (PBDTTPD (P1), 100% alkoy side chain), PBDTT0.29TPD (P2), PBDTT0.59TPD (P3), PBDTT0.76TPD (P4), and PBDTTTPD (P5, 100% alkylthiophene side chain). The P1–P5 polymer donors produced similar PCEs of ~6% in fullerene-based PSCs. In contrast, for the all-PSC systems, the changes in the side chain composition of the polymers induced a strong increasing trend in the power conversion efficiencies (PCEs), from 2.82% (P1), to 3.16% (P2), to 4.41% (P3), to 5.32% (P4), and to 6.60% (P5). The significant increase in the PCEs of the all-PSCs was attributed mainly to improvements in the short-circuit current density (J_sc) and fill factor (FF). The 2D conjugated side chains promoted localized molecular orientation and ordering relative to the P_D/P_A interfaces and improved domain purity, which led to enhanced exciton dissociation and charge transport characteristics of the all-PSCs. Our observations highlight the advantage of incorporating 2D conjugated side chains into polymer donors for producing high-performance all-PSC systems.

INTRODUCTION

All-polymer solar cells (all-PSCs), in which the active layer consists of both an electron-donating polymer (P_D) and an electron-accepting polymer (P_A), have gained growing interest because of their promising advantages including enhanced complementary light absorption from the P_D and P_A components, facile tunability of energy levels of P_D and P_A, and high thermal/mechanical stability.1–3 The power conversion efficiencies (PCEs) of all-PSCs have improved significantly in a brief span of years, with PCEs now in the range of 7–9%.3–22 This rapid progress has been made possible by the effective use of the strategies developed and the lessons learned in extensive studies of fullerene-based PSCs. For example, one of the major hurdles limiting the PCEs of all-PSCs, that is, undesirable large-scale phase separation of polymer blends in bulk-heterojunction (BHJ) layers, was improved in part by approaches used frequently to increase the efficiency of polymer/fullerene solar cell (fullerene-PSC) systems. These approaches include controlling the molecular weight and side chains of the polymer components3,23–32 and the use of P_D/P_A pairs with low interfacial tension.33

One intriguing and important issue remains to be addressed, particularly for the design of high-performance all-PSCs. Unlike fullerene acceptors that have ball-like symmetric molecular geometry (e.g., phenyl-C_66-butyric acid methyl ester (PCBM)), P_A have highly anisotropic (planar) conjugated chemical structures.24,25 This feature associated with P_A often hampers efficient charge separation of Coulombically bound excitons at the P_D/P_A interface of all-polymer blends due to the lack of face-to-face alignment of P_D and P_A desire to afford...
overlapping π-orbitals that reduce the binding energy barrier of the excitons.\textsuperscript{24,34–37} However, achieving such alignment between \( P_D \) and \( P_A \) at the interface during solvent-assisted formation of the active layer is nontrivial, hence leading to severe geminate charge recombination in all-PSCs. It is indeed one of the most dominant loss mechanisms in all-PSCs, though very few studies have addressed these issues to date.\textsuperscript{34,36}

Here we demonstrate the important role of 2D alkylthienyl conjugated side chains of polymer donors in manipulating the polymer packing, ordering and orientation relative to the \( P_D/P_A \) interface as well as the polymer composition variation in the BHJ domains. To systematically investigate the impact of side chains having 2D conjugation on the performance of all-PSC devices, we synthesized a series of poly(benzo[1,2-b:4,5-b]-dithiophene-thieno[3,4-c]pyrrole-4,6-dione (PBDTTPD) polymer donors containing different compositions of alkoxy and alkylthienyl side chains appended to the BDT backbone (Figure 1). We selected the PBDTTPD polymer backbone as a model system because PBDTTPD with both alkoxy and 2D conjugated alkylthienyl side chains produced similar, high PCEs (6–7%) with comparable short-circuit current density (\( J_{SC} \)) values in fullerene-based PSCs.\textsuperscript{51–53} Increasing the fraction of alkylthienyl side chains in the polymer donors from 0 to 100 mol% enhanced the photovoltaic performances of naphthalene-diimide-thiophene polymer acceptor (P(NDI2HD-T)) based all-PSCs from 2.82 to 6.60%. The significantly improved \( J_{SC} \) and fill factor (FF) values are attributed to enhanced charge transport and generation in the active layers and are the main contributors to the improved PCEs of all-PSCs. From grazing incidence X-ray scattering (GIXS) and resonant soft X-ray scattering (RSoXS) experiments, increasing trends in the \( J_{SC} \) factor (FF) values are attributed to enhanced charge transport and generation in the active layers and are the main contributors to the improved PCEs of all-PSCs.

