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A Difluorobenzoxadiazole Building Block for Efficient **Polymer Solar Cells**

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Conjugated polymers are widely used in many types of organic electronic devices including polymer solar cells (PSCs). The advance of the PSC field has been largely driven by the development of donor polymers, which are typically constructed based on electron-rich and electron-deficient building blocks using the so-called donor-acceptor (D-A) copolymer strategy.^[1] During the past decade, many building blocks have been developed and successfully applied to construct high-performance donor polymers.^[2] Currently, the best power conversion efficiency (PCE) of single-junction PSCs is 10.8%,^[2e] which is nevertheless lower than silicon solar cells or emerging perovskite solar cells.^[3] In a previous analysis, 15% PCE is predicted to be achievable in a single junction PSC.^[4] This is based on optimization of three key parameters, which are external quantum efficiency (EQE), fill factor (FF), and energy loss.^[4,5] In the state-of-the-art PSC, a new strategy to control and optimize the blend morphology was demonstrated based on a polymer that exhibits temperaturedependent aggregation.^[2e] This approach has led to excellent EQE values higher than 80% and an FF of ≈75%, which have fulfilled the requirement to achieve a 15% efficient PSC. However, the relatively low open-circuit voltage (V_{OC}) is the limiting factor of the efficiency, which is 0.77 V with an optical band gap of 1.65 eV. The large V_{OC} loss (≈ 0.9 eV) is far higher than what is currently considered to be required (0.6 eV). This indicates that improving the $V_{\rm OC}$ is a promising route to enhance the performance of the state-of-the-art PSC.

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To achieve higher V_{OC} and reduce energy loss, it is important to explore new building blocks to construct novel conjugated polymers. In several previous reports, it was shown that replacing the benzothiadiazole (BT) unit by its analogue benzoxadiazole (BX) could lead to a higher V_{OC} for the PSC devices while maintaining an almost identical optical bandgap.^[6] However, the polymers based on the BX building block generally vielded inferior PSC performance compared with their BT analogues.^[6] On the other hand, an important derivative of the BT unit is difluorobenzothiadiazole (ffBT) that has been widely explored for applications in PSCs, including the state-of-theart single junction^[2e] and tandem^[7] PSCs, ITO-free flexible PSCs,^[8] additive/annealing-free PSCs,^[9] and so on.^[2d,10] The success of the ffBT-based polymers can be attributed to their high polymer crystallinity and thus hole mobility, which lead to several cases of thick-film PSCs with high fill factors and efficiencies.^[2d,e,10c,g] The success of the ffBT unit may inspire one to develop a similar fluorinated building block based on BX, which could potentially combine the advantages of high polymer crystallinity/mobility and high Voc without changing the bandgap. However, the synthesis of the difluorobenzoxadiazole (ffBX) unit is challenging and there has been no report of the ffBX-based conjugated polymers.

Here we report the synthesis and initial use of the ffBX building block to construct a donor polymer for PSCs. Using ffBX as the acceptor unit and guaterthiophene with 2-decyltetradecyl (2DT) alkyl chains as the donor unit, a new donor polymer was synthesized that exhibits the typical temperaturedependent aggregation property. The properties of the ffBX polymer were studied with temperature-dependent UV-vis absorption and density functional theory (DFT) calculations, and compared to the results of the ffBT polymer. Solar cell devices were fabricated using the ffBX polymer and PC71BM as the active layer materials. A V_{OC} of 0.88 V was achieved, which is 0.11 V higher than the previous state-of-the-art solar cells while the optical bandgap remains unchanged, which contribute to a high solar cell efficiency up to 9.4%. The polymer indeed exhibits high crystallinity, high mobility, and favorable backbone orientation in blend films, which enable a respectable performance with a thick film.

