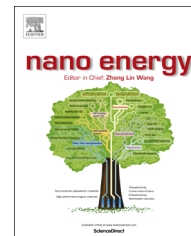




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COMMUNICATION

Dramatic performance enhancement for large bandgap thick-film polymer solar cells introduced by a difluorinated donor unit



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Abstract

We report a large bandgap (1.9 eV) donor-acceptor copolymer (named Pfft2-FTAZ) that enables polymer solar cells with a high power conversion efficiency of 7.8%. An important structural feature of the Pfft2-FTAZ polymer is a difluorinated donor unit (3,3'-difluoro-2,2'-bithiophene, or fft2) that introduces several surprising and/or beneficial effects. By comparing Pfft2-FTAZ with the analog polymer (PT2-FTAZ) without fluorination on the bithiophene donor unit, it is found that the fft2 unit effectively lowers the HOMO and LUMO energy levels of the polymer and slightly reduces optical bandgap. It also introduces strong interchain aggregation for the polymer in solution, which leads to a highly crystalline polymer film and reasonably high hole transport mobility. On the other hand, the Pfft2-FTAZ: fullerene blend still exhibits a reasonably small polymer domain size suitable for polymer solar cell operation. All these

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positive factors combined leads to dramatically enhanced performance for the polymer solar cells with the power conversion efficiency increasing from 2.8% for PT2-FTAZ to 7.8% for PffT2-FTAZ. The high PSC performance of PffT2-FTAZ makes it a promising candidate for high efficiency tandem PSCs.

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Introduction

Polymer solar cells (PSCs) have attracted much research attentions from both academia and industry during the past two decades due to their promise in low-cost solar energy conversion [1-7]. State-of-the-art PSCs consist of the bulk-heterojunction (BHJ) films containing a conjugated polymer and a fullerene derivative that separate excitons and transport holes and electrons respectively [8-14]. To date, single-junction PSCs can achieve power conversion efficiencies (PCE) of about 10% [15-20] and elaborately designed tandem PSCs consisting of large and small bandgap polymer materials can achieve PCEs of about 11% [21-24]. Most conjugated polymers used in PSCs are based on an electron donating (donor or D) and an electron accepting (acceptor or A) comonomer unit. It is convenient to use such D-A alternating copolymer strategy to obtain polymers with low optical bandgaps as the highest occupied molecular orbital (HOMO) level of the polymer is mostly located on the donor unit and the lowest unoccupied molecular orbital (LUMO) level mostly on the acceptor unit [9-11,25,26]. By modifying the donor or acceptor unit of a D-A polymer, the HOMO and LUMO levels of the polymer can be effectively tuned. Tuning the HOMO, LUMO levels and the bandgaps of conjugated polymers is highly important for achieving the best performing single-junction and tandem PSCs [27-30].

Fluorination has been a common method to modify D-A conjugated polymers, which has shown to be effective in tuning the energy levels of polymers accompanied by other positive effects including enhanced polymer crystallinity and mobility [31-39]. There are several reports on

fluorinating the acceptor unit of the D-A polymers. For example, You and coworkers reported that difluorination of benzothiadiazole unit lead to lower HOMO level and thus enhanced open circuit voltage (V_{OC}) of the solar cell as well as increased polymer stacking in the solid state [35]. On the other hand, there were few successful attempts in directly fluorinating the donor part of D-A conjugated polymers, which has yielded improved performance for the PSC devices [40]. It was believed in one case that a perfluorinated polymer backbone (with fluorine on both the donor and accept units) lead to poor PSC performance due to excessive self-organization property and fluorophobicity effect of the polymer [41].

