JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

Terthiophene-Based D−A Polymer with an Asymmetric Arrangement of Alkyl Chains That Enables Efficient Polymer Solar Cells

Huawei Hu,[†,§,#] Kui Jiang,[†,#] Guofang Yang,[†] Jing Liu,[†] Zhengke Li,[†] Haoran Lin,[†] Yuhang Liu,[†] Jingbo Zhao,[†] Jie Zhang,[∥] Fei Huang,[∥] Yongquan Qu,[‡,§] Wei Ma,[*,‡] and He Yan[*,†,⊥]

[†] Department of Chemistry and Energy Institute, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

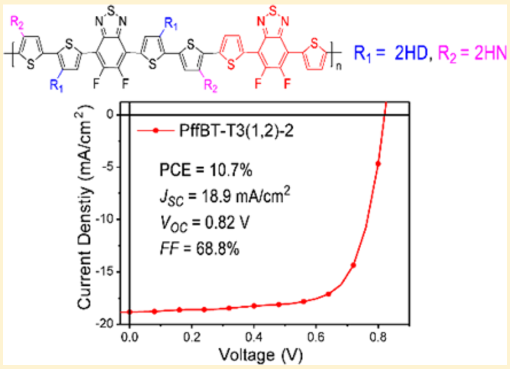
[‡] State Key Laboratory for Mechanical Behavior of Materials, and [§] Center for Applied Chemical Research, Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

[∥] Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, People's Republic of China

[⊥] HKUST-Shenzhen Research Institute, No. 9 Yuexing first RD, Hi-tech Park, Nanshan, Shenzhen 518057, China

Ⓢ *Supporting Information*

ABSTRACT: We report a series of difluorobenzothiadizole (ffBT) and oligothiophene-based polymers with the oligothiophene unit being quaterthiophene (T4), terthiophene (T3), and bithiophene (T2). We demonstrate that a polymer based on ffBT and T3 with an asymmetric arrangement of alkyl chains enables the fabrication of 10.7% efficiency thick-film polymer solar cells (PSCs) without using any processing additives. By decreasing the number of thiophene rings per repeating unit and thus increasing the effective density of the ffBT unit in the polymer backbone, the HOMO and LUMO levels of the T3 polymers are significantly deeper than those of the T4 polymers, and the absorption onset of the T3 polymers is also slightly red-shifted. For the three T3 polymers obtained, the positions and size of the alkyl chains play a critical role in achieving the best PSC performances. The T3 polymer with a commonly known arrangement of alkyl chains (alkyl chains sitting on the first and third thiophenes in a mirror symmetric manner) yields poor morphology and PSC efficiencies. Surprisingly, a T3 polymer with an asymmetric arrangement of alkyl chains (which is later described as having an "asymmetric bi-repeating unit") enables the best-performing PSCs. Morphological studies show that the optimized ffBT-T3 polymer forms a polymer:fullerene morphology that differs significantly from that obtained with T4-based polymers. The morphological changes include a reduced domain size and a reduced extent of polymer crystallinity. The change from T4 to T3 comonomer units and the novel arrangement of alkyl chains in our study provide an important tool to tune the energy levels and morphological properties of donor polymers, which has an overall beneficial effect and leads to enhanced PSC performance.



■ INTRODUCTION

Polymer solar cells (PSCs) based on conjugated polymers and fullerene derivatives have been extensively investigated due to their unique advantages, including mechanical flexibility, light weight, large area and low cost fabrications.[1−4] Over the past decade, great efforts have been spent to maximize the performance of PSCs;[5−15] an important approach has been tuning of the energy levels and optical band gaps of the donor polymers using a donor−acceptor (D−A) copolymer strategy.[16−21] In addition, the selection of proper alkyl chains is essential because they have great influence on the molecular weights, intermolecular interactions, charge transport, and polymer:fullerene morphology, which all play significant roles in the performance of PSCs.[22−26]

Difluorobenzothiadizole (ffBT)-based D−A copolymers have emerged as one of the most successful families of donor polymers that enable the fabrication of high-efficiency PSCs. Wei You and co-workers reported that fluorination of the benzothiadizole unit effectively lowered both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the polymers,[27,28] and that the extent of the shift in the HOMO and LUMO levels could be finely tuned by the density of fluorination on the backbone of the polymer.[29] A similar electronic effect upon fluorination was also observed for the PTB7 polymer family with the HOMO and LUMO levels of the polymers significantly reduced upon fluorination.[11,30,31] We recently reported a D−A copolymer based on ffBT and quaterthiophene (T4), named PffBT4T-2OD, that in several

Received: August 13, 2015

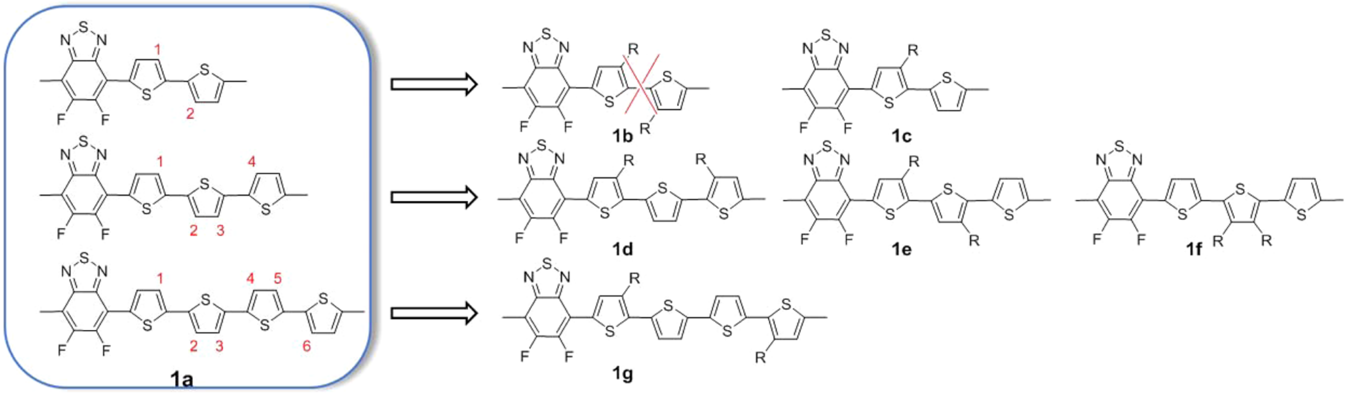
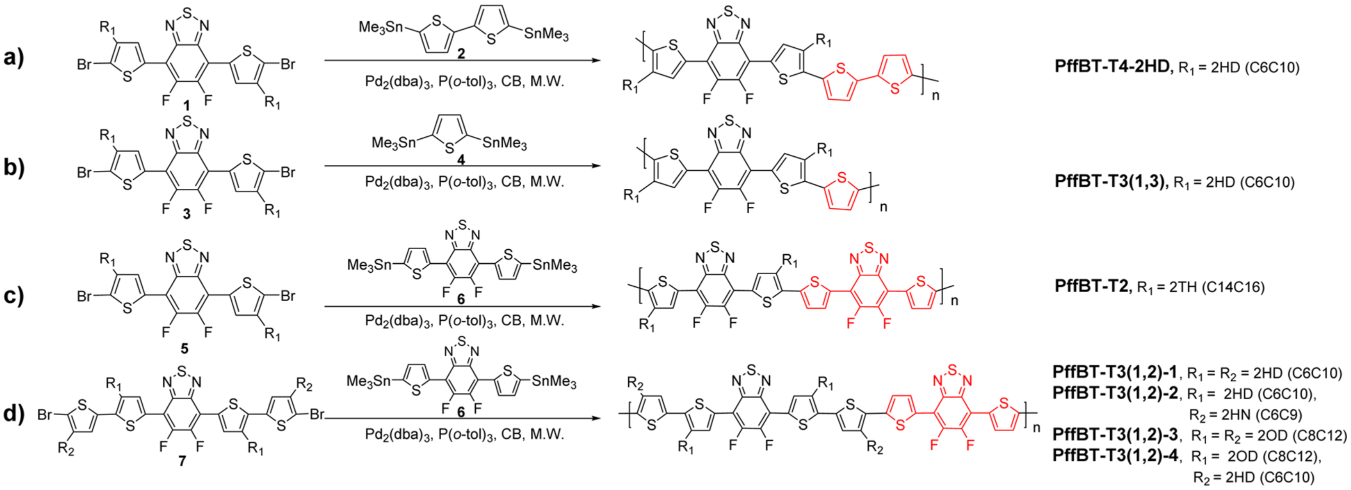