The polymer synthesized here is poly[(5,6-difluoro-2,1,3-benzoxadiazol-4,7-diyl)-alt-(3,3"'-di(2-decyltetradecyl)-2,2';5',2";5",2"'-quaterthiophen-5,5"'-diyl)] (PffBX4T-2DT). Although the ffBX building block is structurally similar to ffBT, the synthetic strategies are completely different. Here we developed a novel synthetic route to synthesize the ffBX unit, which is shown in Figure 1. Traditionally, the 2,1,3-benzoxadiazole 1-oxide unit was synthesized by thermal decomposition of 1-azido-2nitrobenzene^[11] or oxidative ring closure of o-nitroaniline





Figure 1. Structures and synthetic route of the monomer and polymer.

promoted by sodium hypochlorite in an alcoholic alkali hydroxide solution (Figure S1, Supporting Information).^[11b,12] We prefer to use the second method because it avoids using sodium azide, which is explosive and highly toxic. However, when the commonly used procedure^[12b,c,13] was followed. the fluorine atoms on the substrate 1 unfortunately underwent nucleophilic substitution by alkyloxy groups (Figure S1, Supporting Information). This undesired conversion was also observed by other groups recently, which makes the synthesis of fluorinated benzofuroxan challenging.^[11d,14] To address this issue, we attempted to use aprotic polar solvents instead of alcohols to suppress the nucleophilic substitution and finally found that tetrahydrofuran is an ideal choice to afford the desired product in high yields. In the second step, the reduction of 5,6-difluoro-2,1,3-benzoxadiazole 1-oxide 2 by triethyl phosphite readily gives 5,6-difluoro-2,1,3-benzoxadiazole 3. Next, the bromination of 3 was the first choice in order to utilize the ffBX building block to construct various organic semiconductors. Unfortunately, attempts to directly brominate 3 were not successful, even under harsh conditions. Therefore, we developed a two-step bromination procedure of 3. The hydrogens on the benzene ring are first replaced by trimethylsilyl groups. The obtained 4 was treated with N-bromosuccinimide in sulfuric acid to produce 5 rapidly. Suzuki-Miyaura cross-coupling reaction offers 6, which was then brominated to furnish the monomer 7. The polymer was finally obtained by microwave-assisted Stille cross-coupling reaction. All new compounds are unambiguously characterized by ¹H, ¹³C, ¹⁹F NMR, and mass spectrometry.

The polymer PffBX4T-2DT exhibits much poorer solubility than its ffBT-based analogue with the same alkyl chains (C10C14, PffBT4T-2DT,^[10d] Figure S2, Supporting Information). While PffBT4T-2DT is soluble in warm chloroform. PffBX4T-2DT is only soluble in warm chlorobenzene or *o*-dichlorobenzene (DCB). Rather, the solubility of PffBX4T-2DT is similar to the state-of-the-art donor polymer PffBT4T-2OD^[2e] (Figure S2, Supporting Information), which has shorter alkyl chains (C8C12). They also exhibit comparable absorption coefficients (Figure S3, Supporting Information). Energy levels of PffBX4T-2DT were characterized by cyclic voltammetry (CV; Figure S4, Supporting Information). The polymer exhibits a deep highest occupied molecular orbital (HOMO) level of -5.51 eV, which is 0.12 eV lower than that of PffBT4T-2OD. The lowest unoccupied molecular orbital (LUMO) level was difficult to obtain from the CV measurement due to unreliable reduction data. The optical bandgap was calculated to be 1.66 eV based on the film absorption onset (747 nm), which is almost identical to that of PffBT4T-2OD (1.65 eV). The LUMO level was then calculated to be -3.85 eV. These results reveal that replacing ffBT with ffBX lowers both the HOMO and LUMO levels without changing the optical bandgap of the polymer.

Temperature-dependent absorption spectra of PffBX4T-2DT in DCB solution are shown in **Figure 2**a, which indicates a similar temperature-dependent aggregation property to that reported previously.^[2e] At 100 °C, the polymer is fully disaggregated, showing an absorption peak at 553 nm and an onset of 653 nm. As the temperature decreases, a new peak at \approx 700 nm



Figure 2. a) Normalized temperature-dependent UV–vis absorption spectra of 0.02 mg mL⁻¹ PffBX4T-2DT in DCB. The inset indicates temperatures (units: °C). b) UV–vis absorption spectra of PffBX4T-2DT in DCB at 30 °C and as a film processed from a warm DCB solution. c) Plot of "relative aggregation strength" versus solution temperature. "Relative aggregation strength" is defined as the relatively intensity of the emerging absorption peak at \approx 700 nm during the solution cooling process.