Experimental results

Here we report the results of dramatically enhanced polymer solar cell performances introduced by a difluorinated donor unit. We design a new large bandgap D-A polymer (named PffT2-FTAZ) based on a difluorinated bithiophene donor unit (ffT2) combined with difluorinated benzotriazole (FTAZ) as the acceptor unit (Figure 1a). By comparing the properties of the PffT2-FTAZ with its close analog polymer (PT2-FTAZ) without fluorination on the bithiophene (T2) unit, it is clear that the difluorination on donor unit introduces several beneficial effects that improve the polymer solar cell performances. 1) difluorination on the bithiophene unit lowers both the HOMO and LUMO levels, which increases the V_{OC} and reduces the V_{OC} loss of the PSCs; 2) the ffT2 unit also slightly reduces the optical

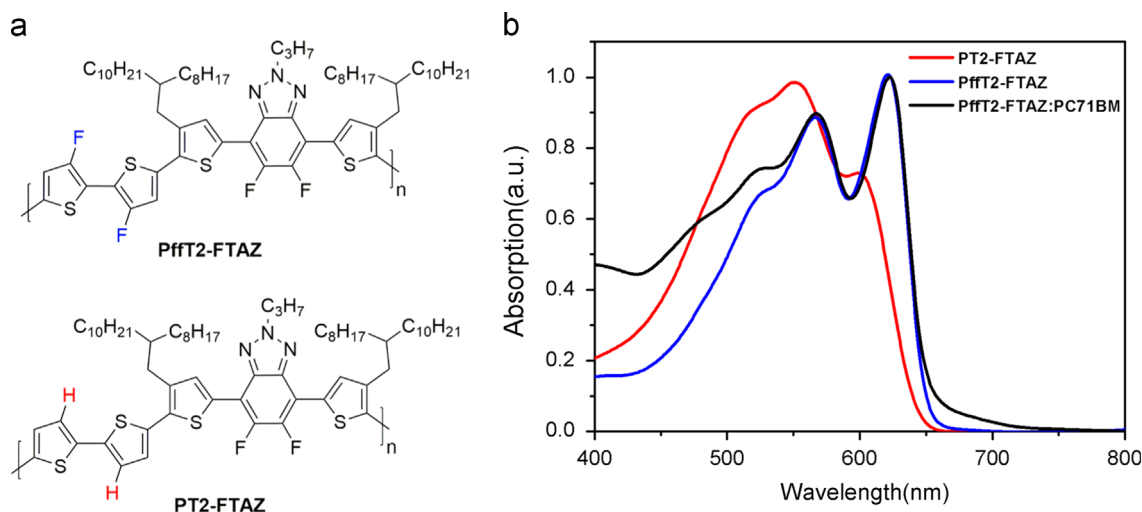


Figure 1 (a) Chemical structures and (b) UV-vis absorption spectra (in thin films) of PffT2-FTAZ, PT2-FTAZ and PffT2-FTAZ:PC₇₁BM blend film.

bandgap of the polymer, which is beneficial for light harvesting; 3) PffT2-FTAZ shows strong interchain aggregation in solution and intense π - π stacking in the solid film that enables higher crystallinity and hole transport mobility; 4) the polymer: fullerene blend still exhibits a reasonably small polymer domain size for efficient exciton dissociation. With these positive effects, the ffT2 donor unit enables a dramatic enhancement of power conversion efficiency from 2.8% to 7.8% for the PffT2-FTAZ based large bandgap PSCs, which exhibit an impressive fill factor (FF) of near 0.7 for a thick active layer (250 nm).

Results and discussion

The UV-vis absorption spectra of the two polymer films are shown in Figure 1b. The absorption onset of PffT2-FTAZ in thin film is about 660 nm, indicating a large bandgap of 1.88 eV. The PffT2-FTAZ polymer exhibits three main absorption peaks, with the 0-0 peak at 620 nm being the strongest. The λ_{onset} and λ_{max} values of PffT2-FTAZ are red-shifted by 20 and 68 nm respectively compared with those of PT2-FTAZ. Although the red-shift of absorption onset is relatively small, the change in absorption maximum point is quite dramatic due to the appearance of the strong 0-0 transition peak for PffT2-FTAZ indicative of *J*-aggregation [42]. The broadened and strengthened absorption of PffT2-FTAZ in the 600-700 nm range should significantly enhance the light harvesting ability of PffT2-FTAZ based solar cells. The absorption wavelengths, optical bandgaps, HOMO and

