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Increased open circuit voltage in fluorinated benzothiadiazole-based alternating conjugated polymers†

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Small band-gap conjugated polymers based on monofluoro- and difluoro-substituted benzothiadiazole were developed. Highly efficient polymer solar cells (PCE as high as 5.40%) could be achieved for devices made from these polymers.

Polymer solar cells (PSCs) have been widely investigated recently due to their potential for light-weight, low-cost, and large-scale roll-to-roll processing.¹ Power conversion efficiencies (PCEs) of more than 7% have been reached based on bulk hetero-junction (BHJ) PSCs, in which a blended film of an electron-rich conjugated polymer and an electron-deficient fullerene acts as the active BHJ layer.²

Open circuit voltage (V_{oc}) is an important device parameter in determining the overall performance of a PSC. In general, V_{oc} is proportional to the difference between the highest occupied molecular orbital (HOMO) of a polymer and the lowest unoccupied molecular orbital (LUMO) of fullerene, although some device engineering factors, such as the type of cathode material and exciton non-radiative recombination, may also affect the V_{oc} of a BHJ PSC.³ A V_{oc} can be increased either by increasing the LUMO of fullerene or decreasing the HOMO of the polymer. There are several reports regarding the development of fullerene derivatives with higher LUMO levels than the commonly used PCBM to achieve higher V_{oc} . However, low band-gap polymers tend to have low-lying HOMO, which are commonly accompanied by low-lying LUMO. Hence, the difference between the LUMO levels of a polymer and fullerene frequently results in inefficient charge separation, leading to low J_{sc} . On the other hand, a higher LUMO in a low band-gap polymer also accompanies with a higher HOMO giving a lower V_{oc} . Therefore, it is a challenge to fine tune the band-gap and energy levels of a polymer to have high V_{oc} and J_{sc} in BHJ PSCs.

It is well known that the introduction of an electron-withdrawing group into the polymer backbone can lower its energy levels.⁴ The change of HOMO and LUMO energy levels is dependent on where the position of the electron-withdrawing group is on the D–A polymer. Among numerous electron-withdrawing groups, the use of fluorine has been proven to be effective in lowering the HOMO energy level and resulting in higher V_{oc} and improved performance in fluorinated poly(benzodithiophene-thienothiophene)s.^{4a} To investigate the effect of F atom on other acceptors, herein we have introduced it onto the benzothiadiazole (BT) unit to synthesize the monofluoro- and difluoro-substituted BT units, which were then copolymerized with the indacenodithiophene (IDT) donor to obtain two new conjugated polymers (PIDT–FBT and PIDT–DFBT). Fig. 1 shows the chemical structures of the polymers.

The synthetic route of monofluoro- (FBT) and difluoro-BT (DFBT) is shown in Scheme 1. Starting from 2,5-dibromo-3-fluorobenzene and 2,5-dibromo-3,4-difluorobenzene, compounds **1** and **5** toward FBT and DFBT, respectively, were synthesized in three steps as shown in the ESI.† The selective nitration of **1** and **5** in the mixture of HNO₃ and conc. H₂SO₄ afforded **2** and **6** with >85% yield. Next, the trifluoroacetyl was de-protected in **2** and **6**, by refluxing in aqueous H₂SO₄ to give **3** and **7**. The NO₂ groups were further reduced by SnCl₂ to result in diamines **4** and **8**, respectively. Finally, the ring closure of diamines **4** and **8** with SOCl₂ in pyridine generated the monofluoro- and difluoro-substituted BT monomers, FBT and DFBT, respectively, in >80% yield. The distannyl IDT **9** was synthesized by following the same method reported previously.⁵ The polymers PIDT–FBT and PIDT–DFBT (Scheme 1) were synthesized *via* the Stille polycondensation of **9** with FBT or DFBT, respectively, using toluene as solvent and Pd₂(dba)₃/P(*o*-tol)₃ as catalyst. Purification of PIDT–FBT and PIDT–DFBT was conducted by Soxhlet extraction of

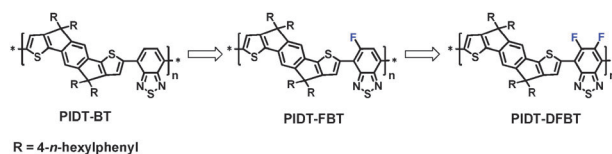


Fig. 1 The chemical structures of PIDT–BT, PIDT–FBT and PIDT–DFBT. (PIDT–FBT is a regiorandom polymer.)