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emerges, which reveals a strong aggregation in solution. At 30 °C, this absorption feature (located at 706 nm) becomes the strongest peak in the spectrum, which corresponds to a bathochromic shift of more than 150 nm compared with the spectrum at 100 °C. The absorption onset (754 nm) also exhibits a bathochromic shift of more than 100 nm. It is interesting to note that both the absorption peak and onset of the polymer solution at 30 °C exhibit slight redshift compared to those of the film absorption spectra (Figure 2b), which is rarely observed for conjugated polymers. The blueshift of film absorption relative to the solution absorption (at 30 °C) indicate that the polymer was not fully aggregated during the spincasting process from a warm solution, as the polymer solution is kinetically quenched before the polymer reaches the level of aggregation as is in solution at 30 °C. On the other hand, the absorption of the polymer solution was recorded for a very dilute solution after it reaches complete thermal equilibrium. Therefore, the polymer can reach a greater extent of aggregation in the solution UV-vis experiment than that achievable in a dynamic spincoating experiment. This is similar to the observation in our previous report, where there is a smaller bathochromic shift of the film absorption when the films were spincast at high rates/higher temperatures.^[2e]

It is found that the temperature-dependent absorption spectra of PffBX4T-2DT are generally similar to those of the PffBT4T-2OD (Figure S5, Supporting Information). However, the temperature at which the aggregation starts to occur is significantly higher for PffBX4T-2DT than for PffBT4T-2OD. To clearly investigate the difference in the aggregation temperatures of the polymers, the normalized intensity of the emerging peak (at 706 nm for PffBX4T-2DT and 699 nm for PffBT4T-2OD) relative to the intensity of the peak absorbance at 100 °C was described as the "relative aggregation strength" of the two polymers at different temperatures. The "relative aggregation

strength" was plotted against the solution temperatures in Figure 2c. Alternatively, a simple plot of the absorption coefficients against temperature (Figure S6, Supporting Information) leads to similar results as the two polymers have comparable absorbance at 100 °C. It is clear that the two polymers reach a comparable level of relative aggregation strength at 30 °C. However, the onset of aggregation strength is at ≈80–90 °C for PffBX4T-2DT, whereas at 60 °C for PffBT4T-2OD. This indicates a significantly stronger tendency for PffBX4T-2DT to aggregate in solution. Considering that the alkyl chains used in PffBX4T-2DT were even longer than that of PffBT4T-2OD, the stronger aggregation tendency of PffBX4T-2DT is originated from the replacement of the sulfur atom with oxygen in the ffBT unit.

To investigate the conformation of the two flanking thiophene rings, a single crystal of ffBX2T was obtained and analyzed by X-ray diffraction (Figure S7, Supporting Information). The result reveals that the two thiophenes exhibit a trans conformation, which is the same as reported previously for ffBT2T.^[10c] The trans conformation of the two thiophenes is important to avoid a zigzag conformation of the polymer backbone (Figure S8, Supporting Information), which would be detrimental for polymer packing and charge transport.^[10c] Two representative compounds, ffBX2T and ffBT2T, were thus simulated with DFT calculations at a level of B3LYP/6-31G*. The energy barriers for trans to cis conversion for ffBX2T and ffBT2T in gas phase are similar (≈20 kJ mol⁻¹, Figure S9, Supporting Information). The directions of the dipole moments are inverse to each other for ffBX2T and ffBT2T, indicating the effect of the high electronegativity of oxygen atom compared with sulfur (Figure S10, Supporting Information). The value of the dipole moment of ffBX2T (1.54 Debye) is significantly larger than ffBT2T (0.70 Debye). The larger dipole moment will lead to stronger intermolecular interaction and may be one of the reasons for



Figure 3. DFT optimized conformation of a) ffBX4T trimer and b) ffBT4T trimer.

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Figure 4. a) Current-voltage and b) EQE curves of an optimized PffBX4T-2DT:PC71BM solar cell.

the stronger aggregation of ffBX-based polymer than ffBT-based polymer.

