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# Tailored donor-acceptor polymers with an A-D1-A-D2 structure: controlling intermolecular interactions to enable enhanced polymer photovoltaic devices

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**KEYWORDS:** A-D1-A-D2 polymer, stepwise syntheses, regioselectivity, intermolecular interactions, polymer photovoltaics

**ABSTRACT:** Extensive efforts have been made to develop novel conjugated polymers that give improved performance in organic photovoltaic devices. The use of polymers based on alternating electron donating and electron accepting units not only allows the frontier molecular orbitals to be tuned to maximize the open-circuit voltage of the devices, but also controls the optical band gap to increase the number of photons absorbed and thus modifies the other critical device parameter – the short circuit current. In fact, varying the non-chromophoric components of a polymer is often secondary to the efforts to adjust the intermolecular aggregates and improve the charge-carrier mobility. Here, we introduce an approach to polymer synthesis that facilitates simultaneous control over both the structural and electronic properties of the polymers. Through the use of a tailored multi-component acceptor-donor-acceptor (A-D-A) intermediate, polymers with the unique structure A-D1-A-D2 can be prepared. This approach enables variations in the donor fragment substituents such that control over both the polymer regiochemistry and solubility is possible. This control results in improved intermolecular  $\pi$ -stacking interactions and therefore enhanced charge-carrier mobility. Solar cells using the A-D1-A-D2 structural polymer show short-circuit current densities that are twice that of the simple, random analogue while still maintaining an identical open-circuit voltage. The key finding of this work is that polymers with an A-D1-A-D2 structure offer significant performance benefits over both regioregular and random A-D polymers. The chemical synthesis approach that enables the preparation of A-D1-A-D2 polymers therefore represents a promising new route to materials for high efficiency organic photovoltaic devices.

## ■ INTRODUCTION

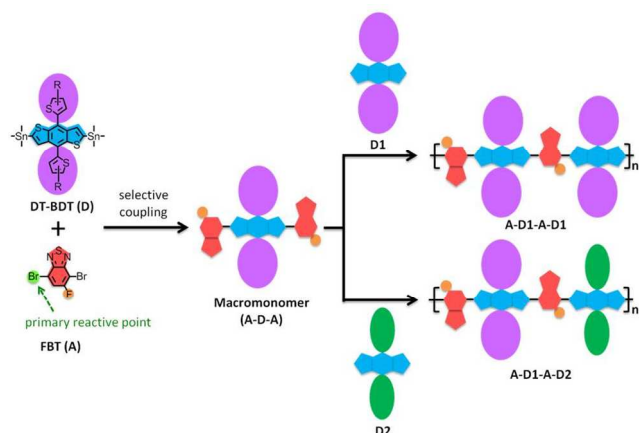
Bulk heterojunction (BHJ) organic photovoltaics (OPVs), based on blends of conjugated polymers and soluble fullerene derivatives, have attracted attention due to their unique advantages of solution-processability, flexibility, light weight, large area and low cost production.<sup>1</sup> Over the last few years, organic chemists and material scientists have been working towards developing novel molecular structures and device architectures to improve the performance of photovoltaic devices.<sup>2</sup> To maximize the performance of OPV devices,<sup>3</sup> attention has shifted beyond just the molecular formula to other considerations such as molecular weight characteristics,<sup>4</sup> chemical and thermal stabilities,<sup>5</sup> end-group contributions,<sup>6</sup> extrinsic impurities,<sup>7</sup> as well as intra- and intermolecular charge carrier mobilities.<sup>8</sup> In addition, strategies such as the use of annealing processes or additives,<sup>9</sup> as well as the use of interfacial materials,<sup>10</sup> have been employed.

Progress due to advances in the chemical structure of materials has mainly come through the use of a donor-acceptor (D-A) approach - polymers based on alternating fragments of electron rich and electron poor groups. This combination allows the molecular orbitals to be tuned so as to enable intramolecular charge transfer (ICT).<sup>11</sup> The open circuit voltage ( $V_{oc}$ ) of OPVs is directly related to the gap between the highest occupied molecular orbital (HOMO) of the polymer and lowest unoccupied molecular orbital (LUMO) of the fullerene. Tuning of the polymer molecular orbitals therefore enables the  $V_{oc}$  to be maximized. While straightforward in design and practice, the use of simple, D-A polymers has

a number of drawbacks. Firstly, conventional polycondensation polymerizations do not allow regioselectivity when asymmetric monomers are employed. As such, there is no control over the orientation of functional groups with respect to each other. Regioregular polymers have a regular, alternating structure whereas random polymers have substituents that are randomly oriented along the chain. It is well known that variations in molecular order reduce intermolecular  $\pi$ -stacking interactions that in turn can limit charge transport through polymer films.<sup>12</sup> A second disadvantage of simple D-A polymers is that there are only two variables, the solubilising groups on the acceptor and donor fragments. This means that the solubility of the polymer can only be altered by changing all of the solubilising groups on a donor or acceptor fragment at once. Such a change could dramatically alter the properties of the polymer. A recent perspective article emphasised how the size and topology of side chains as well as the orientation of repeating units can influence the macroscopic properties of polymers.<sup>13</sup>