Figure 1. (a) Chemical structures of the repeating units for T2-, T3-, and T4-based polymers. (b–g) Illustration of possible arrangements of alkyl chains on the oligothiophene units.

Scheme 1. Synthetic Routes to the Polymers Presented in This Study



cases allowed the fabrication of high-efficiency (>10%) PSCs when the polymer was combined with different fullerenes.[5] The PffBT4T-2OD polymer features second-position branched alkyl chains (2OD) sitting between the thiophenes in the T4 unit. Such a T4-2OD structure motif introduces a highly temperature-dependent aggregation property (for the PffBT4T-2OD polymer) that can be used to achieve a near-optimum polymer:fullerene morphology and highly efficient PSCs. It is important to note that most high-efficiency PSCs were achieved on the basis of a solution containing an additive named 1,8-diiodooctane,[5,8,11,32] which is a toxic and persistent (due to its high boiling point) chemical that is undesirable in industry processes. The PSC community is actively looking for an approach to achieve high-efficiency PSCs without using any additives.

In this work, we report a D–A polymer based on ffBT and terthiophene with an asymmetric arrangement of alkyl chains that enables the fabrication of highly efficient PSCs up to 10.7% without any additives. The main design rationale for the new polymers is to increase the beneficial electronic effects of ffBT units by reducing the number of thiophene rings per repeating unit and thus increasing the effective density of ffBT units in the polymer backbone. This should enable further decrease in the HOMO and LUMO levels of the ffBT-oligothiophene polymers.

■ RESULTS AND DISCUSSION

Materials Synthesis and Optoelectronic Properties. Density functional theory (DFT) calculations were carried out on several polymer backbones (Figure 1a) that have an increasing density of the ffBT units. The calculated HOMO and LUMO levels are −4.82 and −2.98, −4.88 and −3.02, and −4.96 and −3.11 eV, for the T4, T3, and T2 polymers, respectively. The results of these DFT calculations indeed support that deeper HOMO and LUMO levels can be obtained as the density of the ffBT units increases.

Motivated by the positive results of the DFT calculation, several ffBT polymers based on T4, T3, and T2 units were synthesized. To obtain polymers that are soluble and easily processable for the fabrication of solar cells, it is important to attach branched alkyl chains on the beta positions of the thiophene rings.[33] The use of second-position branched alkyl chains between the thiophene rings is critical, because they are the key structural feature that enables the highly temperature-dependent aggregation property of the polymers.[5] Several possible arrangements of alkyl chains are illustrated in Figure 1b–g. For the positioning of the alkyl chains, the first principle is to avoid putting two alkyl chains on the "head-to-head" positions of two adjacent thiophenes.[34,35] For example, when positions 1 and 2 in the T2 polymer (Figure 1b) are attached with branched alkyl chains, the two thiophene units will be strongly twisted due to the steric hindrance effect caused by the two head-to-head alkyl chains (shown in Figure 1b). Therefore, the T2 polymer has only one possible alkyl chain arrangement (Figure 1c). The common approach for the T4 polymer is to attach alkyl chains on the beta positions of the first and fourth thiophenes and allow the alkyl chains to point inside toward the second and third thiophene rings in a C2 symmetric manner (Figure 1g). For the T3 polymers, there are three possible arrangements of alkyl chains on the terthiophene unit as shown in Figure 1d–f. Among these three possible arrangements, a reasonable and commonly used arrangement is to attach two alkyl chains on the first and third thiophene units in a mirror symmetric manner with reference to the T3 unit (Figure 1d), as reported in the literature.[36,37] Another possibility is to attach the alkyl chains on the first and second thiophene units in a head-to-tail manner (Figure 1e) to form an asymmetric T3 unit. This type of head-to-tail arrangement of alkyl chains is not commonly seen in D–A-type donor polymers, but was used to construct small molecule donors that yielded organic solar cells with high fill factor (FF) and PCEs.[38] Surprisingly, we found that this unusual arrangement of alkyl chains (Figure 1e) enabled a completely different and more favorable polymer:fullerene morphology and thus dramatically enhanced the performance of the PSCs as compared to the reported approach of symmetric arrangement of alkyl chains on the T3 unit as shown in Figure 1d. (Note that the polymer in Figure 1f was not successfully synthesized because the thiophene monomer substituted with two long-branched alkyl chains is extremely difficult to synthesize and purify.)

The synthesis of the new polymers involved in this study is illustrated in Scheme 1. The T4 polymer and the T3 polymer with alkyl chains on the first and third thiophenes (PffBT-T3(1,3)) can be synthesized via a commonly used synthetic route from the dibromide of 5,6-difluoro-4,7-bis(thiophen-2-yl)-2,1,3-benzothiadiazole (T-ffBT-T) and the distannyl reagent of thiophene or bithiophene. However, the synthesis of the T2 polymer or the other T3 polymers must be performed via a different route involving the distannyl reagent of T-ffBT-T. Note that each repeating unit of the T4 and T3(1,3) polymers contains only one ffBT unit, whereas the repeating units of the T2 and T3(1,2) polymers contain two ffBT units that are not chemically equivalent due to the different positions of the alkyl chains relative to those of the ffBT units. In some sense, the T3(1,2) polymers can be described as having an "asymmetric bi-repeating unit".