To further investigate the backbone conformation and electronic structure of the polymers, the theoretically optimal structures of both ffBX4T and ffBT4T trimer were calculated at the B3LYP/6-31G* level of theory. It was found that the ffBT4T trimer exhibits a more twisted structure (Figure 3). The S-C-C-S dihedral angle between the two thiophenes separated by an alkyl chain (arrows in Figure 3) is 162° for ffBT4T trimer but 172° for ffBX4T trimer. This result reveals a more coplanar structure of PffBX4T-2DT, which is likely one of the origins of its stronger tendency to aggregate in solution. The HOMO/LUMO levels from the calculations are -3.04 eV/-4.83 eV and -2.93 eV/ -4.73 eV for the ffBX4T and ffBT4T trimers, respectively. The ≈0.1 eV downshifted HOMO/LUMO levels and the nearly identical bandgap are in good agreement with the electrochemical characterization data. It is also interesting to note that the distribution of the frontier orbitals is similar for the two trimers (Figure S11, Supporting Information), but the electrostatic potential map of ffBX4T trimer is dramatically different from that of ffBT4T trimer (Figure S12, Supporting Information), probably due to the high electronegativity of oxygen. This observation is consistent with the reverse dipole direction of the ffBX unit.

Bulk-heterojunction PSCs were fabricated with an inverted device structure of ITO/ZnO/PffBX4T-2DT:PC71BM/V2O5/ Al. The active layer was spincast from a warm solution of DCB with 1% 1,8-diiodooctane (DIO) with a D:A weight ratio of 1:1.2. An absorption spectrum of the blend film is shown in Figure S13 (Supporting Information). The current-voltage curve is shown in Figure 4a. The V_{OC} of the best cell is 0.88 V, which is 0.11 V higher than that in the state-of-the-art PSC based on PffBT4T-2OD. At the same time, a good short-circuit current (J_{SC}) of 15.9 mA cm⁻² and FF of 0.67 were achieved, leading to an excellent overall performance of 9.4% (Table 1). One reason of the lower J_{SC} compared with the state-of-theart PffBT4T-2OD:PC71BM device is the film thickness in the optimized PffBX4T-2DT:PC71BM device, which is 250 nm and lower than that of PffBT4T-2OD:PC71BM film (300 nm). As a result, the maximum EQE (Figure 4b) of the optimized PffBX4T-2DT:PC71BM device is 74%, which is lower than that of PffBT4T-2OD:PC₇₁BM. When the film thickness was increased to 300 nm, the FF decreased significantly while the improvement on J_{SC} was negligible, which resulted in an inferior PCE of 8.7% (Table 1). The inferior FF values and a poorer performance at 300 nm thick film are probably due to a lower charge carrier mobility of PffBX4T-2DT than PffBT4T-2OD. Hole mobility was measured using the space charge limited current (SCLC) method to be 5.2×10^{-3} cm² V⁻¹ s⁻¹ in a blend film (Figure S14, Supporting Information), which is indeed lower than that for PffBT4T-2OD. Nevertheless, the SCLC hole mobility of PffBX4T-2DT is reasonably high compared to other high-performance donor polymers,^[2d-g,i,15] which allows it to achieve a respectable FF for an active layer with 250–300 nm thickness. The good performance at 300 nm is also among the best of reported thick-film PSCs.^[2d-f,i] In light of the high $V_{\rm OC}$ of devices based on PffBX4T-2DT, this polymer is a promising donor material and may exhibit better PSC performance than PffBT4T-2OD with further optimization.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was used to investigate the polymer packing and texture. In a pure PffBX4T-2DT film (Figure 5a), the polymer exhibits high crystallinity with (100)-(500) lamellar stacking peaks clearly visible (sector averages shown in Figure S15, Supporting Information). The (010) diffraction peak is found in both the in-plane and out-of-plane directions, indicating a bimodal face-on and edge-on texture of the polymer backbone. The intensity ratio, taking into account Ewald's sphere corrections, indicates a preferential edge-on texture. In contrast, in a blend film of PffBX4T-2DT:PC₇₁BM, the polymer exhibits a predominantly face-on orientation relative to the substrate (Figure 5b). It is clear that the addition of fullerene promoted a more preferred face-on polymer backbone orientation, which is favorable for PSCs.^[10c,16] The π - π stacking distance in the blend film is calculated to be 3.57 Å, which is among the smallest values for conjugated polymers,^[2e,17] despite the long alkyl chains used.