One insight into the design rules for all-PSCs was gained from our previous studies and those of others: the vast majority of high-performance all-PSCs used polymer donors appending 2D conjugated side chains (i.e., thienyl or phenyl groups).\textsuperscript{3,4,6–9,34,36,38} These \( P_A \)s typically surpass the performance of all-PSCs based on \( P_D \)'s with alkoxy side chains, even though both polymers with alkoxy- and 2D conjugated-side chains have been used extensively to produce high PCEs in fullerene-PSCs. For example, in our earlier work, all-PSCs based on the PTB7-Th with alkylthienyl side chains (PCE = 4.60%) outperformed those based on the PTB7 with alkoxy side chains (PCE = 2.54%),\textsuperscript{33} while high PCEs of \( \sim10\% \) were achieved in both PTB7 and PTB7-Th based fullerene-PSCs.\textsuperscript{39,40} Hou and co-workers reported that the efficiency of PBDT-BDD-T:PNDI all-PSCs having a \( P_D \) with conjugated alkylthienyl side chain (5.8%) was twice as high as compared to that of PBDT-BDD:PNDI all-PSCs with a \( P_D \) having alkoxy side chain (2.4%).\textsuperscript{34} These observations have two implications: (i) there exists different efficiency-determining principles between fullerene- and all-PSCs that are most likely linked to different morphological aspects in the active layers (e.g., interfacial orientation, as discussed above), and (ii) morphological aspects of all-PSCs can be modulated by engineering the side chains of conjugated polymers. It is expected that efforts to develop correlations between side chain structure, morphology, and device performance for all-PSCs will establish material design criteria for high-performance all-PSCs; however, very few studies have addressed these issues to date.\textsuperscript{34,36}

Here we demonstrate the important role of 2D alkylthienyl conjugated side chains of polymer donors in manipulating the polymer packing, ordering and orientation relative to the \( P_D/P_A \) interface as well as the polymer composition variation in the BHJ domains. To systematically investigate the impact of side chains having 2D conjugation on the performance of all-PSC devices, we synthesized a series of poly(benzo[1,2-b:4,5-b]-dithiophene-thieno[3,4-c]pyrrole-4,6-dione (PBDTTPD) polymer donors containing different compositions of alkoxy and alkylthienyl side chains appended to the BDT backbone (Figure 1). We selected the PBDTTPD polymer backbone as a model system because PBDTTPD with both alkoxy and 2D conjugated alkylthienyl side chains produced similar, high PCEs (6–7%) with comparable short-circuit current density (\( J_{SC} \)) values in fullerene-based PSCs.\textsuperscript{51–53} Increasing the fraction of alkylthienyl side chains in the polymer donors from 0 to 100 mol% enhanced the photovoltaic performances of naphthalene-diimide-thiophene polymer acceptor (P(NDI2HD-T)) based all-PSCs from 2.82 to 6.60%. The significantly improved \( J_{SC} \) and fill factor (FF) values are attributed to enhanced charge transport and generation in the active layers and are the main contributors to the improved PCEs of all-PSCs. From grazing incidence X-ray scattering (GIXS) and resonant soft X-ray scattering (RSoXS) experiments, increasing trends in the population of face-on orientated polymers in the thin film blends, localized molecular orientation and ordering relative to the \( P_D/P_A \) interface, and composition variations (i.e., the average purity of the polymer domains) in the BHJ active layer were observed with increasing content of alkylthienyl side chains in the polymer donors.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{P D} & \textbf{feed ratio} & \textbf{actual ratio}\textsuperscript{a} & \textbf{M_n (kg/mol)}\textsuperscript{b} & \textbf{D (M_n/M_w)}\textsuperscript{b} & \textbf{E_g (eV)}\textsuperscript{c} & \textbf{HOMO (eV)}\textsuperscript{d} & \textbf{LUMO (eV)}\textsuperscript{d} \\
\hline
P1 & 1:0 & 1:0 & 28.8 & 1.9 & 1.86 & -5.44 & -3.58 \\
P2 & 0.75:0.25 & 0.71:0.29 & 30.2 & 2.2 & 1.85 & -5.45 & -3.60 \\
P3 & 0.50:0.50 & 0.41:0.59 & 31.1 & 2.7 & 1.86 & -5.48 & -3.62 \\
P4 & 0.25:0.75 & 0.24:0.76 & 31.2 & 2.7 & 1.87 & -5.49 & -3.62 \\
P5 & 0:1 & 0:1 & 25.9 & 2.3 & 1.88 & -5.54 & -3.66 \\
\hline
\end{tabular}
\caption{Properties of P1–P5}
\end{table}