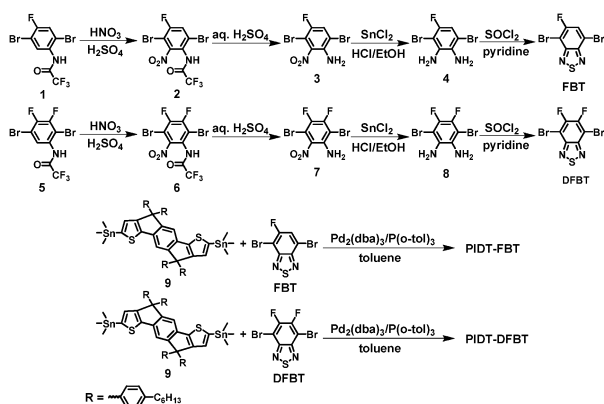
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Scheme 1 Synthetic routes of monomers and polymers.

the crude product with acetone and hexane to remove oligomers and residual catalyst. It is noted that PIDT-FBT is a regio-random polymer because of the asymmetrical FBT unit. PIDT-BT was synthesized as previously reported with a number-average molecular weight (M_n) of 28 kDa.⁶ All polymers possess good solubility in organic solvents, such as chloroform, chlorobenzene, and dichlorobenzene, which was benefiting from the tetrahexylbenzene groups on the IDT unit. The molecular weights of PIDT-FBT and PIDT-DFBT were measured using GPC with THF as an eluent. The M_n of PIDT-FBT and PIDT-DFBT are determined to be 32.9 kDa and 61.4 kDa with the polydispersity indices (PDI) of 3.70 and 3.04, respectively. The DSC measurements showed that there were no thermal transitions found between 20 and 300 °C for both polymers.

Fig. 2 shows the UV-Vis absorption spectra of PIDT-FBT and PIDT-DFBT in chloroform solutions and in thin films. The UV-Vis spectrum of PIDT-BT is also shown for comparison. All polymers showed two similar characteristic peaks resulting from similar polymer main chains. The band at the longer wavelength was attributed to the intramolecular charge transfer (ICT) from IDT to BT unit. In chloroform solution, as shown in Fig. 2a, PIDT-FBT shows almost the same absorption peaks (413 nm and 644 nm) and onset (715 nm) as those of PIDT-BT. Similarly, the absorption spectra of PIDT-FBT and PIDT-BT in thin film also possess the same peaks and onset. The main peak and absorption onset of PIDT-FBT and PIDT-BT in thin films are 649 nm and 720 nm, respectively, with an optical band-gap of 1.72 eV. The results showed that the introduction of monofluoro-substituent onto PIDT-FBT showed a little effect on the polymer optical properties. The same band-gap of PIDT-FBT and PIDT-BT also indicates that the F atom in PIDT-FBT lowered both HOMO and

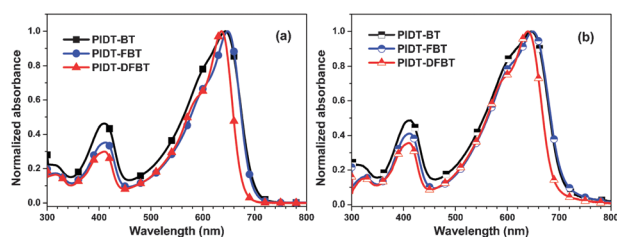


Fig. 2 UV-Vis spectra of polymers in chloroform solution (a) and thin film states (b).