Regarding the size of the alkyl chains, the common choices of second branched alkyl chains include 2HD (2-hexyldecyl, C6C10), 2OD (2-octyldodecyl, C8C12), and 2DT (2-decyltetradecyl, C10C14). The general guideline of the choice of alkyl chain is to minimize the size of the branched alkyl chains, because unnecessarily long alkyl chains may cause many negative effects, including a reduced absorption coefficient, a lower domain purity, and lower efficiency for PSCs.[5,39,40] At the same time, it is necessary to use an alkyl chain that is sufficiently large to provide sufficient solubility for the polymer. For the T3 polymers, the choices of alkyl chains are 2HD and 2HN (2-hexylnonyl, C6C9). For the T4 polymers, the choices of alkyl chains are 2HD and 2OD. However, the T2 polymers with 2HD, 2OD, and even 2DT alkyl chains exhibit extremely poor solubility. Therefore, an especially long alkyl chain of 2TH (2-tetradecylhexadecyl, C14C16) must be incorporated in the T2 polymer structure to obtain a polymer that is possible to process. In this work, we first examine the differences in the properties of PffBT-T4-2HD, PffBT-T3(1,2)-1, and PffBT-T2, which correspond to the T4, T3, and T2 polymers, respectively. Note that PffBT-T4-2HD and PffBT-T3(1,2)-1 were selected to compare the differences in the properties between the T4 and T3 polymers, because PffBT-T4-2HD and PffBT-T3(1,2)-1 have the same 2HD alkyl chains and allow a fair comparison between the solubility properties of the T4 and T3 polymers.

The optical bandgaps and energy levels of the investigated polymers (summarized in Table 1) were estimated on the basis of the film UV–vis absorption spectra (Figure 2) and cyclic voltammetric measurements (Figure S3). As shown in Figure 2, all of the polymers exhibited an absorption peak at ~640 nm, while PffBT-T4-2HD and PffBT-T2 showed another absorption peak at about 693 and 713 nm, which originate from the strong polymer aggregation, as demonstrated in a previous report.[5] On the other hand, when the oligothiophene unit changes from T4 to T3 then to T2, the effective density of ffBT unit is increased, and the electronic effect of the ffBT unit is thus enhanced, which led to lower HOMO and LUMO levels and also red-shifted absorption. This is the reason that PffBT-T2 exhibits red-shifted absorption compared to PffBT-T4-2HD. Similar observations on the different properties of polymers based on odd and even oligothiophene units have been reported for isoindigo polymers.[41] The T3 polymers indeed exhibit deeper HOMO and LUMO levels than the T4 polymers, which is consistent with the shift in HOMO levels predicted by the DFT calculations and with the change in the open circuit voltages (V_{OC}) of the corresponding PSCs (which will be shown later). A deeper HOMO level and smaller bandgaps should help to achieve higher V_{OC} and larger short-circuit current (J_{SC}) for the PSCs. It is important to note that the LUMO level of the T2 polymer is −3.77 eV, which might

Table 1. Molecular Weight and Electrochemical Properties of Polymers

polymer	M_n (kDa)	M_w (kDa)	E_{HOMO} (eV)[a]	$E_{g,opt}$ (eV)[b]	E_{LUMO} (eV)[c]
PffBT-T4-2HD	13.9	25.8	−5.21	1.65	−3.56
PffBT-T3(1,3)	37.7	56.0	−5.35	1.60	−3.75
PffBT-T3(1,2)-1	72.2	129.0	−5.31	1.63	−3.68
PffBT-T3(1,2)-2	66.1	109.6	−5.31	1.63	−3.68
PffBT-T2	58.4	98.0	−5.38	1.61	−3.77

[a] Measured by cyclic voltammetry. [b] Estimated on the basis of film absorption onset. [c] Calculated by using HOMO and $E_{g,opt}$.

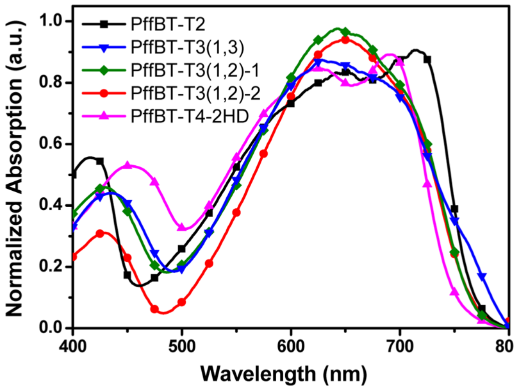


Figure 2. Normalized UV–vis absorption spectra of polymer films.

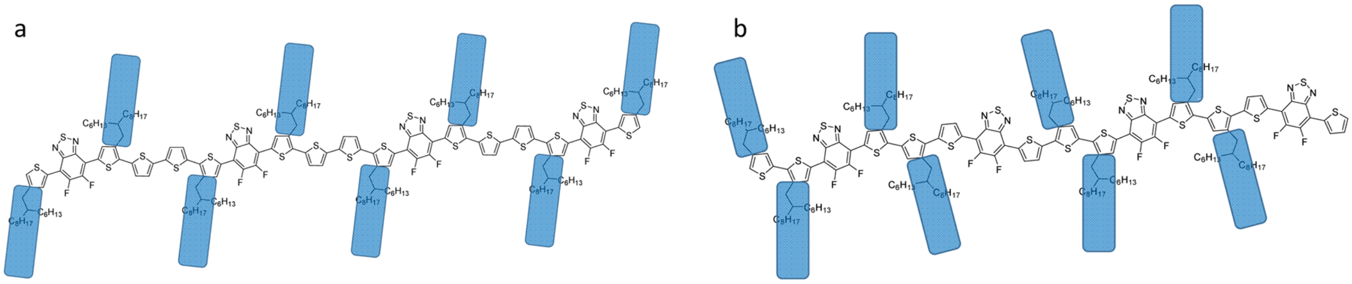


Figure 3. Illustration of the orientations of alkyl chains on the PffBT-T4-2HD (a) and PffBT-T3(1,2)-1 (b) polymers.

Table 2. Photovoltaic Properties of PSCs Based on Polymers/PC$_{71}$BM[a]

polymer	μ_h (cm^2 V^{-1} s^{-1})	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PffBT-T4-2HD	1.3×10^{-3}	0.73 ± 0.01	14.8 ± 0.2	64.4 ± 0.6	7.0 ± 0.2
PffBT-T3(1,3)	6.7×10^{-4}	0.77 ± 0.01	10.6 ± 0.3	45.3 ± 0.9	3.7 ± 0.2
PffBT-T3(1,2)-1	1.2×10^{-3}	0.82 ± 0.01	18.5 ± 0.2	64.1 ± 0.7	9.7 ± 0.3
PffBT-T3(1,2)-2	2.4×10^{-3}	0.82 ± 0.01	18.7 ± 0.2	68.3 ± 0.5	10.5 ± 0.2
PffBT-T2	8.0×10^{-4}	0.88 ± 0.01	10.1 ± 0.3	48.6 ± 0.5	4.3 ± 0.2
PffBT-T4-2OD	1.3×10^{-2}	0.77 ± 0.01	18.2 ± 0.2	73.2 ± 0.7	10.2 ± 0.3

[a] The values for V_{OC}, J_{SC}, and FF are the averages of about 15 devices.