The design strategy conceived in this work is illustrated in Scheme 1. We present a stepwise synthetic strategy, based on an intermediate A-D-A intermediate, which provides simultaneous control over both the polymer regiochemistry and solubility. In this terminology, “A” represents an electron accepting group and “D” represents an electron donating group. This route provides access to a series of  $\pi$ -conjugated polymers based on both A-D1-A-D1 and A-D1-A-D2 structures. In the latter, two different donor fragments (D1 and D2) are used and the structure of the polymer is controlled. In side-by-side comparisons we demonstrate that by

controlling the orientation of substituents and the amount of non-chromophoric components in the polymer, the macromolecular interactions can be enhanced which in turn lead to significant improvements in the short-circuit current densities of the OPVs.



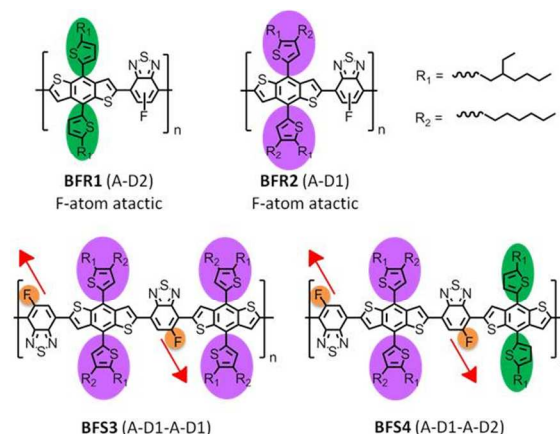
**Scheme 1.** Design strategy based on an A-D-A intermediate. The different coloured ellipses on D1 and D2 represent different substituents.

As outlined above, our strategy enables two different donor fragments to be used while still maintaining an alternating D-A structure. Janssen *et al.* have recently shown that combining the properties of multiple D-A copolymer systems can have advantageous benefits.<sup>14</sup> Patil *et al.* have described an A1-D-A2-D polymer for use in OFETs where optimized chain packing and the formation of large crystalline domains in the solid state dramatically enhanced charge-carrier mobility.<sup>15</sup> Our design strategy is distinct in that it extends on these ideas by also providing a means to control the regiochemistry of the polymer through the fixed orientation of the acceptor fragments. To demonstrate the strategy we sought donor and acceptor fragments that would i) enable variation in the positioning of side chains and ii) enable controllable reactivity in an asymmetric monomer. After a review of the literature dithienyl-benzo[1,2-b:4,5-b']dithiophene (DT-BDT)<sup>16</sup> and 5-fluoro-2,1,3-benzothiadiazole (FBT)<sup>17</sup> were selected as they could satisfy both requirements. Compared with other well-known donor units, such as silafluorene<sup>18</sup> or dithienosilole,<sup>19</sup> in which two out-of-plane side chains have to be located on the fused heteroatom between the aromatic rings, the DT-BDT unit can provide multiple positions for solubilizing substituents with varied out-of-plane dihedral angles. For the acceptor fragment, mono-fluoro substituted benzothiadiazole (FBT) is one of only two reported acceptor units (the other is pyridalthiadiazole<sup>20</sup>), which demonstrates asymmetric reactivity between ortho- and meta-positions.