LUMO levels of the polymers are summarized in Table 1. The HOMO and LUMO levels of PffT2-FTAZ are -5.43 eV and -3.55 eV, 0.13 and 0.19 eV lower than those of PT2-FTAZ, respectively. Considering the LUMO level of PC₇₁BM is at about -4.0 eV, the reduction of the LUMO level of PffT2-FTAZ reduces the LUMO offset and thus decreases the V_{OC} loss of the solar cells. At the same time, the LUMO offset between PffT2-FTAZ and PC₇₁BM should be large enough to ensure efficient electron transfer from PffT2-FTAZ to PC₇₁BM [10,27].

It is a somewhat surprising that modifying the donor unit of triazole-based polymer is more effective in lowering the LUMO than the HOMO level and introduces a significant LUMO change of 0.19 eV. The general theory for D-A conjugated polymers is that modifying the donor unit is more effective in tuning the HOMO level and a similar effect applies to modifying the acceptor unit for tuning LUMO levels [43-45]. The ffT2 donor unit appears to be a useful building block in tuning LUMO levels and could be combined with other acceptor units to obtain D-A polymers with smaller LUMO offsets with PCBM. Regarding bandgaps, previous studies reported increased bandgaps (up to 0.08 eV [35]) upon the fluorination of the acceptor unit of the D-A polymers [32,35-37,39]. For PffT2-FTAZ, however, the effect of fluorination on bandgap is different: the fluorination on the donor unit of PT2-FTAZ slightly reduces the optical bandgap of the polymer.

Polymer solar cells based on PffT2-FTAZ and PC₇₁BM are fabricated in an inverted device structure of ITO/ZnO/active layer/V₂O₅/Al. The *J*-*V* curve and external quantum

Table 1 Optical and electrochemical properties of polymers.

Polymer	λ_{onset}^a [nm]	λ_{max}^a [nm]	Bandgap ^b [eV]	E_{HOMO}^c [eV]	E_{LUMO}^d [eV]
PT2-FTAZ	640	552	1.94	-5.30	-3.36
PffT2-FTAZ	660	620	1.88	-5.43	-3.55

^aAbsorption wavelengths of polymer thin films.

^bOptical bandgaps determined by λ_{onset} .

^cMeasured by cyclic voltammetry.

^dCalculated with the following equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + \text{Bandgap}$.

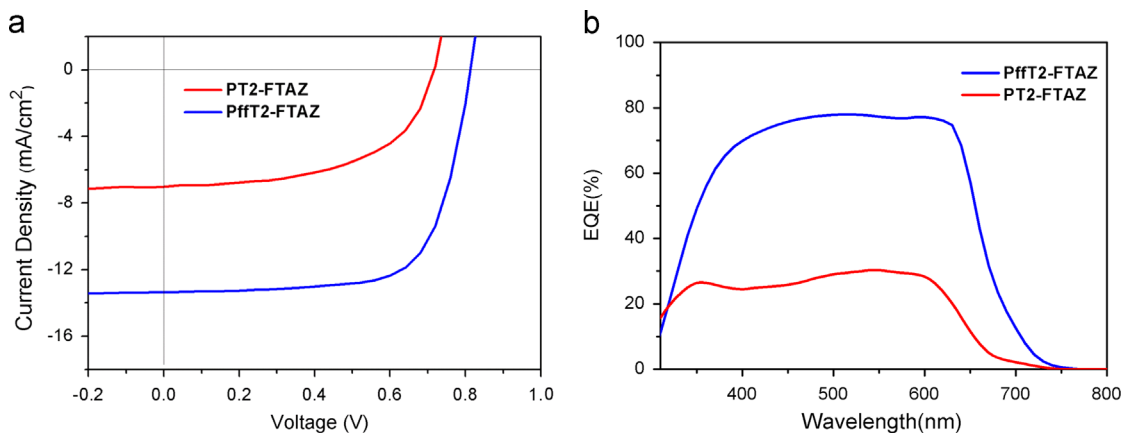


Figure 2 (a) Current density (*J*)-voltage (*V*) characteristics and (b) external quantum efficiency (EQE) spectra of BHJ solar cells from 1:1.2 w/w blend of PffT2-FTAZ:PC₇₁BM and PT2-FTAZ:PC₇₁BM in DCB with 2.5% DIO.