Table 3. Summary of GIWAXS Data[a]

materials	(100) *d* spacing (Å) [±0.01]	(100) coherence length (Å) [±3.0]	(010) *d* spacing (Å) [±0.01]	(010) coherence length (Å) [±0.7]	percentage of face-on area (%) [±2]
PffBT-T4-2HD:PC$_{71}$BM	18.18	170.4	3.50	78.4	0
PffBT-T3(1,3):PC$_{71}$BM	21.61	159.1	3.47	48.4	68
PffBT-T3(1,2)-1:PC$_{71}$BM	19.81	80.1	3.67	31.9	100
PffBT-T3(1,2)-2:PC$_{71}$BM	19.27	85.1	3.65	39.7	100
PffBT-T2:PC$_{71}$BM	24.09	129.1	3.48	75.8	100
PffBT-T4-2OD:PC$_{71}$BM	22.22	235.4	3.55	78.5	100

[a] The values in brackets represent typical errors of the measurements.

be too deep to provide a sufficient LUMO offset with PCBM (LUMO, −4.0 eV), because it is commonly believed that a LUMO offset of 0.3 eV is needed to ensure highly efficient exciton dissociations for polymer:fullerene cells.[42,43]

Polymer Solubility and Crystallinity. The following discussions mainly focus on the comparison of the T3 and T4 polymers, both of which exhibit reasonably good PSC performance. The properties and performance of the T2 polymer will be explained separately in a later paragraph. (Regarding the T2 polymer, it exhibits an extremely poor solubility as compared to the T3 and T4 polymers, because it has only one branched alkyl chain for each ffBT repeating unit and the T3 and T4 polymers have two branched alkyl chains for each repeating unit. The extremely poor solubility of the T2 polymer partially contributes to the poor PSC performance of the PffBT-T2-based devices.) Comparing the T3 and T4 polymers with the same 2HD alkyl chains (PffBT-T4-2HD and PffBT-T3(1,2)-1), the PffBT-T3(1,2)-1 polymer exhibits a significantly enhanced solubility. The M_n of PffBT-T4−2HD is only 14 kDa; yet it could not be dissolved in hot toluene but is only soluble in hot chlorobenzene. In contrast, the PffBT-T3(1,2)-1 polymer with the same 2HD alkyl chains can be readily dissolved in toluene even though the polymer molecular weight is 5 times higher. The PffBT-T4-2HD polymer is found to be significantly more crystalline by grazing incidence wide-angle X-ray scattering (GIWAXS). As shown later, the (100) coherence length (CL) of PffBT-T4-2HD is about 17 nm, which is double that for the PffBT-T3(1,2)-1 polymer. In addition, the temperature-dependent aggregation properties of the T3 and T4 polymers are also compared. It can be clearly seen in Figure S1 that the PffBT-T4-2HD polymer exhibits a strong absorption peak at 693 nm at room temperature, which indicates strong polymer aggregation in solution at room temperature. The PffBT-T3(1,2)-1 does not exhibit such an aggregation peak, indicating much weaker aggregation of the PffBT-T3(1,2)-1 polymer in solution.

The greater solubility of the PffBT-T3(1,2)-1 as compared to the PffBT-T4-2HD polymer is consistent with its lower crystallinity and weaker aggregation. It has been commonly observed in polymer semiconductors that polymers with greater crystallinity often exhibit lower solubility because stronger $\pi-\pi$ stacking between polymer chains makes it more difficult to dissolve the polymers.[44,45] From the perspective of chemical structure, it is also reasonable for the PffBT-T4-2HD polymer to have greater crystallinity and stronger lamellar packing because the quaterthiophene comonomer (with two 2HD alkyl chains) has a C2 symmetry, which allows the PffBT-T4-2HD polymer to form a regioregular polymer structure. As shown in Figure 3a, the 2HD alkyl chains have a regular and parallel arrangement, which can help the interdigitation of the alkyl chains along the lamellar packing direction. The role of C2 symmetric monomers in the formation of regioregular polymer structures is well described in the literature.[5,45−47] In contrast, the T3 unit is not C2 symmetric, and the 2HD alkyl chains on the PffBT-T3(1,2)-1 are not all parallel, which contributes to the lower extent of crystallinity of the PffBT-T3(1,2)-1

DOI: 10.1021/jacs.5b08556
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

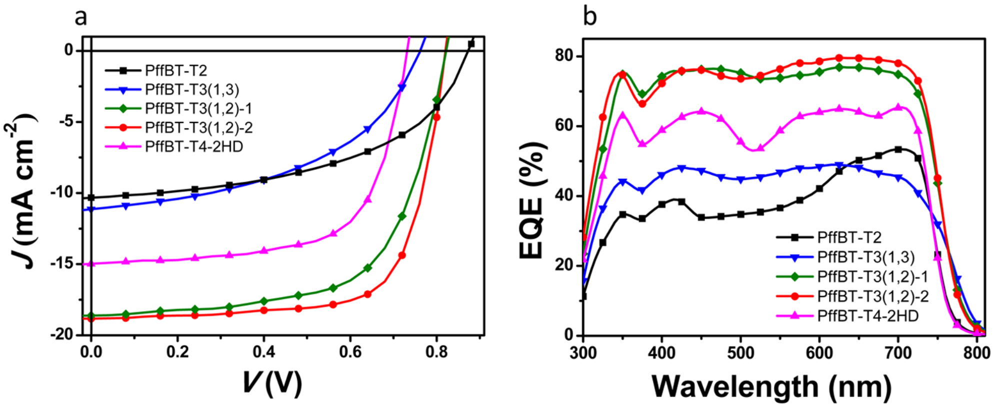


Figure 4. (a) Current−voltage plots under illumination with AM 1.5G solar simulated light (100 mW/cm^2) and (b) EQE spectra of the BHJ solar cells with PC$_{71}$BM.

polymer. As a result, the extent of alkyl chain interdigitation is significantly stronger for the PffBT-T4-2HD polymer than for the PffBT-T3(1,2)-1 polymer, as evidenced by the small lamellar stacking distance of the PffBT-T4-2HD polymer film (data summarized in Table 3).

Photovoltaic Performance. The performance of the PSC devices was investigated using an inverted device structure (ITO/ZnO/polymer:PC$_{71}$BM/V$_2$O$_5$/Al). The characteristic current density−voltage curves of the optimized devices based on these five materials are presented in Figure 4a. For the T4 polymer with 2HD alkyl chains (PffBT-T4-2HD), a PCE of 7.0% (7.2% max) with a V_{OC} of 0.73 V, a J_{SC} of 14.8 mA cm^{-2}, and a FF of 64.4% was obtained. The PffBT-T4-2HD polymer has very poor solubility, which makes it difficult to process and to obtain good device performance. Previous studies have shown that the optimal choice of alkyl chain for the T4 polymer is 2OD and that it is important to obtain reasonably high molecular weights to achieve high-efficiency devices. The performance of the T4 polymer with 2OD alkyl chains has been reported and listed in Table 2 (the average efficiency of PffBT-T4-2OD:PC$_{71}$BM devices is 10.2%). In comparison, the T3 polymer exhibits significantly enhanced solubility. As a result, even the T3 polymer with the 2HD alkyl chain exhibits excellent solubility for device processing. For PffBT-T3(1,2)-1, a V_{OC} as high as 0.82 V was observed, and combined with its high J_{SC} of 18.5 mA cm^{-2} and FF of 64.1%, a high PCE of 9.7% (10.0% max) was obtained. As the solubility of PffBT-T3(1,2)-1 is still more than sufficient, the size of the alkyl chains on PffBT-T3(1,2)-1 could be further reduced to minimize the negative effects of alkyl chains. For this reason, a T3 polymer with a combination of 2HD and 2-hexylnonyl (2HN) alkyl was synthesized (structure shown in Scheme 1). Devices based on PffBT-T3(1,2)-2 showed a PCE of 10.5% (10.7% max) with V_{OC} = 0.82 V, J_{SC} = 18.7 mA cm^{-2}, and FF = 68.3%. Both the J_{SC} and the FF are better for the cells based on PffBT-T3(1,2)-2 than for the cells based on PffBT-T3(1,2)-1. The V_{OC} of the T4-polymer-based cells is 0.77 V, and that of the cells based on T3 polymers is about 0.82 V; this difference can be attributed to the deeper HOMO level of the T3 polymers. In addition, the onset of the absorption and external quantum efficiency (EQE) spectra (Figure 4b) of the T3 polymers is red-shifted by ∼10 nm as compared to that of the T4 polymers, which contributes to the enhanced J_{SC} of the PffBT-T3(1,2)-2 cells. Importantly, the high performance of the PffBT-T3(1,2)-2-based cells was achieved without using the undesirable DIO additive in the active layer processing. These results clearly indicate the beneficial effects of reducing the number of thiophenes and increasing the effective density of the ffBT units.