## RESULTS AND DISCUSSION

**Synthesis.** To begin, we prepared two DT-BDT monomers (D1 and D2, Figure S3 in the Supporting Information) as donor units with various substituted alkyl-chains, as well as the acceptor monomer, 3,6-dibromo-5-fluoro-2,1,3-benzothiadiazole (FBT) (A, Figure S3). By using direct or stepwise synthesis methods, four novel DT-BDT-FBT based conjugated polymers with either random (BFR1 and BFR2) or regioregular (BFS3 and BFS4) orientations in the polymer backbone were achieved, Scheme 2. The random and regioregular labels refer to the orientation of the fluorine atom on the FBT fragment with respect to the donor fragment. The synthetic routes are shown in Figure S3. The branched 2-ethylhexyl chain was firstly used on the DTBDT units

in an attempt to ensure adequate solubility of the target polymers. Unfortunately, the first random copolymer BFR1 demonstrated limited solubility and could not be processed using common solvents. Accordingly, an extra linear hexyl chain was added to the design, resulting in the second random copolymer BFR2 with high solubility in chloroform, chlorobenzene and dichlorobenzene. Polymer BFR2 is a control for comparison with the regioregular polymers BFS3 and BFS4.



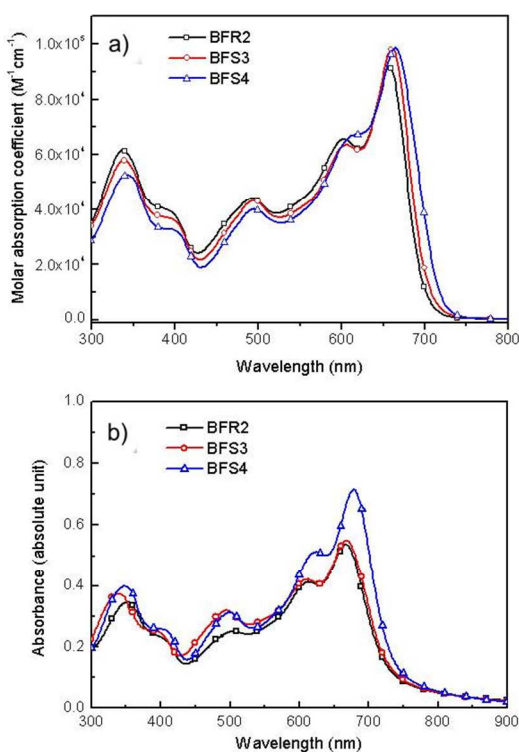
**Scheme 2.** The repeat units of the DT-BDT-FBT based polymers (random F-atom arranged BFR1 and BFR2, regioregular BFS3 and BFS4). The coloured ellipses highlight the different solubilizing groups and the red arrows emphasise the regiochemical control.

Polymers BFS3 and BFS4 were prepared in a two-step route via an A-D1-A intermediate. Control over the structure of the intermediate was achieved due to the preferential reaction of the Pd-catalysed Stille coupling at the position meta- to the fluorine atom on the FBT group. This asymmetric reactivity gave the A-D1-A intermediate in yields as high as 90%. The proposed regiochemical structure was confirmed by 2D NMR spectroscopy (Figure S4). No proton peaks were observed from A or D1 starting materials or from their polymeric side product. The A-D1-A intermediate was then used to prepare the two regioregular, conjugated polymers BFS3 and BFS4. Coupling A-D1-A with monomer D1 and D2, respectively, varied the amounts of pendant side chains while keeping the basic conjugated polymer backbone unchanged. BFR2 and BFS3 are structural isomers differing only in the fact that in the latter the position of the fluorine atom is controlled while in the former it is random. Polymer BFS4 has a lower proportion of non-chromophoric groups while still maintaining high solubility in common solvents.

**Thermal, Optical and Optoelectrical Properties.** High temperature gel permeation chromatography (HT-GPC) was employed to evaluate the molecular weight distribution of the conjugated polymers. Although the random polymer BFR1 showed poor solubility and could not be analyzed, the other three polymers were soluble in 1,2,4-trichlorobenzene which is used as the eluent in the HT-GPC system. The regioregular polymer BFS4 was prepared with a high molecular weight with  $M_n = 46$  kDa and PDI = 2.8. For comparison, batches of the two regioregular polymers BFS3 and BFS4 were synthesised with similar molecular weights and polydispersity as the random counterpart BFR2. (Figure S5).

The molar extinction coefficients of the three, soluble, conjugated polymers in chloroform solutions with a concentration of  $10^{-6}$  M and the absolute absorbance spectra of neat, 100 nm thick films are shown in Figure 1 and the data listed in Table 1. In dilute solu-