\textsuperscript{a}Values were determined by elemental analysis. \textsuperscript{b}Values were determined by GPC. \textsuperscript{c}Values were determined by UV–vis absorption spectra of thin films. \textsuperscript{d}Values were determined by UPS. \textsuperscript{e}Values were determined by LUMO = HOMO + \( E_g \).
A series of PBDTT-TPD polymer donors with different contents of alkoxy and alkylthienyl side chains was designed to investigate the effects of 2D conjugated side chains on the photovoltaic performance of all-PSCs (Figure 1). The side chain composition of the polymers was adjusted by varying the feed ratios of the 4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT) and 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b,4,5-b′]-dithiophene-2,6-diyl)bis(trimethylstannane) (BDTT) monomers from 0 to 100 mol %, which produced five polymer donors: PBDT-TPD (P1, 0% BDTT), PBDTT0.28-TPD (P2, 29% BDTT), PBDTT0.59-TPD (P3, 59% BDTT), PBDTT0.76-TPD (P4, 76% BDTT), and PBDTT-TPD (P5, 100% BDTT) (Figure S1). The BDT:BDTT ratios incorporated into the polymers were determined by elemental analysis, and the results showed good correlation with the molar feed ratios of BDT/BDTT monomers (Table 1). Detailed synthetic procedures are provided in the Supporting Information.

The optical properties of thin polymer films of P1–P5 were measured by gel permeation chromatography (GPC) (Table 1), and they exhibited similar Mn values (25.9–31.2 kg/mol). P(NDI2HD-T) polymer acceptor was synthesized following the previously reported procedure, and the Mw and D values of P(NDI2HD-T) were 65 kg/mol and 2.2, respectively. Ultraviolet photoelectron spectroscopy (UPS) was used to measure the highest occupied molecular orbital (HOMO) energy levels of P1–P5 (Table 1, Figure S2). The HOMO energy levels of the polymers were determined to be -5.44 eV for P1, -5.45 eV for P2, -5.48 eV for P3, -5.49 eV for P4, and -5.54 eV for P5. The lowest occupied molecular orbital (LUMO) energy levels were estimated from the optical bandgaps (Eg), and the LUMO levels of polymers were -3.58 eV for P1, -3.60 eV for P2, -3.62 eV for P3, -3.62 eV for P4, and -3.66 eV for P5. Both the HOMO and LUMO levels were found to decrease as the BDTT content in the P5s increased, which is likely because the π-electrons can be effectively delocalized along the extended π-conjugation of the BDTT units.