Table 1. Solar cell performance of PffBX4T-2DT:PC_{71}BM at different thicknesses. The averages and standard derivations were calculated from at least five devices.

Thickness [nm]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF	PCE (best PCE) [%]
110±10	$\textbf{0.878} \pm \textbf{0.004}$	13.6 ± 0.2	$\textbf{0.72} \pm \textbf{0.01}$	8.6±0.2 (8.9)
250 ± 10	$\textbf{0.875} \pm \textbf{0.003}$	15.8 ± 0.1	$\textbf{0.66} \pm \textbf{0.02}$	9.1 ± 0.3 (9.4)
300 ± 10	$\textbf{0.867} \pm \textbf{0.006}$	15.9 ± 0.1	$\textbf{0.62} \pm \textbf{0.01}$	8.5 ± 0.2 (8.7)



Figure 5. 2D GIWAXS patterns of a) a pure PffBX4T-2DT film and b) a PffBX4T-2DT:PC₇₁BM blend film. c) R-SoXS profile of a PffBX4T-2DT:PC₇₁BM film.

In addition, the (500) laminar peak is not observed in the blend film, indicating more disorder. To characterize the cumulative lattice disorder in the π - π stacking direction, the out-of-plane (010) coherence length of the polymer was calculated using Scherrer equation^[18] to be 6.7 nm for the blend film. The high crystallinity of PffBX4T-2DT is in accordance with its strong π - π stacking and strong aggregation. Additionally, resonant soft X-ray scattering (R-SoXS) was used to investigate the spatial dimensions of the phase-separated domains.^[19] The Lorentz corrected R-SoXS profile of a blend film is shown in Figure 5c (a plot without Lorentz correction can be found in Figure S16, Supporting Information). A peak at 0.085 nm⁻¹ was observed, corresponding to the long period and thus (center-to-center) domain spacing of 74 nm in real space. Note that the morphology of PSCs is a complicated conundrum and involves many morphological parameters including domain size, domain purity, polymer backbone orientation relative to the substrate, and molecular orientation relative to donor:acceptor interfaces. From our preliminary morphology characterization, it appears that the high polymer crystallinity and favorable backbone orientation may contribute to the good performance of our PSCs. But other morphology parameters and possible vertical segregation are yet to be studied in detail and need to be fully optimized to realize the high potential of PffBX4T-2DT.

In summary, we developed a synthetic route to ffBX that was then used to construct conjugated polymers for PSCs. Incorporating the ffBX unit and 2nd position branched alkyl chains, a conjugated polymer PffBX4T-2DT was synthesized that exhibits the typical temperature-dependent aggregation and thus achieved efficient thick-film PSCs. Replacing the ffBT unit with ffBX, both the HOMO and LUMO levels of the polymer are significantly reduced while the optical bandgap of the polymer remains unchanged. Compared with its ffBT-based analogue polymer, PffBX4T-2DT exhibits a stronger aggregation tendency in solution and a higher crystallinity in blend films, which originates from its stronger intermolecular interaction and a more planar backbone. Solar cell devices were fabricated with PffBX4T-2DT as the donor polymer, which yielded high PCEs up to 9.4% for a thick (250 nm) active layer. Importantly, the $V_{\rm OC}$ of the PffBX4T-2DT-based PSCs were increased by 0.11 V compared to that of the PffBT4T-2OD-based cells while the optical bandgap remains unchanged. This shows that it is still possible to reduce the energy loss in the state-of-the-art PffBT4T-2OD PSCs. Morphology studies revealed a high polymer crystallinity and predominantly face-on orientation of the polymer backbone with respect to the substrate. Due to the structural simplicity and synthetic accessibility of ffBX, its deeper energy levels than those of ffBT, and the success achieved by many ffBT-based polymers, ffBX is a versatile and promising building block for constructing conjugated polymers, and might thus be widely used in future studies of PSCs as well as other organic electronic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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