tions, the main absorption band of polymer **BFS4** is bathochromically shifted and broadened to some extent in comparison to that of its analogue **BFS3** and random counterpart **BFR2**. This difference can be attributed to enhanced intermolecular  $\pi$ - $\pi$  interactions resulting from the reduced size of the pendant side groups and the regioregular arrangement of the polymer main chain.<sup>21</sup> In the solid state absorption spectra these differences were even more pronounced. The maximum absorption edge of **BFR2** and **BFS3** were at 778 nm and 783 nm, respectively, and 793 nm for **BFS4**. Furthermore, the absorption intensity of **BFS4** as a thin film was higher than the other two polymers, an observation that is consistent with the reduction of the proportion of non-chromophoric alkyl-chains in the polymer.<sup>22</sup> The onset of the film absorbance spectra were used to estimate the HOMO-LUMO gaps of the three polymers, **BFR2**, **BFS3**, and **BFS4**. Photoelectron spectroscopy in air (PESA) was applied to estimate the highest occupied molecular orbital (HOMO) of these conjugated polymers in thin films (Figure S6)<sup>23</sup> The experimentally determined HOMO values and the calculated LUMO levels are summarized in Table 1. It is clear that the variations to the polymers described here do not have a significant effect on the energy levels of the materials.



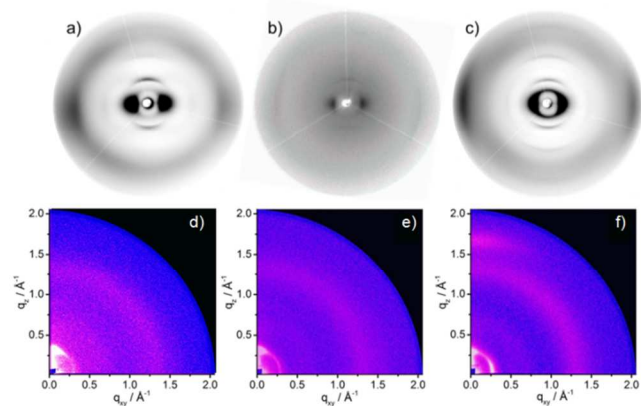
**Figure 1.** UV-Vis absorption spectra of DT-BDT-FBT polymers. a, Molar absorptivities ( $\epsilon$ ) of **BFR2** (square), **BFS3** (round) and **BFS4** (triangle) in  $10^{-6}$ M chloroform solutions. b, Absolute absorbance spectra of the corresponding polymers in 100 nm films.

**Table 1.** Optical, optoelectronic and frontier molecular orbital level data.

Polymer	$\lambda_{\max}$	$\lambda_{\text{edge}}$	$\lambda_{\max}$	$\lambda_{\text{edge}}$	$E_g^{\text{opt}}$	HOMO	LUMO
	(nm)	(nm)	(nm)	(nm)			
	Solution <sup>[a]</sup>		Film <sup>[b]</sup>		(eV) <sup>[c]</sup>	(eV) <sup>[d]</sup>	(eV)
<b>BFR2</b>	656	733	667	778	1.59	5.20	3.61
<b>BFS3</b>	661	744	668	783	1.58	5.20	3.62
<b>BFS4</b>	665	749	678	793	1.56	5.15	3.59

[a]  $10^{-6}$  M in chloroform solution, [b] 100 nm thick film, [c] calculated from  $\lambda_{\text{edge}}$  of film, [d] estimated by PESA.

**Intermolecular Interactions.** The organisation of the regioregular polymers **BFR2**, **BFS3** and **BFS4** in the bulk solid state was investigated by using two-dimensional, wide-angle X-ray scattering (2D-WAXS) measurements (Figure 2a-c).<sup>29</sup> Fibers of the neat polymers were macroscopically aligned by extrusion and no further thermal pre- or post-annealing processes were applied in order to ensure the same thermal treatment as during the device fabrication. At 30 °C the polymers revealed a characteristic pattern with reflections being distributed in the equatorial and meridional planes.<sup>30</sup> However, significant differences in intensity and position of the reflections were evident for both systems. The positions of the reflections of **BFR2** and **BFS3** in the equatorial small-angle and wide-angle region are similar (Figures 2a,b and S7). However, **BFS3** displayed only a faint 2D pattern due to its poor scattering. For both polymers, the equatorial small-angle reflections were attributed to a chain-to-chain distance of 19.65 Å between the lamellar structures; the broad wide-angle scattering intensity on the same plane was ascribed to a quite large stacking distance of 4.18 Å and the meridional, middle-angle position scattering reflection, corresponding to a d-spacing of 12.0 Å for **BFR2** and 12.65 Å for **BFS3**, was assigned to the length of the single DT-BDT repeat unit of polymer chain.<sup>22</sup> By contrast, **BFS4** exhibited sharper, more distinct and a higher number of reflections with a chain-to-chain distance of 24.51 Å, much smaller stacking distance of 3.66 Å and an unchanged repeating spacing between DT-BDT units of 12.8 Å (Figure 2c and S7). Thus, the significantly closer packing and higher crystallinity for **BFS4** in the bulk are in agreement with the absorption data and could be related to the polymer structure.