Morphological Characterization and Correlation to Device Performances. *Comparison of T3- and T4-Based Polymers.* To further understand the performance differences between polymers in this study, GIWAXS and resonant soft X-ray scattering (RSoXS)[48,49] were used to reveal the relationship between device performance and the polymer:fullerene morphology. First, the morphology and the poor performance of PffBT-T4-2HD were investigated. For the PffBT-T4-2HD polymer, although it exhibits better interdigitation and higher crystallinity than the PffBT-T3(1,2) polymers, the low face-on percentage of the PffBT-T4-2HD:PC$_{71}$BM blend should reduce the charge transport ability of the polymer in the vertical direction, which hurts the mobility of the polymer despite its high crystallinity. As a result, the hole mobility of the polymer is 1.3×10^{-3} cm^2 V^{-1} s^{-1}, which is even lower than the PffBT-T3(1,2) polymers. Moreover, the PffBT-T4-2HD polymer has very poor solubility, which makes it difficult to process and to obtain good device performance. Our R-SoXS data also show that the average domain purity of the PffBT-T4-2HD:PC$_{71}$BM blend is ∼78% of that in the PffBT-T4-2OD:PC$_{71}$BM film. The low domain purity also contributes to the lower FF of PffBT-T4-2HD:PC$_{71}$BM-based cells. Next, the morphology of the T3 polymers was studied and compared to that of the T4 polymers (PffBT-T4-2HD or PffBT-T4-2OD). The change of the oligothiophene unit from T4 to T3 has both positive and negative effects on the polymer:fullerene morphology. The negative effect is that the two PffBT-T3(1,2) polymers are significantly less crystalline than the T4-based polymers, as explained in an earlier paragraph. The positive effect is that the median domain sizes (estimated by RSoXS, Figure 5) of the polymer:fullerene blends based on the T3 polymers are reduced from 40 nm for PffBT-T4-2OD to about 31 nm for PffBT-T3(1,2)-1 and 23 nm for PffBT-T3(1,2)-2. The reduced domain size should be beneficial for the performance of PSCs because the 40 nm domain size of PffBT-T4-2OD is slightly larger than the generally accepted optimal domain size (∼20 nm) for PSCs.[50−52] On the other hand, the reduced extent of polymer crystallinity led to slightly lower FF (68.3%) for the PSCs based on T3 polymers than for their T4 counterparts (73.2%). Still, the FF of 68.3% for PffBT-T3(1,2)-2 is an impressive value, as the thickness of the active layer is relatively

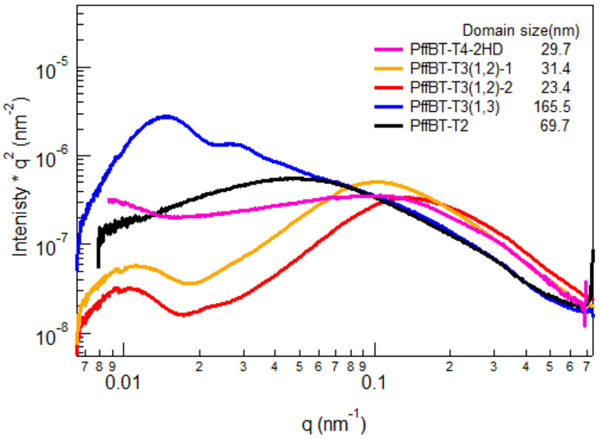


Figure 5. R-SoXS data of polymer:$PC_{71}BM$ blend films.

thick (~250 nm). It is well-known that achieving high FFs for thick-film PSCs is quite challenging. The lower FF of PffBT-T3(1,2)-2-based cells is consistent with its reduced space charge limited current (SCLC) hole mobility in comparison with that of PffBT-T4-2OD. As shown in Table 2, the SCLC hole mobilities of PffBT4T-2OD and PffBT3T(1,2)-2 are about 1.2×10^{-2} and 2.4×10^{-3} cm^2 V^{-1} s^{-1}, respectively. Nevertheless, the overall PSC performance of the devices based on PffBT-T3(1,2)-2 is improved because the benefits of an increased V_{OC}, widened absorption ranges, and a reduced domain size outweigh the loss in FF due to the weaker polymer crystallinity.[28,45] As shown in Figure 4b, the EQE spectrum of PffBT3T(1,2)-2-based devices is red-shifted by ~10 nm as compared to that of PffBT-T4-2HD, which can be attributed to the red-shifted absorption onset of PffBT3T(1,2)-2 (761 nm versus 752 nm for PffBT-T4-2HD). The results show that a change of the comonomer structure from T4 to T3 provides an important tool to optimize the energy levels and the morphology of the polymer:fullerene blends, which results in an overall beneficial effect that led to enhanced PSC efficiencies even without using the DIO additive. Previous study[48] has shown that the use of DIO is critical for PTB7:$PC_{71}BM$-based materials to achieve small domain sizes of ~20 nm that is optimal for PSC operation. In our study, however, the blend of PffBT-T3(1,2)-2:$PC_{71}BM$ exhibits an optimal domain size without using the DIO additive in the solution.