efficiency (EQE) data are depicted in Figure 2. The V_{OC} , short circuit current (J_{SC}), fill factor (FF) and efficiency data are listed in Table 2. Compared with PT2-FTAZ based devices, PffT2-FTAZ based devices have average V_{OC} increased from 0.73 V to 0.80 V. The J_{SC} is dramatically enhanced from 5.3 mA/cm² to 13.3 mA/cm² due to stronger and wider absorption, and more importantly, much higher EQE for the PffT2-FTAZ based cells. For the best performance device, a V_{OC} of 0.82 V, a J_{SC} of 13.6 mA/cm², a FF of 0.71 and an efficiency of 7.8% was achieved. The 7.8% PCE achieved with the PffT2-FTAZ polymer is one of the best efficiencies achieved for large bandgap (~ 1.9 eV) PSCs. It is important to note the good performance of PffT2-FTAZ is achieved with an active layer thickness of 250 nm. The FF value of 0.70 for a 250 nm thick PSC is among the best values achieved thus far for PSCs [46-48]. Note that the PffT2-FTAZ:PC₇₁BM-based cells exhibit significant EQE (Figure 2b) in the wavelength region (680-740 nm), which is beyond the absorption range of PffT2-FTAZ. This is due to the absorption of PC₇₁BM, as evidenced by the small “tail” of the absorption for PffT2-FTAZ:PC₇₁BM blend film in the 660-740 nm range as shown in Figure 1b. As the active layer is relatively thick (250 nm), a small extent of absorption by PC₇₁BM in the 660-740 nm can result in significant red-shift of the EQE spectra of PffT2-FTAZ:PC₇₁BM-based cells compared to that of the corresponding cells based on PffT2-FTAZ:PC₆₁BM (shown in Figure S3).

To understand the origin of the great performance of PffT2-FTAZ, we first look into the aggregation properties of the polymers. The temperature-dependent UV-vis absorption spectra of PffT2-FTAZ and PT2-FTAZ are compared in

Figure 3. The UV-vis absorption spectra of PffT2-FTAZ's solution in 1,2-dichlorobenzene (DCB) exhibits a gradually progressing but dramatic red-shift when solution is cooled from 100 °C to room temperature. During the cooling process of the solution, two very strong 0-0 and 0-1 transition peaks appear in the absorption spectra. At the end of the cooling process, the 0-0 transition peak dominates the absorption spectra of the solution and the absorption spectrum of the room temperature solution is quite similar to that of the solid film. Considering a previous report of a fluorinated polymer which shares similar properties, [49] we suggest that the polymer PffT2-FTAZ can form strong interchain aggregation in solution. In contrast, the PT2-FTAZ polymer does not exhibit any sign of such interchain aggregation in solution. Because the molecular weights (determined by GPC) of PffT2-FTAZ ($M_n=41$ kDa, $M_w=71$ kDa) is even lower than those of PT2-FTAZ ($M_n=81$ kDa, $M_w=151$ kDa), the stronger aggregation tendency in solution must be induced by the fffT2 unit. Clearly, the fluorination on the T2 donor unit completely changes the aggregation behavior of the polymer, which could be partially explained by higher planarity of the fffT2 unit as a result of the F-S interaction between F atom on the bithiophene unit and adjacent S atom [50,51]. It's worth noting that the concentration of the polymer solution is near 1×10^{-6} M and the aggregation is still strong enough to be observed under such dilute condition.