The gradually decreasing HOMO levels from P1 to P5 are beneficial for yielding higher open-circuit voltage (VOC) values in all-PSC devices. The optical properties of thin films of P1–P5 were compared in Figure S3. All of the optical densities exhibited broad and strong absorption bands in the range of 300–700 nm with similar maximum absorption coefficients in the range of (4.3–5.2) × 10^5 cm^-1. The intensity of the absorption peak at 615 nm was found to increase slightly with increasing amounts of alkylthienyl units in P1 to P5, attributed mainly to the enhanced intermolecular π–π interactions of the 2D conjugated alkylthienyl side chains of BDTT (Figure S3b).

However, the overall light absorption properties of the polymers remain relatively constant as a function of BDTT content. The absorption edges were essentially unchanged as a function of side chain composition, producing similar optical band gaps of 1.85–1.88 eV.

To evaluate the performance of P1–P5-based all-PSCs, we fabricated normal-type solar devices with an ITO/PEDOT:PSS/active layer/LiF/Al architecture. P(NDI2HD-T) was chosen as the P3 because of its good compatibility and high photovoltaic performance with PBDTT-TPD P5. For P1–P5-based all-PSCs, the optimal P3/P1 ratio and active layer thickness were determined to be 1.3:1 (w/w) and 100–110 nm, respectively. The polymer blends were dissolved in chloroform, and 1 vol % 1, 8-diodooctane (DIO) was added to the blend solutions to optimize the BHJ morphology. Device fabrication is detailed in the Supporting Information. The device performance of the all-PSCs is summarized in Table 2, and the current density–voltage (J–V) and the external quantum efficiency (EQE) curves are displayed in Figure 2. Interestingly, we found that there was a linear trend between PCE and BDTT content in the P5s: PCEs were increased from 2.82% for P1, 3.16% for P2, 4.41% for P3, 5.32% for P4, and 6.60% for P5. The Voc increased from 0.96 (P1) to 0.99 (P3), and to 1.04 (P5), as a result of the decreased HOMO levels of the polymers as a function of BDTT content. However, we noted that the simultaneously increased Jsc and FF values were the dominant factors responsible for the strong correlation between the side chain composition of the P3s and the PCEs. For example, the P1 device afforded low Jsc and FF values of 7.35 mA/cm^2 and 0.40, respectively, whereas the P5 device yielded much higher values of 11.13 mA/cm^2 and 0.57, which were 51% and 43% increases, respectively. The EQE spectra of the P1–P5 devices supported the increasing Jsc values with BDTT content in the P5s (Figure 2b). While all of the devices yielded broad EQE responses from 300 to 700 nm, the EQE values progressively increased in the order of P1, P2, P3, P4, and P5-based all-PSCs. The integrated Jsc values from the EQE spectra correlated well with the Jsc values measured from the solar cell devices, within 5% error.