LUMO levels at about the same strength. The absorption spectra of PIDT-DFBT in both chloroform and thin film (Fig. 2a and b), however, showed blue-shift peaks compared with those of PIDT-FBT. The ICT peaks of PIDT-DFBT are 636 nm and 639 nm, respectively, in solution and in film, which blue-shifted ~10 nm compared to that of PIDT-FBT. The onset of PIDT-DFBT in film was 698 nm, corresponding to a band-gap of 1.78 eV. The larger band-gap compared to that of PIDT-FBT is believed to be the stronger effect of two F atoms on the HOMO energy level than for the PIDT-FBT polymer, therefore, having a further lower HOMO and a similar LUMO compared to that of PIDT-FBT.

The HOMO and LUMO energy levels of PIDT-FBT and PIDT-DFBT were determined by cyclic voltammetry (CV) with Pt as a counter electrode and Ag/Ag⁺ as a reference electrode in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s⁻¹. The CV curves of PIDT-FBT and PIDT-DFBT in thin films were shown in Fig. 3. PIDT-FBT and PIDT-DFBT showed the similar oxidation and reduction behaviours with good reversible peaks. The HOMO and LUMO energy levels of PIDT-FBT were determined to be -5.38 eV and -3.64 eV, respectively, with ferrocene as reference. By comparing with the HOMO (-5.23 eV) of PIDT-BT,^{6a} the HOMO of PIDT-FBT is 0.15 eV deeper through the introduction of a F atom onto the BT unit. The LUMO energy level of PIDT-FBT is -3.64 eV, which is 0.12 eV deeper than that of PIDT-BT (-3.52 eV). The similar decrease of the HOMO and LUMO energy levels in PIDT-FBT compared with that of PIDT-BT echoed the similarity of band-gap observed in absorption. Similarly, the HOMO and LUMO energy levels of PIDT-DFBT were calculated to be -5.48 eV and -3.67 eV, respectively. Again, further decreases in both HOMO and LUMO energy levels were found, but with a larger decrease of the HOMO value than that of the LUMO, thus, leading to the larger band-gap. From the results, it can be concluded that the F substitution effectively lowered the HOMO levels of PIDT-FBT and PIDT-DFBT, which may have a positive effect on V_{oc} in PSC. In addition, the differences (>0.5 eV) of LUMO levels between polymers and PCBM (-4.20 eV) are still adequate for efficient charge transfer, even for the lower LUMO in PIDT-DFBT.

The photovoltaic properties of the polymers were investigated in the device structure of ITO/PEDOT:PSS/polymer:PC₇₁BM (1 : 3 wt)/Ca/Al. The detailed device fabrication is described in the ESI.† The PIDT-BT device was also fabricated under the

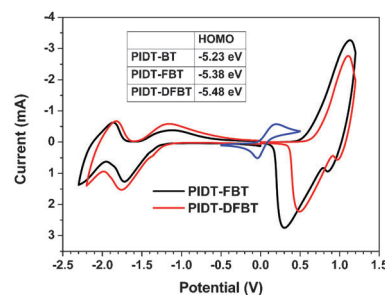


Fig. 3 CV curves of polymers PIDT-FBT and PIDT-DFBT (the CV curve of ferrocene is shown as a blue line).

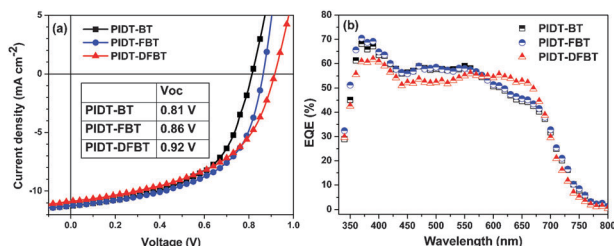


Fig. 4 J - V (a) and EQE (b) curves of polymer/PC₇₁BM devices.