The polymer crystallinity and π - π stacking orders of the polymers in films were characterized using grazing incidence wide-angle X-ray scattering (GIWAXS) technique. The GIWAXS 2-D mapping of polymer films are shown in Figure 4.

Table 2 Photovoltaic properties of BHJ polymer solar cells.

Polymer: PC ₇₁ BM	V_{OC} [V]	J_{SC} [mA/cm ²]	FF	PCE [%]	PCE _{max} [%]
PT2-FTAZ	0.73 (± 0.02)	5.3 (± 1.8)	0.55 (± 0.04)	2.1 (± 0.7) ^a	2.8
PffT2-FTAZ	0.80 (± 0.02)	13.3 (± 0.5)	0.69 (± 0.02)	7.5 (± 0.3) ^b	7.8

^aAverage value from 6 individual devices.

^bAverage value from 10 individual devices.

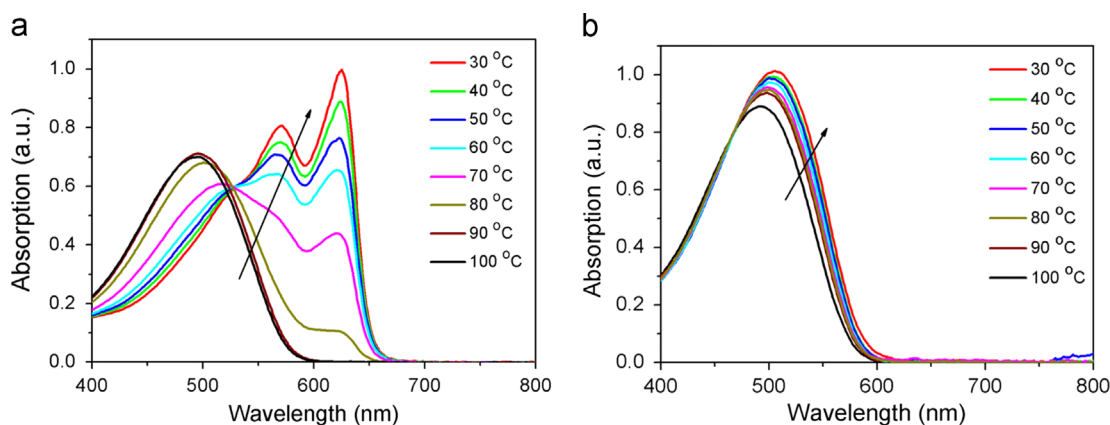


Figure 3 (a) UV-vis absorption spectra evolutions of PffT2-FTAZ in dichlorobenzene solution. (Cooling process, from 100 °C to 30 °C.) (b) UV-vis absorption spectra evolutions of PT2-FTAZ in dichlorobenzene solution. (Cooling process, from 100 °C to 30 °C.)

The patterns show that the (010) diffraction peak of PffT2-FTAZ on q_z axis is much more intense than the corresponding (010) peak of PT2-FTAZ on q_{xy} axis. Also, through calculation with (010) peak values, the π - π stacking distance of PffT2-FTAZ is estimated to be 3.6 Å, smaller than that of PT2-FTAZ (3.8 Å). These data support stronger π - π interaction of the PffT2-FTAZ polymers in the solid state, which is consistent with observation of strong interchain aggregation of PffT2-FTAZ in solution.

To evaluate the hole transport ability of the polymers, hole-only devices were fabricated utilizing device structure of ITO/ V_2O_5 /active layer/ V_2O_5 /Al and the hole mobility was estimated using space-charge-limited current (SCLC) method. [52] The SCLC hole mobility of PffT2-FTAZ polymers is $1.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is significantly higher than that of PT2-FTAZ ($3.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). (Figure S2) The relatively high hole mobility of PffT2-FTAZ allows the PSC devices to achieve a high fill factor and PCE, even when the active layer is as thick as 250 nm [31,53]. As the result of the thick active layer, the EQE of the cell is as high as 77%, which is one of the best values achieved for large bandgap PSCs to date [6,54,55]. The PffT2-FTAZ polymer should be promising for industrial applications, because of its ability to maintain high efficiency in thick-film PSCs.