Comparison between the T3 Polymers. It is important that the three T3 polymers can achieve significantly different PSC performance despite the relatively small differences in their chemical structures. In a previous study, a series of T3-based polymers were investigated,[53] but the alkyl chains of the reported T3 polymers were arranged in a symmetric manner on the T3 unit. In our study, the T3 polymer (PffBT-T3(1,3)) with a known and symmetric arrangement of alkyl chains exhibits the worst performance. In such an arrangement, the two 2HD alkyl chains are pointed toward each other in a head-to-head manner with only one thiophene spacer. This could resulte in a significant steric hindrance effect and thus limit the molecular weight of the polymer. The M_n of PffBT-T3(1,3) is 37.7 kDa, which is significantly lower than that of the other two T3-based polymers. It is also found that the polymer:fullerene domain size (estimated by RSoXS) for PffBT-T3(1,3) is 165 nm, which is excessively large for optimal PSC operation. It is noted that the V_{OC} of PffBT-T3(1,3) is slightly lower than that of PffBT-T3(1,2)-1. It has been generally accepted that the V_{OC} of PSCs not only depends on the HOMO level of the polymer, but also other factors such as radiative and nonradiative recombination loss.[54] As the PffBT-T3(1,3):$PC_{71}BM$ blend exhibits an excessively large domain size, the recombination loss in the PffBT-T3(1,3):$PC_{71}BM$ blend could be significantly larger than that of the PffBT-T3(1,2)-1 (or -2):$PC_{71}BM$ blend. This could an important reason why the V_{OC} of PffBT-T3(1,3):$PC_{71}BM$ cell is lower than that estimated by its HOMO level. PffBT-T3(1,3) exhibits greater crystallinity than the other two T3 polymers, as shown by its large (010) and (100) CL. However, the hole mobility of PffBT-T3(1,3) is the worst (6.7×10^{-4} cm^2 V^{-1} s^{-1}), because it does not have a preferential face-on orientation like those of the other two T3 polymers. In contrast, both PffBT-T3(1,2)-1 and PffBT-T3(1,2)-2 films exhibit a (010) peak that is preferentially located in an out-of-plane direction. These negative morphological features can largely explain the poor PSC performance of cells based on PffBT-T3(1,3).

Our comparison of the structures, morphology, and performance of the other two T3 polymers PffBT-T3(1,2)-1 and PffBT-T3(1,2)-2 also provide interesting results. While PffBT-T3(1,2)-1 has two 2HD alkyl chains, PffBT-T3(1,2)-2 has one 2HD alkyl chain and one slightly shorter 2HN alkyl chain on each terthiophene repeating unit. The design rationale of PffBT-T3(1,2)-2 is to slightly reduce the alkyl chains and the solubility of PffBT-T3(1,2)-1 and thus to increase the crystallinity and hole mobility of the polymer. Indeed, the GIWAXS data show that the (010) CL of PffBT-T3(1,2)-2 increases to 3.97 nm, whereas that of PffBT-T3(1,2)-1 is 3.19 nm. The (010) *d*-spacing of PffBT-T3(1,2)-2 is also slightly reduced from 3.67 to 3.65 Å. The lamellar stacking of PffBT-T3(1,2)-2 is also stronger than that of PffBT-T3(1,2)-1; the (100) CL increases from 8.01 to 8.51 nm, and the (100) *d*-spacing decreases from 19.81 to 19.27 nm. The SCLC hole mobility of PffBT-T3(1,2)-2-based cells is 2.4×10^{-3} cm^2 V^{-1} s^{-1}, which is double that of the cells based on PffBT-T3(1,2)-1 (1.2×10^{-3} cm^2 V^{-1} s^{-1}). Although the greater crystallinity of PffBT-T3(1,2)-2 than PffBT-T3(1,2)-1 is the expected result of the reduced alkyl chain size, it is surprising to observe that the domain size of polymer:fullerene blends is significantly smaller for PffBT-T3(1,2)-2 (23.5 nm) than for PffBT-T3(1,2)-1 (31 nm). The reduced domain size of PffBT-T3(1,2)-2 is possibly due to the fact that the polymer contains a mixture of 2HD and 2HN alkyl chains, which appears to have a positive effect on reducing the domain size of polymer:fullerene blends. In addition, the topography of the polymer:fullerene films is investigated by atomic force microscopy (Figure S2); it reveals that the blend films exhibit a smooth surface with reasonable domain sizes except for PffBT-T3(1,3):$PC_{71}BM$, which is in agreement with the RSoXS data.

Comparison between T2 polymer with T3/T4 polymers. For the T2-based polymer, its PSC performance is significantly worse than that of the best T3 and T4 polymers. First, the solubility of the T2-based polymers is extremely poor, because there is only one alkyl chain for each ffBT unit. As a result, when 2HD or 2OD alkyl chains were used on the T2 polymer backbone, the solubility of the obtained polymers is too poor to be soluble in hot chlorobenzene. Even when a much longer 2DT alkyl chain is used on the T2 polymer backbone, the polymer obtained is only slightly soluble in boiling chlorobenzene. The M_n of the T2 polymer with 2DT alkyl chains is only 5 kDa, because the molecular weight is limited by the poor solubility of the polymer. As a result, an excessive long alkyl chain (2TH) is used on the T2 polymer backbone to obtain a polymer that has reasonably high molecular weight and good solubility. In a previous report,[5] excessively long alkyl chains have been shown to have many negative effects such as impure domains and poor lamellar stacking. As the 2DT alkyl chain was already proved to be excessively long and to have caused several negative effects in our report, the current 2TH alkyl chains have six additional carbons as compared to 2DT and are likely to cause more serious negative effects. In addition, the LUMO level of the T2-based polymer is −3.77 eV, which may be too deep to offer a sufficient LUMO offset to ensure efficient exciton dissociation.

Effect of the Molecular Weight and Related Discussion. It is well-known that polymer molecular weight is an important material parameter that could influence polymer aggregation and the morphology of the polymer:fullerene blend.[55−58] Therefore, it is important to study the effect of molecular weights on the performance of the PffBT-T3(1,2)-2 polymer. While the polymer batch with the best 10.7% efficiency has a M_n of 66.1 kDa, a lower molecular weight (M_n = 47.8 kDa) polymer batch was intentionally synthesized for comparison (Table S1). First, the lower molecular weight polymer batch exhibits a better solubility as it can be extracted using chloroform. In contrast, the higher molecular weight polymer is not soluble in hot chloroform and can only be extracted using hot toluene or chlorobenzene. The temperature-dependent aggregation properties of these two polymer batches are then compared in Figure S1. Overall, the shape and the trend of red-shift for the UV−vis absorption spectra of the two polymer batches are rather similar. The absorption spectra of the higher molecular weight polymer are only slightly different with a small shoulder at about 730 nm (Figure S1). PSC devices were fabricated based on the lower molecular weight PffBT-T3(1,2)-2 polymer, and a respectably high efficiency of 10.2% was obtained. These results show that the PffBT-T3(1,2)-2 polymer can yield high-performance (>10%) PSCs when the polymer batches have lower polymer molecular weight and very different solubility properties. This is an important advantage for the scale-up of polymer batches as there is less stringent requirement to control the molecular and solubility properties of the polymer.

It is also noted that some polymers in Table 1 have significantly lower molecular weights than PffBT-T3(1,2)-2. Therefore, it is important to clarify whether the lower molecular weight is the reason that caused their inferior PSC performance. For the PffBT-T4-2HD polymer (M_n = 13.9 kDa), our main conclusion was that it exhibits much poorer solubility than the PffBT-T3 polymers. If the low molecular weight version of PffBT-T4-2HD already exhibits dramatically lower solubility than the PffBT-T3 polymer, the solubility of the higher molecular weight version should be even worse. To prove this point, we attempted to synthesize the PffBT-T4-2HD polymer with higher molecular weights. Because of the poor solubility of the PffBT-T4-2HD polymer, it tends to solidify in the polymerization reaction glassware once the molecular weight reaches a certain level. It is thus generally challenging to synthesize polymers with higher molecular weights. By further synthesis optimizations, a PffBT-T4-2HD polymer batch was obtained with a high M_n of 65.6 kDa. Not surprisingly, the solubility of this polymer batch is much poorer and its processing is extremely difficult as compared to the low molecular weight batch. For the processing of the polymer:fullerene solution, the lower molecular weight PffBT-T4-2HD polymer can be processed at 110 °C, but the higher molecular weight polymer requires the solution and substrate be preheated at 130−140 °C (the substrate also needs to attached onto a preheated metal chuck and spun together on the spin-coater; the preheated metal chuck serves as a "heat reservoir" to slow the cooling of the substrate during the spin-coating process) to obtain a workable active layer film. The poor solubility of the high molecular weight PffBT-T4-2HD polymer led to lower PSC efficiencies of 6.2% (6.4% max).