It is worth noting that the PCE trends of all-PSCs differed greatly from those of fullerene-PSCs constructed with the same P5s (i.e., P1 and P5). We fabricated P1- and P5-based fullerene-PSCs following the same procedure as above. The PCEs of both P1- and P5-based fullerene-PSCs were not sensitive to side chain structure, yielding similar PCEs of ~6% and comparable Jsc values of ~12 mA/cm^2 (Table S1). Additionally, previous work by Beaujuge et al. supported our observations. They reported the PCE of PBDT-TPD (P1)-based fullerene-PSCs to be 7.5%, which exceeded that of the fullerene-PSC fabricated with PBDTT-TPD having 2D side chains (6.5%). Taken together with the photovoltaic performance of the P1–P5-based all-PSCs reported herein, this report suggests that the drastic contrast in the photovoltaic performances of the P1–P5 all-PSCs originated from different underlying working principles in all-PSCs and fullerene-PSCs. Further, since the light absorption properties of the P1–P5-based all-PSCs were similar (Figure S4), it was expected that the electrical properties (i.e., charge transport and exciton dissociation) of the BHJ active layers would be the dominant factor in determining the photovoltaic performance.
Investigated to gauge the geminate recombination losses in the 10e (PSCs, the hole (μa), and electron (μb) mobilities were measured using the space-charge limited current (SCLC) method (Table S2). We found an increasing trend in the average μa as a function of BDTT content, from 5.42 × 10−4 cm2 V−1 s−1 for P1, to 6.35 × 10−4 cm2 V−1 s−1 for P2, to 7.98 × 10−4 cm2 V−1 s−1 for P3, to 1.43 × 10−5 cm2 V−1 s−1 for P4, and to 4.41 × 10−5 cm2 V−1 s−1 for P5. However, the μb values of the P1–P5:P(NDI2HD-T) blend films were almost constant, that is, (5.05–6.45) × 10−5 cm2 V−1 s−1. As such, the P5:P(NDI2HD-T) blend afforded well-balanced electron and hole mobilities (μa/μb = 1.26). Next, the exciton dissociation probability (P(E,T)) of the P1–P5:P(NDI2HD-T)-based all-PSCs was investigated to gauge the geminate recombination losses in the devices. The photocurrent densities (Jph) of the devices were measured against biased voltages between −6 and +2 V under illumination (100 mW cm−2) and in the dark, and the Jph versus effective voltage (Veff) curves were plotted (Figure 3), where Jph applied bias. The P(E,T) values were obtained by calculating the ratio of Jph at the short circuit condition (Veff = V0) and the saturated photocurrent density Jph sat.46–49 P(E,T) values for the P1–P5 devices were calculated to be 62, 64, 68, 70 and 80%, respectively. Taken together, the increased exciton dissociation and improved charge transport as a function of the incorporation of BDTT contributed to the enhancement in Jsc and FF, and thus the resulting PCEs in P5 all-PSCs.

Charge transport and exciton dissociation in all-PSCs are strongly correlated with structural and morphological characteristics. To investigate the polymer packing structure, orientation, and blend morphology in P1–P5 all-PSCs, complementary analyses using GIXS, RSoXS, atomic force microscopy (AFM), and photoluminescence (PL) spectroscopy were performed. First, GIXS was used to investigate the molecular packing and the crystallinity of P1–P5 in both neat polymer films and their blends with the P(NDI2HD-T) polymer acceptor. We prepared P1–P5 thin films on Si/PEDOT:PSS substrates by spin-coating from chloroform. Figure S5 displays the 2D GIXS patterns of P1–P5 films and their line cuts in the in-plane and out-of-plane directions. All of the polymers were found to exhibit clear (100) reflection peaks in the in-plane direction with lamellar spacings (d100) of 2.14 nm (P1), 2.25 nm (P2), 2.29 nm (P3), 2.33 nm (P4), and 2.39 nm (P5) (Table 3). The lamellar spacings gradually increased due to increased amounts of extended 2D side chains in the BDTT units. We compared the coherence length (Lc) of the crystalline domains of P1–P5 measured from the in-plane (100) lamellar stacking peaks using the Scherrer equation (Table 3).50–52 A monotonic increase in Lc values was observed as a function of BDTT content, from 8.5 nm (P1), to 9.7 nm (P3), and 11.3 nm (P5). This result suggests that the 2D conjugated alkyldienyl side chains are beneficial in that they induce the formation of larger crystallites in thin films. Importantly, we observed significant differences in the packing orientation of the polymer crystallites between P1–P5 films. The P1 film produced distinct (010) π–π

Figure 2. (a) J–V curves and (b) EQE responses of P1–P5:P(NDI2HD-T) all-PSCs.

Figure 3. Photocurrent density (Jph) versus effective voltage (Veff) of P1–P5 all-PSCs.