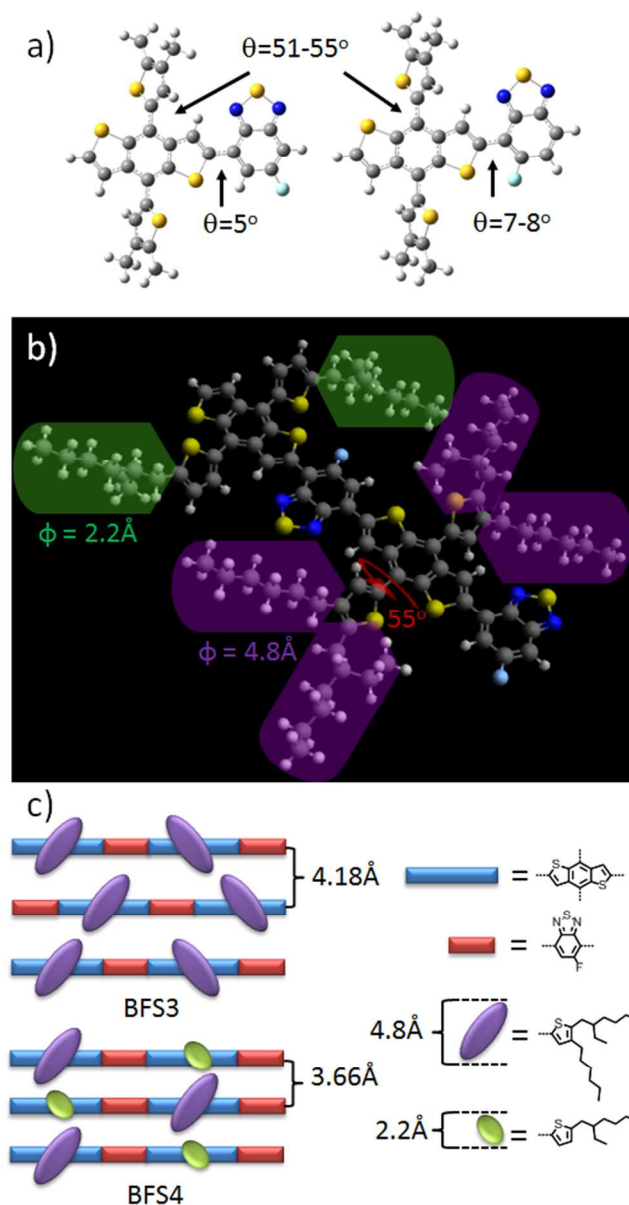
**Figure 2.** Two-dimensional WAXS patterns of filament extruded polymers of a) **BFR2**, b) **BFS3** and c) **BFS4** at 30 °C and GIWAXS patterns of d) **BFR2/PC<sub>61</sub>BM**, e) **BFS3/PC<sub>61</sub>BM** and f) **BFS4/PC<sub>61</sub>BM** thin films.

To gain further information about the organisation in the solar cell, grazing incidence WAXS (GIWAXS) on thin films was performed (Figure 2d-f). The thin films were prepared in the same way as for the devices including the PEDOT:PSS surface and the blending with PC<sub>61</sub>BM and 1,8-diiodooctane. In both cases, the order was lower than in the bulk as indicated by the lack of higher order reflections. This could be attributed to the spin-coating process. Nevertheless, a significant distinction in surface organisation between the polymers could be derived. The meridional position of the wide-angle scattering intensity at  $q_{xy} = 0 \text{ \AA}^{-1}$  and  $q_z = 1.72 \text{ \AA}^{-1}$  in the pattern for **BFS4** (Figures 2f and S8), which was related to the stacking distance of 3.66 Å, was characteristic for a face-on arrangement of the backbones towards the surface. In accordance with this alignment, the chain-to-chain reflections appeared in the small-angle equatorial plane. Additional meridional small-angle



reflections were due to an edge-on orientation of a certain misaligned polymer fraction leading to a mixed organization with a coexistent face- and edge-on arrangement in the film.<sup>31</sup> It is expected that a face-on polymer arrangement favors the charge carrier perpendicular to the surface as is the case in a solar cell. By contrast, **BFR2** and **BFS3** reveal only a meridional small-angle scattering intensity and no  $\pi$ -stacking reflection indicating low order in edge-on arranged polymer lamellae (Figures 2d, 2e and S8). Therefore, with respect to both factors, better packing and face-on orientation, the data suggests that **BFS4** is more optimized for solar cell applications than **BFS3**.