The morphologies of the polymer: fullerene blends were investigated using atomic force microscopy (AFM). The polymer domain size of PffT2-FTAZ based polymer: fullerene blend is observed to be 30-40 nm (Figure 5a). On the other hand, the PT2-FTAZ: fullerene blend films exhibit large scale phase segregation on the scale of about 300 nm as shown in the AFM images of Figure 5b. Note that the PT2-FTAZ: fullerene blend films exhibit a whitish foggy appearance by visual observation, which is consistent with the highly rough surface as revealed by AFM. These data combined show that PffT2-FTAZ not only exhibits high crystallinity but also maintains reasonably small polymer domains and exhibits good intermixing with PC_{71}BM , which should be one main reasons why the PffT2-FTAZ polymer enables high PSC efficiency.

Intriguingly, despite the fact PffT2-FTAZ has four fluorine atoms in each repeating unit, it still forms a good BHJ morphology, high EQE and PCE. In a previous report, a perfluorinated polymer (PTBF3) that has three fluorine atoms in its repeating unit exhibited low PCE due to poor morphology and fluorophobicity effect [41]. The different PSC performances of PffT2-FTAZ and PTBF3 could be explained by several possible reasons. Firstly, while PTBF3

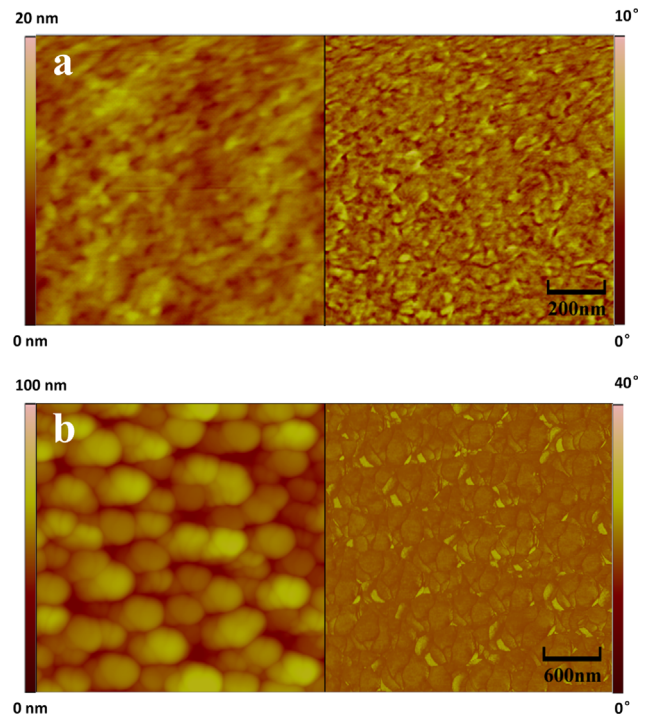


Figure 5 (a) AFM image of a PffT2-FTAZ: PC_{71}BM blend film ($1 \times 1 \mu\text{m}$), (b) AFM image of a PT2-FTAZ: PC_{71}BM blend film ($3 \times 3 \mu\text{m}$). The surface topography and phase images are displayed on the left and right sides respectively.