Table 3. Morphological Characteristics of P1–P5 Pristine and Blend Films

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<tr>
<th></th>
<th>d100 a</th>
<th>d200 a</th>
<th>Lc (nm)</th>
<th>(nm)</th>
<th>F/E ratio °</th>
<th>domain spacing (nm)</th>
<th>anisotropy parameter b</th>
<th>relative domain purity c</th>
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<tr>
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<td>0.367</td>
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<tr>
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<td>2.29</td>
<td>0.370</td>
<td>9.7</td>
<td>5.3</td>
<td>43.9</td>
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<td>0.74</td>
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<tr>
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<tr>
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<td>10.1</td>
<td>52.4</td>
<td>-0.31</td>
<td>0.74</td>
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</table>

Values associated with pristine films. bValues associated with blend films. Relative face-on/edge-on ratio (F/E) was derived from the (010) peak area of P1–P5 in the range of χ = 0°–45° and χ = 45°–90°.
stacking reflection peaks in both the in-plane and out-of-plane directions, indicating that both edge-on and face-on orientations of P1 crystallites were present in the thin film. With increasing BDTT content, the (010) peak in the in-plane direction began to disappear, and, simultaneously, the (010) peak in the out-of-plane direction became stronger. Therefore, the P5 polymer film contained mostly face-on oriented crystallites. High-order peaks of lamellar stacking up to (300) were observed in P1 thin films, and these peaks decreased monotonically with increasing BDTT content, which confirmed the sequential changes observed in the molecular orientation as a function of BDTT content.

On the basis of the understanding of the para-crystalline behaviors of P1–P5, we investigated the polymer packing structures in P1–P5:P(NDI2HD-T) blend films by GIXS (Figure 4). All samples were prepared under identical conditions used to fabricate optimized devices. Consistent with the observations in the pristine thin films, higher order (h00) lamellar reflection peaks up to (400) in the out-of-plane direction (qz) and pronounced (010) π−π stacking peaks in the in-plane direction (qxy) were seen in the polymer donors with low BDTT contents (e.g., P1 and P2). However, as the BDTT content increased, both peaks faded and a monotonic increase in the intensity of the (010) π−π stacking peaks was observed in the qz direction (inset of Figure 4b). This indicated that the intrinsic molecular orientation of P1–P5 was preserved in the blend films with the P(NDI2HD-T) polymer acceptor. The P(NDI2HD-T) P_A also exhibited strong face-on packing in thin films (Figure S6), and the (001) peak in the qxy direction associated with the P(NDI2HD-T) backbone was preserved in the blend films (Figure 4c). Consequently, it is postulated that the P5 donor with strong face-on orientation likely produced well-defined, face-to-face alignment with P(NDI2HD-T) acceptor at the P_D/P_A interfaces, whereas the P1 donor with mixed orientations led to the misoriented P_D/P_A interfaces.

To quantify the differences in the molecular orientation of P1–P5 in thin films, the pole figures for each of the polymers were obtained (Figure 5). The GIXS patterns for P1, P3, and P5 pristine films were used to elucidate the quantitative differences between polymer orientation in thin films. The pole figure was obtained as follows. First, the (010) π−π stacking peak intensities of P1, P3, and P5 as a function of azimuth angles (χ) and pronounced (010) π−π stacking peaks in the in-plane direction (qxy) were seen in the polymer donors with low BDTT contents (e.g., P1 and P2). However, as the BDTT content increased, both peaks faded and a monotonic increase in the intensity of the (010) π−π stacking peaks was observed in the qz direction (inset of Figure 4b). This indicated that the intrinsic molecular orientation of P1–P5 was preserved in the blend films with the P(NDI2HD-T) polymer acceptor. The P(NDI2HD-T) P_A also exhibited strong face-on packing in thin films (Figure S6), and the (001) peak in the qxy direction associated with the P(NDI2HD-T) backbone was preserved in the blend films (Figure 4c). Consequently, it is postulated that the P5 donor with strong face-on orientation likely produced well-defined, face-to-face alignment with P(NDI2HD-T) acceptor at the P_D/P_A interfaces, whereas the P1 donor with mixed orientations led to the misoriented P_D/P_A interfaces.

Figure 4. (a) 2D GIXS patterns of P1–P5:P(NDI2HD-T) all-PSCs and their line cuts in the (b) out-of-plane and (c) in-plane directions.