Computational analysis of the D-A dimer fragment in the two regioregular polymers (**BFS3** and **BFS4**) by density functional theory (DFT)<sup>27</sup> at the B3LYP/6-31+G(d,p) level of theory estimated that the dihedral angle between donor and acceptor units is only 5-7°, meaning that the polymer backbones should be planar (Figure 3a). The pendant thiophene unit on the **BDT** unit displayed a calculated dihedral angle around 51-55°. This means that the alkyl substituents may hinder close packing of the polymer chains. We then used a semi-empirical AM1 method<sup>28</sup> to calculate the volume of space occupied by the various alkyl chains. For the bis-substituted donor fragment the combination of the para-substituted ethylhexyl and meta-substituted hexyl chains occupy a sphere with a maximum diameter of 4.8 Å (Figure 3b). By contrast, for the mono-substituted donor fragment, with only a single para-substituted ethylhexyl group, the maximum size of a sphere occupied by the alkyl chains is significantly smaller, around 2.2 Å. As noted previously, the 2DWAXS analysis showed that stacking distance reduced by around 0.52 Å from 4.18 Å for **BFS3** to 3.66 Å for **BFS4** for un-annealed bulk organization. For **BFS3**, every donor fragment features the large (4.8 Å) bis-substituted group. Two adjacent bis-substituted groups when aligned directly would fill a space that is larger than the measured  $\pi$ - $\pi$  stacking distance. It is therefore likely that, in **BFS3**, the donor fragments in adjacent chains are offset with respect to each other (Figure 3c). By contrast, the presence of the smaller, mono-substituted donor fragment in **BFS4** should not hinder the close approach of donor units on adjacent chains as the sum of the calculated maximum distance occupied by a large and small donor unit  $[(4.8 + 2.2 \text{ Å})/2] = 3.5 \text{ Å}$  is less than the measured stacking distance of 3.66 Å. It has previously been shown that D-A polymers are known to prefer an arrangement where D and A groups on adjacent chains align with the same groups above and below in a columnar fashion.<sup>29</sup> By reducing the steric bulk of the substituents in **BFS4** we postulate that an arrangement closer to an aligned, columnar structure (Figure 3c) is possible and is indeed consistent with the WAXS data. Such an outcome is directly attributable to the structural control provided by our synthetic method.

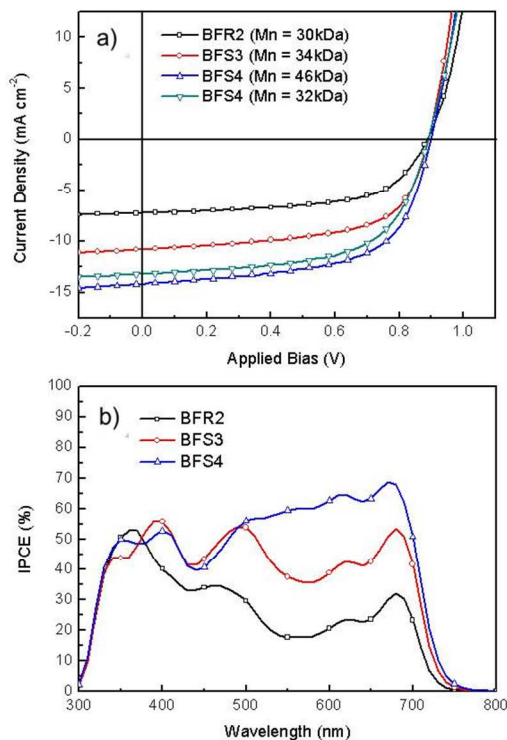


**Figure 3.** Computational representations. a, B3LYP/6-31+G(d,p) calculation of D-A dimer fragments. b, 3D simulation (semi-empirical AM1 model) of repeating unit A-D1-A-D2 in **BFS4**. c, Schematic edge-view illustration of the possible supramolecular organization in **BFS3** and **BFS4**.