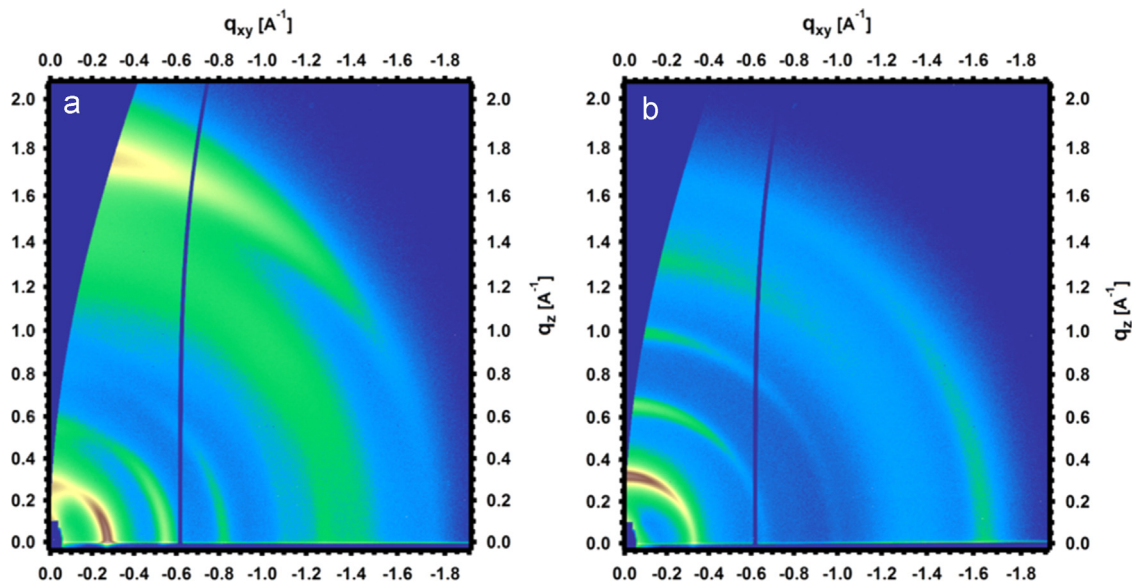


Figure 4 (a) GIWAXS image of PffT2-FTAZ polymer thin film, (b) GIWAXS image of PT2-FTAZ polymer thin films.

has a perfluorinated polymer backbone, the fluorine “density” of PffT2-FTAZ is smaller, which is, four hydrogen atoms and four fluorine atoms in each repeating unit. Therefore, the fluorophobicity effect is limited, if any, for PffT2-FTAZ. Secondly, the structure of PTBF3 contains fused aromatic unit with large planar structure, which, combined with the effect of planar conformation aroused by two fluorine atoms, lead to very strong driving force for the development of long-range ordered structure and thus cause excessively large polymer domains. The donor unit of PffT2-FTAZ does not have the large fused aromatic structure of PTBF3 and thus exhibits less tendency to form large domains. In addition, as PffT2-FTAZ exhibits a temperature-dependent aggregation behavior, the extent of its aggregation can be controlled by processing the polymer solution at elevated temperature to prevent the formation of excessively large domains.

With the performances and properties described above, PffT2-FTAZ should be a promising donor material for tandem PSCs. State-of-the-art double-junction tandem PSCs consist of a front cell with a relatively large bandgap polymer and a back cell with a smaller bandgap polymer [22]. Although hundreds of low or medium bandgap polymers have been developed for PSCs, there are relatively limited choices of highly efficient large bandgap donor polymers [22,56-60]. Comparing with commonly used large bandgap polymer material P3HT, PffT2-FTAZ exhibit much higher J_{SC} and EQE values while maintaining high FF (~ 0.7) under similar thickness condition (~ 250 nm). In the 10.6% tandem cell report, the performance and J_{SC} of the P3HT front cell is relatively weak thus the overall performance and J_{SC} of the tandem cell is limited by the P3HT front cell [22]. By replacing P3HT with PffT2-FTAZ, the J_{SC} of the front cell should be largely increased, and the enhanced front cell J_{SC} should have a chance to improve the overall performance of the tandem PSCs.

Conclusion

To conclude, the PffT2-FTAZ polymer exhibits lower HOMO and LUMO levels than the corresponding PT2-FTAZ polymer and the optical bandgap is also slightly reduced. These changes lead to higher V_{OC} , smaller V_{OC} deficit, wider absorptions and thus higher J_{SC} for the PffT2-FTAZ polymer based bulk-heterojunction solar cell. The fluorination on donor unit of the polymer result in a strong J -aggregation of the polymer in solution, which leads to enhanced polymer crystallinity and high hole transport mobility. For the blend morphology, the polymer can still form polymer domains with suitable domain size. This large bandgap polymer material with a 7.8% PCE achieved in single-junction solar cell should be a leading candidate to replace P3HT and build next-generation tandem polymer solar cells.