Influence of Alkyl Chains. To summarize the effect of alkyl chains for the T4 polymer, the 2HD chain is too short and caused poor solubility, while the 2DT chain is too long and introduced other negative morphology effects.[5] The optimal alkyl chain should be the one that is the shortest possible while ensuring sufficient solubility for processing. Apparently, the 2OD chain is a better choice of alkyl chain than 2HD for the T4 polymer. For the PffBT-T3(1,2) polymers, however, the solubility of the polymer family is greatly enhanced due to the less regular polymer structure and thus lower polymer crystallinity. As a result, the T3 polymers with 2HD or slightly shorter chains are still highly soluble for device processing. Therefore, the optimal alkyl chain for the T3 polymers is not 2OD; instead, it should be 2HD or even shorter chains. To further support this point, we synthesized the T3 polymers with 2OD alkyl chains or a mixture of 2OD and 2HD alkyl chains (shown in Scheme 1). These two polymers exhibit better solubility even in dichloromethane. It has been demonstrated in our work and it is general rule of the PSC field that donor polymers with too good solubility do not work efficiently in PSCs. Not surprisingly, the PCE decreases dramatically with longer alkyl chains (Table S1).

Comparing the optimal polymer in the T3 family (PffBT-T3(1,2)-2) with the best one in the T4 family (PffBT-T4-2OD), when using the same $PC_{71}BM$ as the acceptor, the performance of PffBT-T4-2OD is about 10.5%, while the PCE of PffBT-T3(1,2)-2 is 10.7%. However, it is important to point out that the 10.5% efficiency of PffBT-T4-2OD was achieved using DIO, which is a problematic high-boiling and halogenated additive that is not desirable in industry processes. In contrast, the 10.7% PCE of PffBT-T3(1,2)-2 can be achieved without using any additives at all. This offers a tremendous advantage for the easy processing and optimization of PSCs. Because of its higher V_{OC} and wider absorption range than the T4 polymer, the PffBT-T3(1,2)-2 polymer should have more room to further increase its FF and J_{SC} and thus PCE upon extensive device optimizations.

■ CONCLUSIONS

In summary, a series of ffBT and oligothiophene-based D−A copolymers are synthesized and systematically studied. It is shown that the T3 polymer with an asymmetric arrangement of alkyl chains enables highly efficient thick-film PSCs with PCE up to 10.7%. In addition, this high efficiency of T3 polymer-based PSCs was achieved without using any processing additives, which greatly simplifies the processing of PSCs and makes the polymer more suitable for industry applications. By reducing the number of thiophene units per repeating unit, the HOMO and LUMO levels of the polymers are reduced and the absorption onsets of the polymer films are also slightly red-shifted. These positive changes contribute to higher V_{OC} and J_{SC} values for the T3 polymer than for the T4 polymers. By comparing the three T3 polymers that differ in the positions and size of their alkyl chains, it is surprisingly found that the T3 polymer with an unusual head-to-tail arrangement of alkyl chains on the first and second thiophenes exhibits a more favorable morphology and dramatically enhanced performance than the T3 polymer with mirror-symmetric alkyl chains on the first and third thiophenes. Our study also shows that the change from a T4 to a T3 comonomer unit introduces significant differences in the energy levels, solubility, crystallinity, polymer:fullerene morphology, and PSC performances between the T3 and T4 polymers. The polymer design rationales (using a T3 unit with an asymmetric arrangement of alkyl chains) demonstrated in our work provide an effective approach to tune the energy levels and morphology of donor polymers that can be adopted to further increase the efficiency of PSCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08556.

> Synthetic procedures and characterization data of monomers and polymers; temperature-dependent UV absorption of polymer in solution; GIWAXS and AFM images; and details for all device characterizations (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*msewma@mail.xjtu.edu.cn

*hyan@ust.hk

Author Contributions

[#]H.H. and K.J. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was partially supported by the National Basic Research Program of China (973 Program; 2013CB834705 and 2014CB643501), the Hong Kong Research Grants Council (T23-407/13-N, N_HKUST623/13, and 606012), the National Science Foundation of China (nos. 21374090, 51361165301, 21504006, and 21534003), and HKUST president's office through SSTSP scheme (project ref number: EP201). X-ray data were acquired at beamlines 7.3.3[59] and 11.0.1.2[60] at the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

■ REFERENCES

(1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(2) Thompson, B. C.; Frechet, J. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.

(3) Brabec, C. J.; Gowrisanker, S.; Halls, J. J.; Laird, D.; Jia, S.; Williams, S. P. *Adv. Mater.* **2010**, *22*, 3839.

(4) Søndergaard, R.; Hösel, M.; Angmo, D.; Larsen-Olsen, T. T.; Krebs, F. C. *Mater. Today* **2012**, *15*, 36.

(5) Liu, Y.; Zhao, J.; Li, Z.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H.; Ade, H.; Yan, H. *Nat. Commun.* **2014**, *5*, 5293.

(6) Wienk, M. M.; Kroon, J. M.; Verhees, W. J.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, R. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3371.

(7) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.

(8) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497.

(9) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222.

(10) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297.

(11) Chen, H.-Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649.

(12) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, *22*, E135.

(13) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. *Nat. Photonics* **2012**, *6*, 593.

(14) 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.

(15) Guo, X.; Zhou, N.; Lou, S. J.; Smith, J.; Tice, D. B.; Hennek, J. W.; Ortiz, R. P.; Navarrete, J. T. L.; Li, S.; Strzalka, J.; Chen, L. X.; Chang, R. P. H.; Facchetti, A.; Marks, T. J. *Nat. Photonics* **2013**, *7*, 825.

(16) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.

(17) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletete, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732.

(18) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868.

(19) Huang, Y.; Guo, X.; Liu, F.; Huo, L.; Chen, Y.; Russell, T. P.; Han, C. C.; Li, Y.; Hou, J. *Adv. Mater.* **2012**, *24*, 3383.

(20) Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723.

(21) McCulloch, I.; Ashraf, R. S.; Biniek, L.; Bronstein, H.; Combe, C.; Donaghey, J. E.; James, D. I.; Nielsen, C. B.; Schroeder, B. C.; Zhang, W. *Acc. Chem. Res.* **2012**, *45*, 714.

(22) Huang, W. Y.; Lee, C. C.; Wang, S. G.; Han, Y. K.; Chang, M. Y. *J. Electrochem. Soc.* **2010**, *157*, B1336.