Figure 5. Pole figures from the (010) peak area of P1, P3 and P5 films; the fractions correspond to the relative ratios of integrated 0−45° and 45−90° peaks to the summed area.
thin films in portions of 69 and 31%, respectively, resulting in an F/E ratio of 2.2. Upon incorporation of BDTT monomers with 2D side chain, the primarily edge-on orientation was transformed gradually to a face-on orientation. Thin films of P5 had the highest face-on population of 91%, corresponding to an F/E ratio of 10.1. The high population of face-on structures can promote vertical charge transport in all-PSCs.53 The high population of face-on structures can promote vertical charge transport in all-PSCs.53

The high population of face-on structures can promote vertical charge transport in all-PSCs.53–55 In addition, this feature of P5 film is anticipated to promote the formation of face-to-face alignment of the P0 and P1 at the interface and facilitate efficient exciton dissociation.

To gain deeper insight into the impact of 2D side chains on the interfacial orientation of polymers in all-PSCs, transmission RSoXS experiments were performed at different photon energies. RSoXS with a polarized soft X-ray beam allows probing of the in-plane, localized molecular orientation and ordering of the components relative to the P0/P1 interface through analysis of scattering anisotropy.11,34,56–58 First, we prepared P1, P3, P5, and P(NDI2HD-T) pristine films and acquired near edge X-ray absorption fine structure (NEXAFS) profiles to assign bond transition energies of the polymers (Figure S7). All of the polymers exhibited a strong bond transition at a photon energy of 287.5 eV, which is commonly associated with combined contributions of carbon–hydrogen or carbon–sulfur 1s→π* C–H or C–S bond transitions.59 The pronounced peaks at 285.4 eV photon energy were also observed in the P1, P3, and P5 films, which are related to the 1s→π* C=C bond transitions of the conjugated polymer backbone. Since the P(NDI2HD-T) P0 film did not show a distinct bond transition at 285.4 eV, we selected a photon energy of 285.4 eV to compare the peak characteristics of P1, P3, and P5 in blend films without interference from P0 (Figure S8). When we applied a horizontally polarized soft X-ray beam to the samples, distinct contrast between the scattering anisotropy was observed between the three blends. The scattering ring in the P1 blend film was nearly isotropic, but the anisotropy increased in P3 films, and more so in the P5 blend films. Therefore, the P5 blend film exhibited the most anisotropic pattern with stronger scattering intensity in the horizontal direction. Next, we attempted to obtain quantitative differences in the scattering anisotropy of the three blend films using the integrated scattering intensity (ISI) and the following equation,58 (ISIL−ISIL)//(ISIL+ISIL) (a phenomenological anisotropy parameter). ISI∥ and ISI⊥ were calculated from the average sector line cuts (±10°) of the 2D scattering patterns in the perpendicular and parallel directions, respectively (Figure S9, Table 3). The anisotropy ranged from 0 for the P1 blend, to −0.15 for the P3 blend, and −0.31 for the P5 blend. The magnitude of the anisotropy can be changed only when the 1s→π* C=C transition dipole moments from the polymeric backbones are highly aligned (either horizontally or perpendicularly) with the applied electrical field direction. Therefore, this feature indicates the greatly increased extent of molecular orientational order of P5 chains relative to the P0/P1 interface. In contrast, the isotropic 2D scattering pattern of the P1 film suggests the presence of randomly oriented P1 chains relative to the P0/P1 interface. Additional polarized RSoXS results for the P1, P3, P5, and P(NDI2HD-T) pristine films provided further evidence concerning this observation (Figure S10). In stark contrast to the scattering patterns of the blend films, the P1, P3, P5, and P(NDI2HD-T) pristine films showed nearly isotropic scattering patterns. Therefore, it was concluded that high scattering anisotropy of the P5 blend film was the result of molecular anisotropy relative to the P0/P1 interface, attributed to π−π stacking of P5 with the blended P(NDI2HD-T) near the interface and/or additional aggregation of P5 in the blend film.58 The correlated π-orbitals of P5 and P(NDI2HD-T) at the P0/P1 interface are expected to improve exciton dissociation at the interface, which correlates well with the P(E,T) and Jsc values in the all-PSCs.34–36,60