Experimental section

Materials: the syntheses and characterization of PffT2-FTAZ and PT2-FTAZ can be found in supplemental information.

Absorption spectra of thin films: the UV-Visible absorption spectra of PffT2-FTAZ and PT2-FTAZ solutions and solid

thin films were measured by a Cary 50 UV-vis spectrophotometer.

Fabrication and characterization of polymer solar cell devices: the ITO-coated glass substrates were washed by sequential ultrasonication in water/detergent, water, acetone, and isopropanol for 30 min in each solvent. The washed substrates were further treated with a UV-O₃ cleaner (Novascan, PSD Series digital UV ozone system) for 30 min. A topcoat layer of ZnO (The diethylzinc solution 15 wt% in toluene, diluted by tetrahydrofuran) was spin-coated onto the ITO substrate at a spinning rate of 5000 rpm for 30 s and then baked in air at 150 °C for 20 min. A blend of polymer:PC₇₁BM (1:1.2) at a concentration of 10 mg mL⁻¹ in DCB was prepared by stirring at 110 °C overnight. ITO substrate were pre-heated to about 115 °C and then transferred onto the spincoater to which is attached to a metal chuck that was pre-heated together with the substrate to serve as a “heat reservoir” to slow down the cooling of the substrate before the start of spincoating. A warm (115 °C) solution of polymer blend was then spin-coated on the top of ZnO layer at different speed from 750-900 rpm to achieve an optimal film thickness. All dried thin film was thermally annealed at 100 °C for 5 min inside a N₂-filled glove box. The thickness of active layer is typically 300 nm. After that, a vanadium oxide interlayer (V₂O₅, 20 nm) and an aluminum electrode (Al, 100 nm) were vacuum-deposited at 2.0×10^{-6} Torr. The current density-voltage (J - V) characteristics were measured in air under simulated AM. 1.5 G solar irradiation (100 mW cm⁻², Newport: oriel model 94021A).

The light intensity was adjusted by using a standard silicon reference cell with a KG5 filter. The J - V characteristics of the photovoltaic cells were recorded with a J - V measurement system (Keithley 236). The EQE measurement was performed on a Newport EQE system equipped with a standard Si diode (Oriel lamp model 74125). The configuration of the shadow mask afforded four independent devices on each substrate, and each device had an active layer of ~ 5.9 mm².

AFM characterization: AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All films were coated on ITO glass substrates.

Grazing incidence wide-angle x-ray scattering (giwaxs) characterization: GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared using identical blend solutions as those used in devices on Si substrate. The 10 keV X-ray beam was incident at a grazing angle of 0.12-0.16°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 1 M photon counting detector.

Acknowledgments

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Appendix A. Supporting information

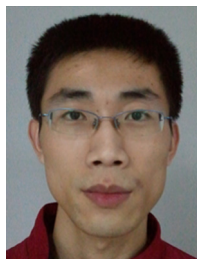
Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2015.05.016>.

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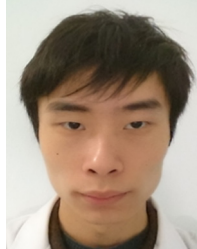
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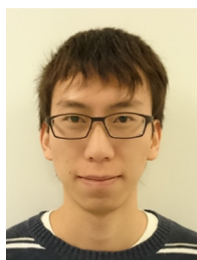
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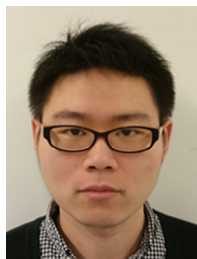


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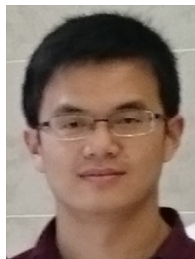
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