**Device Performances.** In order to investigate the influence of the intermolecular interactions of the conjugated polymers on their electronic properties, single charge carrier devices were prepared. The measured current density/voltage (J-V) characteristics were then fitted by using the space-charge-limited current (SCLC) model.<sup>30</sup> At a typical electric field of  $10^5 \text{ V cm}^{-1}$  (corresponding to an applied voltage of 1 V to a 100 nm neat polymer device), the observed occurrence of a SCLC enabled a direct estimate of the hole mobility of  $2.3 \times 10^{-5}$ ,  $2.0 \times 10^{-4}$ , and  $1.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for **BFR2**, **BFS3** and **BFS4**, respectively (Figure S9). At a high voltage of 5 V, **BFS4** also exhibited a field-dependent electron mobility<sup>31</sup> of  $7.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (at  $5 \times 10^5 \text{ V cm}^{-1}$ , Figure S10). Notably, neither of the other two polymers showed any measurable electron mobility. The observation that **BFS4** has both the highest hole mobility and a measurable electron mobility is consistent with the highest order and close  $\pi$ -stacking distance as derived

from the structural analysis, and the structure postulated above whereby the reduced steric bulk permits an arrangement that is closer to a columnar structure. The high charge mobility for **BFS4** is also desirable with respect to increasing the short circuit current density ( $J_{SC}$ ) in OPV devices.

OPV devices were fabricated using these three polymers (**BFR2**, **BFS3** and **BFS4**), in turn, as the electron donor and PC<sub>61</sub>BM as the electron acceptor. The device structure was ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM/PFN/Al. PFN is a polyelectrolyte that is used as an interlayer to assist with charge extraction.<sup>32</sup> The optimized weight ratio of polymer to PC<sub>61</sub>BM is 1:1.4. About 2% (1,8-diodooctane (DIO)/o-dichlorobenzene (o-DCB), v/v) of DIO was added as an additive to enable differential solubility.<sup>33</sup> No thermal pre- or post-annealing processes were applied during the device fabrication. Device J-V characteristics are shown in Figure 4a and the parameters are listed in Table 2. From the J-V curves, a clear improvement of photovoltaic properties was observed in going from the random to the regioregular polymers. The  $V_{OC}$  and fill factor (FF) values were in the same range for the three polymers, a finding that is consistent with their similar HOMO levels, equal D/A ratio and identical device structures. However, the  $J_{SC}$  values for devices based on **BFS4** were significantly increased in comparison with those of **BFS3** and **BFR2**, even with similar molecular weights. Notably, a  $J_{SC}$  as high as 14.20 mA/cm<sup>2</sup> was obtained for devices based on **BFS4** and PC<sub>61</sub>BM. Combined with its high  $V_{OC}$  and FF, a high PCE of 7.38±0.4% (average from 40 devices, simulated sunlight, AM 1.5G, 100 mW cm<sup>-2</sup>) was achieved, the highest measured PCE being 7.80%. To the best of our knowledge, the only reports of higher PCEs from polymer OPV devices make use of the higher cost C<sub>70</sub> derivative.



**Figure 4.** OPV performance of DT-BDT-FBT polymers. a, Photocurrent density–voltage (J-V) curves of **BFR2** (square), **BFS3** (round) and **BFS4** (triangles) under illumination of AM 1.5G, 100 mW cm<sup>-2</sup>. b, IPCE curves of the corresponding OPVs.

To further explore the properties of the devices, the incident photon-to-current efficiency (IPCE) of the devices based on the three

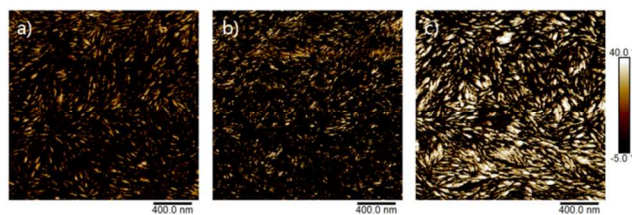
polymers was measured. The IPCE curves are shown in Figure 4b. All the devices exhibited a good response to short-wavelength sunlight in the range 300-450 nm, attributable to the contribution of PC<sub>61</sub>BM.<sup>34</sup> Their photo conversion efficiencies in the long-wavelength range, 450-750 nm, which correspond to the absorption of the polymers,<sup>35</sup> varied from 17-32% to 36-54% and up to 60-68% for **BFR2**, **BFS3** and **BFS4**, respectively. The integrated IPCE curves give calculated  $J_{SC}$ s of 7.5, 10.7 and 14.0 mA/cm<sup>2</sup> for **BFR2**, **BFS3** and **BFS4**, respectively, confirming the accuracy of our photovoltaic measurements. These results are again consistent with the conclusion that the increased structural order and a reduction in the proportion of non-chromophoric side chains are responsible for the significant improvements in device performance.