same conditions for comparison. Fig. 4a displays the J - V curves of the devices that were measured under 100 mW cm^{-2} illumination (AM 1.5G). The PIDT-FBT/PC₇₁BM device showed a V_{oc} of 0.86 V, a J_{sc} of 11.23 mA cm^{-2} and a FF of 56%, leading to an overall PCE of 5.40%. Under the same conditions, however, the PIDT-BT device gave a PCE of 5.02%, with a V_{oc} of 0.81 V, a J_{sc} of 11.23 mA cm^{-2} , and a FF of 55%. An increase of 0.05 V in the V_{oc} of the PIDT-FBT device was found while comparing to that of the PIDT-BT device. It is interesting that both devices showed very similar J_{sc} and FF, therefore, the increased PCE of the PIDT-FBT device over the PIDT-BT device was mainly attributed to the increase of V_{oc} , benefiting from the deeper HOMO energy level of PIDT-FBT. As indicated above, PIDT-DFBT has the deepest HOMO energy level, it is expected that a further increase of V_{oc} would be achieved. As expected, the V_{oc} of the PIDT-DFBT/PC₇₁BM device reached 0.92 V, 0.12 V enhancements compared to that of the PIDT-BT device. Combining a J_{sc} of 10.87 mA cm^{-2} and a FF of 51%, the overall PCE of the PIDT-DFBT device was 5.10%, which is slightly higher than the PIDT-BT device. The comparable performance was also attributed to the significant enhancement of V_{oc} which was offset by the loss in J_{sc} and FF in comparison with the PIDT-BT device. The results clearly indicate that increasing the V_{oc} in PSC by fine tuning the HOMO energy level of the polymer is an effective way to enhance the overall device performance.

The external quantum efficiency (EQE) spectra of the devices were studied to further verify the photoresponse. As shown in Fig. 4b, all devices showed an efficient photoresponse in the range of 340 nm to 750 nm. The highest EQE value of the devices reached $\sim 70\%$ in PIDT-BT and PIDT-FBT devices, and $\sim 60\%$ in the PIDT-DFBT device. A flat EQE value of more than 40% between 350 nm to 700 nm indicates the balanced contribution from both polymer and PC₇₁BM. The almost overlapped EQE curves of PIDT-FBT and PIDT-BT devices are very consistent with the similarities in the measured J_{sc} and FF in both devices. In the PIDT-DFBT device, the low EQE value between 350 nm to 550 nm coming from the PC₇₁BM may be one of the main factors for the measured low J_{sc} .

The hole mobility measured by the space-charge-limited-current (SCLC) method for the polymer/PC₇₁BM BHJ film was investigated using the hole-only device configuration of ITO/PEDOT:PSS/BHJ/MoO₃/Al, where MoO₃ was used as the electron-blocking layer due to its high work-function (-5.40 eV).⁷ The hole mobilities of PIDT-BT, PIDT-FBT and PIDT-DFBT were calculated to be 4.69×10^{-2} , 3.38×10^{-2} , and $2.88 \times 10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$, respectively. It is known that both J_{sc} and FF are partially dependent on the charge

transporting property of the BHJ layer. The similar absorption and hole mobilities of PIDT-FBT and PIDT-BT combined with similar morphology, as revealed by atomic force microscopy (AFM), resulted in similar J_{sc} and FF. Thus, the improved performance of the PIDT-FBT device should come mainly from the increased V_{oc} . In the PIDT-DFBT device, the low FF may be due to the significantly decreased hole-mobility. Similarly, the comparable PCE of the PIDT-DFBT device is mainly due to the very high V_{oc} of 0.92 V.

In conclusion, fluoro-substituted PIDT-FBT and PIDT-DFBT were synthesized and used as the donor polymer in PSCs. PIDT-FBT and PIDT-DFBT showed deep HOMO energy levels of -5.38 eV and -5.48 eV , respectively, after introducing the electron-withdrawing fluorine atoms onto the BT unit. The PCEs of PIDT-FBT and PIDT-DFBT devices reached 5.40% and 5.10%, with high V_{ocs} of 0.86 V and 0.92 V, respectively, compared with the PCE of 5.02% and V_{oc} of 0.81 V in the PIDT-BT device. The high V_{oc} and improved device performance make PIDT-FBT and PIDT-DFBT promising candidates for high-performance PSCs.

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