(23) Yang, L.; Zhou, H.; You, W. *J. Phys. Chem. C* **2010**, *114*, 16793.

(24) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607.

(25) Cabanetos, C.; El Labban, A.; Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Frechet, J. M.; McGehee, M. D.; Beaujuge, P. M. *J. Am. Chem. Soc.* **2013**, *135*, 4656.

(26) Meager, I.; Ashraf, R. S.; Mollinger, S.; Schroeder, B. C.; Bronstein, H.; Beatrup, D.; Vezie, M. S.; Kirchartz, T.; Salleo, A.; Nelson, J.; McCulloch, I. *J. Am. Chem. Soc.* **2013**, *135*, 11537.

(27) Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.; Liu, S.; You, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 2995.

(28) Stuart, A. C.; Tumbleston, J. R.; Zhou, H.; Li, W.; Liu, S.; Ade, H.; You, W. *J. Am. Chem. Soc.* **2013**, *135*, 1806.

(29) Li, W.; Albrecht, S.; Yang, L.; Roland, S.; Tumbleston, J. R.; McAfee, T.; Yan, L.; Kelly, M. A.; Ade, H.; Neher, D.; You, W. *J. Am. Chem. Soc.* **2014**, *136*, 15566.

(30) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S.-T.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 7792.

(31) Son, H. J.; Wang, W.; Xu, T.; Liang, Y.; Wu, Y.; Li, G.; Yu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1885.

(32) He, Z.; Xiao, B.; Liu, F.; Wu, H.; Yang, Y.; Xiao, S.; Wang, C.; Russell, T. P.; Cao, Y. *Nat. Photonics* **2015**, *9*, 174.

(33) Lei, T.; Wang, J.-Y.; Pei, J. *Chem. Mater.* **2014**, *26*, 594.

(34) Maior, R. M. S.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268.

(35) Gill, R. E.; Malliaras, G. G.; Wildeman, J.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*, 132.

(36) Wang, E.; Ma, Z.; Zhang, Z.; Vandewal, K.; Henriksson, P.; Inganas, O.; Zhang, F.; Andersson, M. R. *J. Am. Chem. Soc.* **2011**, *133*, 14244.

(37) Liu, X.; Cai, P.; Chen, Z.; Zhang, L.; Zhang, X.; Sun, J.; Wang, H.; Chen, J.; Peng, J.; Chen, H.; Cao, Y. *Polymer* **2014**, *55*, 1707.

(38) Sun, K.; Xiao, Z.; Lu, S.; Zajaczkowski, W.; Pisula, W.; Hanssen, E.; White, J. M.; Williamson, R. M.; Subbiah, J.; Ouyang, J.; Holmes, A. B.; Wong, W. W.; Jones, D. J. *Nat. Commun.* **2015**, *6*, 6013.

(39) Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Frechet, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 2180.
(40) Li, W.; Hendriks, K. H.; Furlan, A.; Roelofs, W. S.; Meskers, S. C.; Wienk, M. M.; Janssen, R. A. *Adv. Mater.* **2014**, *26*, 1565.
(41) Ho, C.-C.; Chen, C.-A.; Chang, C.-Y.; Darlingcd, S. B.; Su, W.-F. *J. Mater. Chem. A* **2014**, *2*, 8026.
(42) Halls, J. J. M.; Cornil, J.; dos Santos, D. A.; Silbey, R.; Hwang, D. H.; Holmes, A. B.; Bredas, J. L.; Friend, R. H. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *60*, 5721.
(43) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.
(44) Osaka, I.; Abe, T.; Shinamura, S.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 6852.
(45) Osaka, I.; Shimawaki, M.; Mori, H.; Doi, I.; Miyazaki, E.; Koganezawa, T.; Takimiya, K. *J. Am. Chem. Soc.* **2012**, *134*, 3498.
(46) Wang, Y.; Xin, X.; Lu, Y.; Xiao, T.; Xu, X.; Zhao, N.; Hu, X.; Ong, B. S.; Ng, S. C. *Macromolecules* **2013**, *46*, 9587.
(47) Chen, Z.; Cai, P.; Chen, J.; Liu, X.; Zhang, L.; Lan, L.; Peng, J.; Ma, Y.; Cao, Y. *Adv. Mater.* **2014**, *26*, 2586.
(48) Collins, B. A.; Li, Z.; Tumbleston, J. R.; Gann, E.; McNeill, C. R.; Ade, H. *Adv. Energy Mater.* **2013**, *3*, 65.
(49) Ma, W.; Tumbleston, J. R.; Wang, M.; Gann, E.; Huang, F.; Ade, H. *Adv. Energy Mater.* **2013**, *3*, 864.
(50) Hoppe, H.; Niggemann, M.; Winder, C.; Kraut, J.; Hiesgen, R.; Hinsch, A.; Meissner, D.; Sariciftci, N. S. *Adv. Funct. Mater.* **2004**, *14*, 1005.
(51) Shaw, P. E.; Ruseckas, A.; Samuel, I. D. W. *Adv. Mater.* **2008**, *20*, 3516.
(52) Dou, L.; You, J.; Hong, Z.; Xu, Z.; Li, G.; Street, R. A.; Yang, Y. *Adv. Mater.* **2013**, *25*, 6642.
(53) Zhou, N.; Guo, X.; Ortiz, R. P.; Harschneck, T.; Manley, E. F.; Lou, S. J.; Hartnett, P. E.; Yu, X.; Horwitz, N. E.; Burrezo, P. M.; Aldrich, T. J.; Lopez Navarrete, J. T.; Wasielewski, M. R.; Chen, L. X.; Chang, R. P.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2015**, *137*, 12565.
(54) Vandewal, K.; Ma, Z.; Bergqvist, J.; Tang, Z.; Wang, E.; Henriksson, P.; Tvingstedt, K.; Andersson, M. R.; Zhang, F.; Inganäs, O. *Adv. Funct. Mater.* **2012**, *22*, 3480.
(55) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. *Nat. Chem.* **2009**, *1*, 657.
(56) Tong, M.; Cho, S.; Rogers, J. T.; Schmidt, K.; Hsu, B. B. Y.; Moses, D.; Coffin, R. C.; Kramer, E. J.; Bazan, G. C.; Heeger, A. J. *Adv. Funct. Mater.* **2010**, *20*, 3959.
(57) Hendriks, K. H.; Heintges, G. H.; Gevaerts, V. S.; Wienk, M. M.; Janssen, R. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 8341.
(58) Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Labban, A. E.; Tassone, C. J.; Toney, M. F.; Fréchet, J. M. J.; Beaujuge, P. M.; McGehee, M. D. *Adv. Energy Mater.* **2014**, *4*, 1311733.
(59) Alexander, H.; Wim, B.; James, G.; Eric, S.; Eliot, G.; Rick, K.; Alastair, M.; Matthew, C.; Bruce, R.; Howard, P. *J. Phys. Conf. Ser.* **2010**, *247*, 012007.
(60) Gann, E.; Young, A. T.; Collins, B. A.; Yan, H.; Nasiatka, J.; Padmore, H. A.; Ade, H.; Hexemer, A.; Wang, C. *Rev. Sci. Instrum.* **2012**, *83*, 045110.