**Table 2.** Photovoltaic properties of the OPVs based on DT-BDT-FBT polymers/PC<sub>61</sub>BM.

Polymer	Mn (kDa)	PDI	$V_{OC}$ (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	
						Best	Ave <sup>[a]</sup>
<b>BFR2</b>	30	2.2	0.89	-7.25	60.56	3.91	3.74
<b>BFS3</b>	34	2.2	0.90	-10.82	60.81	5.92	5.67
<b>BFS4</b>	32	2.3	0.90	-13.19	60.33	7.16	7.02
<b>BFS4</b> <sup>[b]</sup>	46	2.8	0.90	-14.20	61.05	7.80	7.38

[a] Averaged from at least 40 devices. [b] Results are shown for two different batches of **BFS4**.

The advantageous effect of the A-D1-A-D2 structure on the PCE is most likely also related to the microstructure of the bulk heterojunction blends that are obtained during film deposition. AFM phase images of the photoactive layers reveal clear phase separation arising from aggregated polymer chains (Figure 5). **BFR2**/PC<sub>61</sub>BM and **BFS3**/PC<sub>61</sub>BM phase images are dominated by areas of dark phase (i.e. a low phase value), with needle shaped bright phase regions ranging in length from approximately 10 nm to 200 nm. For **BFS4**/PC<sub>61</sub>BM, the needle shaped regions are more densely packed, leading to larger islands of bright phase and a greater ratio of bright to dark phase for this blend. Thus the bright phases mostly likely correspond to the donor material as we expect closer packing for **BFS4**. The superior device performance of **BFS4** is therefore likely the result of the packing density and frequency of these regions observed herein.



**Figure 5.** AFM phase images of the photoactive layers: a) **BFR2**/PC<sub>61</sub>BM, b) **BFS3**/PC<sub>61</sub>BM and c) **BFS4**/PC<sub>61</sub>BM thin films.

## CONCLUSION

To conclude, we have demonstrated a chemical design approach to improving the performance of organic solar cells. The  $J_{SC}$  of the OPV devices was increased through the use of tailored A-D-A intermediates and a stepwise approach to the synthesis of conjugated polymers. We have shown that the use of A-D1-A-D2 repeating units, as opposed to a typical A-D structure, enables control of the supramolecular interactions within a polymer film. Specifically, our method enables control over both the regiochemistry of the polymer backbone and the amount of non-chromophoric components in the polymer. Through molecular simulations backed by 2D GIWAXS measurements we have pre-



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- (24). Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F. J.; Lotz, B. *J. Am. Chem. Soc.* **2000**, *122*, 5957–5967.
- (25). Zhang, M.; Yang, C.; Mishra, A. K.; Pisula, W.; Zhou, G.; Schmaltz, B.; Baumgarten, M.; Müllen, K. *Chem. Commun.* **2007**, *17*, 1704–1706.
- (26). Mei, J. G.; Kim, D. H.; Ayzner, A. L.; Toney, M. F.; Bao, Z. N. *J. Am. Chem. Soc.* **2011**, *133*, 20130–20133.
- (27). Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (28). Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P.; *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
- (29). (a) Tsao, H. N.; Cho, D. M.; Park, I.; Hansen, M. R.; Mavrinskiy, A.; Yoon, D. Y.; Graf, R.; Pisula, W.; Spiess, H. W.; Müllen, K. *J. Am. Chem. Soc.* **2011**, *133*, 2605–2612. (b) Osaka, I.; Zhang, R.; Sauv e, G.; Smilgies, D. M.; Kowalewski, T.; McCullough, R. D. *J. Am. Chem. Soc.* **2009**, *131*, 2521–2529.
- (30). Rose, A. *Phys. Rev.* **1955**, *97*, 1538–1544.
- (31). (a) Kreouzis, T.; Baldwin, R. J.; Shkunov, M.; McCulloch, I.; Heeney, M.; Zhang, W. *Appl. Phys. Lett.* **2005**, *87*, 172110. (b) Murgatroyd, P. N. *J. Phys. D: Appl. Phys.* **1970**, *3*, 151–156.
- (32). Huang, F. Wu, H. B.; Wang, D. L.; Yang, W.; Cao, Y. *Chem. Mater.* **2004**, *16*, 708–716.
- (33). Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 3619–3623.
- (34). He, Y. J.; Chen, H. Y.; Hou, J. H.; Li, Y. F. *J. Am. Chem. Soc.* **2010**, *132*, 1377–1382.
- (35). Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719–1730.



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