However, extensive interpretation of the chain orientation behaviors, which can be only achieved by appropriate X-ray optical models that require anisotropic optical constants for P1, P3, P5, and P(NDI2HD-T), is beyond the scope of this paper. Recently, Ye et al. thoroughly described the impact of interfacial orientation of the polymer donor (PBDTTBDD-T) on the performance of all-PSCs using polarized RSoXS measurements and optical models.34 They observed strong anisotropic patterns in the PBDTTBDD-T:NDI-based P0 blends with a high anisotropy ratio of −0.45, indicating the face-on alignment of PBDTTBDD-T polymers with respect to the P0/P1 interface. This conclusion is consistent with our observations in this work.

Next we investigated additional morphological characteristics (i.e., the domain spacing and purity) of P1–P5 all-polymer blends using RSoXS at a different photon energy, namely 287.5 eV. At this energy, the material contrast of the blend films was maximized with marginal contribution from mass-thickness differences. Five P1–P5 blend samples were prepared under the optimized device fabrication conditions. RSoXS profiles were plotted as a function of scattering vector q (nm⁻¹) in Figure 6. All of the samples exhibited broad scattering peaks in the range of q = 0.05–0.3 nm⁻¹ and the peaks were centered at similar qpeak values of 0.11–0.15 nm⁻¹. Therefore, the P1–P5 blend films exhibited finely phase-separated BHJ morphologies with similar domain spacings (d = 2π/qpeak) of 43–56 nm (Table 3), which was well-supported by AFM measurements (Figure S11). Also, all of the blend films produced similar PL quenching, suggesting similar domain spacings of the BHJ morphologies of P1–P5 blend films (Figure S12). However, significant differences in the scattering intensities of the P1–P5 blend films were observed. The intensities progressively increased from P1 to P5 blends, indicating a higher purity of Pb and P0P5 domains in blends with Pb5 having higher BDTT contents. The relative root−mean−square composition variation, related to domain purity, is proportional to √ISI (Table 3).61–64 The relative √ISI increased significantly from 0.19 in the P1 blend to 0.74 in the P3 blend, and in the P5 blend, which was used a reference. Thus, the root-mean square composition variations of the P5 blend was determined to be 5.3 times greater than that of the P1 blend. The underlying increased domain purity is attributed to the improved
molecular packing of the P5 polymer, which is in good agreement with UV–vis and GIXS results. The relatively pure domains with finely phase-separated BHJ morphologies of P5 blends yielded improved charge transport and efficient exciton dissociation in all-PSCs.

CONCLUSIONS

In this work, we demonstrated the importance of 2D conjugated side chains (BDTT) for producing efficient all-PSCs based on the model polymer donors, P1–P5. We observed a strong correlation of the BDTT content in the polymer donors with the Jsc and FF values and the resulting photovoltaic performances of the all-PSCs. The increase in BDTT content generated gradual enhancement in the PCEs of all-PSCs from 2.82% (P1), to 3.16% (P2), to 4.41% (P3), to 5.32% (P4), and to 6.60% (P5). From the structural and morphological investigation using GIXS and RSoXS measurements, it was concluded that the use of the π-extended BDTT units enhanced the face-on crystalline domains of P5s in thin films and promoted strong π–π interactions with P_D. These features impacted both the interfacial ordering of the P_Ds and P_P and the relative domain purity in the active blend layer. For example, the P5-based all-polymer blends exhibited the highest coherence length of face-on crystalline domains and the highest domain purity. The dramatic changes in morphological characteristics with side chain composition improved hole mobility and P(η,τ) of P5-based all-PSCs, leading to greatly enhanced Jsc and FF values. The structure–property-performance correlations established in our model system provide important guidelines for designing effective P_Ds and P_P polymers in terms of the side chain structure and demonstrate the importance of controlling the polymer orientation and domain purity to achieve high-performance all-PSCs.

ASSOCIATED CONTENT

Supporting Information

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Materials and methods, detailed experimental procedures, additional data (PDF)

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