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PII: S1566-1199(19)30175-2

DOI: https://doi.org/10.1016/j.orgel.2019.04.010

Reference: ORGELE 5204

To appear in: Organic Electronics

Received Date: 30 January 2019

Revised Date: 9 April 2019

Accepted Date: 9 April 2019

Please cite this article as: C. Jiang, X. Chen, M. Zhao, Y. Li, X. Li, H. Wang, Implication of sidechain fluorination on electronic properties, ordering structures, and photovoltaic performance in asymmetric-indenothiophene-based semiconducting polymers, *Organic Electronics* (2019), doi: https:// doi.org/10.1016/j.orgel.2019.04.010.

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Implication of Side-Chain Fluorination on Electronic Properties, OrderingStructures,andPhotovoltaicPerformanceAsymmetric-Indenothiophene-Based Semiconducting Polymers.

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Abstract

Side-chain fluorination of conjugated polymers has been proved to be a highly effective approach for optimizing optical and electrical properties of the relative polymers. However, current studies on the fluorination are all based on symmetric molecular structures. In this work, two new D-A type photovoltaic polymers, namely PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT, based on asymmetric indenothiophene (IT) donor units with alkoxyphenyl or fluoroalkoxyphenyl substituents were designed and synthesized. Effects of the fluorine substitution in the asymmetric IT donor units on the electronic structure, ordering structure, photovoltaic properties, and charge generation and recombination dynamics were investigated. It is found that side-chain fluorination in the asymmetric donor units of the D-A polymers endowed the relative polymer with a deeper HOMO level, higher and more balanced charge mobilites, increased charge dissociation efficiency and reduced bimolecular recombination. As a result, the bulk heterojunction solar cell based on the blend film of PIT_{Phf} -DT_{ff}BT and PC₇₁BM demonstrated an efficiency of 7.03%, whereas the cell efficiency based on PIT_{Ph}-DT_{ff}BT was only 5.68%. These results indicate that our design strategy by introducing a fluoroalkoxyphenyl unit as side chain to fabricate asymmetric IT-based polymer is efficient in improving the photovoltaic performance. We believe that the results provide new insights into the design of high-performance semiconducting photovoltaic polymers.

Keywords: Asymmetric; Indenothiophene; Side-chain fluorination; Solar cells

Introduction

The past decade has witnessed the rapid improvement in polymer solar cells (PSCs) with advantages of low-cost, light weight, and flexibility.^[1,2] Generally, efficient PSCs adopt a bulk heterojunction structure with a p-type conjugated polymer as donor and a n-type material (fullerene derivatives, nonfullerene small-molecular, conjugated polymers) as acceptor.^[3-7,38] Fullerene derivatives, such as $PC_{71}BM$ ([6,6]-phenylC₇₁butyric acid methyl ester) and ICBA (indene-C₆₀bisadduct), are one of the most widely used acceptor materials in PSCs. The great success of $PC_{71}BM$ or ICBA could be ascribed to their fundamental properties, including high electron affinity and electron mobility, and ability to form appropriate phase separation.^[8,9]A lot of

literatures have focused on the design of highly efficient donors matched with fullerene acceptor, leading to devices with power conversion efficiencies (PCEs) over 10%.^[10-14]

Recently, asymmetric structural materials, including polymer or small-molecule, have caused increasing attention. Compared with symmetric units, asymmetric structures can induce higher dipole moment which can strongly influence molecular self-assembly and resultantly improve the order and crystallinity in BHJ films.^[15] With the increase of dipole moment, the intramolecular charge transfer (ICT) effect will be enhanced, thus resulting in the higher charge carrier mobility.^[16,17] Furthermore, it has been proven that the asymmetric structures also efficiently decrease the highest occupied molecular orbital (HOMO) values of the corresponding polymers,^[18,19]which would be beneficial for higher V_{oc} achieved for the relative devices. For example, in order to achieve a donor unit with a deep HOMO level and good J_{sc} and FF values, Hoang et al.^[20] designed a new BDT monomer, bearing an alkoxy group on one side of the moiety and an alkyl group on the other side. This strategy both reduced the HOMO energy level and maintained J_{sc} and FF compared to the dialkoxy-BDT polymer. Gu et al.^[21] synthesized a new D-A type polymer (PBDT_{Th}-DT_{ff}BT) based on alkylthienyl asymmetric BDT and the well-known 4,7-di(thiophen-2-ethylhexyl)-5,6-difluoro-2,1,3-benzothiadiazole (DT_{ff}BT), the optimized PBDT_{Th}-DT_{ff}BT based device exhibited a V_{oc} of 0.87 V, a J_{sc} of 15.06 mA cm⁻², FF of 70.4% and a high PCE of 9.22%. The PCE is higher than the control polymers which have the same backbone structure but have the 1D (8.3%) or 2D (6.2%) symmetric substituted BDT unit. Guo et al.^[22] designed and synthesized a small molecule named DRBDTCO based on BDT with an asymmetric side chain as donor material for solution-processed bulk heterojunction solar cells. The optimized device exhibits a high PCE of 8.18% with an outstanding FF of 73%. These results demonstrated that the asymmetric BDT unit could be a promising building block for photovoltaic materials with high efficiencies and high fill factors. Indenothiophene (IT), an asymmetric counterpart of indacenothiophene (IDT), was ultilized by Wang et al.^[23] as the donor unit for building D-A copolymers. These PSCs based on IT copolymers were found to exhibit the highest PCE of 9.14%, meanwhile with a high V_{oc} of 1.0 V. Kim et al.^[24] synthesized a new asymmetric n-type semiconducting molecule (PhITBD) with an indenothiophene core. The relative PSC with asymmetric PhITBD displayed improved PCE of 6.57% as compared to those with the symmetric molecular backbone.

In addition, it has been demonstrated that side-chain fluorination of conjugated polymers is a highly effective approach for optimizing optical and electrical properties of the relative polymers, thus improving the photovoltaic performance of fullerene-based PSCs.^[25-32,47] Given the strong electron-withdrawing nature, introduction of fluorine can effectively lower the HOMO and LUMO energy levels while minimally changing energy band gap (E_g), resulting in the enhancement of V_{oc} .^[27,29,33-35,39-41] In addition, it is also believed that the fluorine atom offers noncovalent attractive interactions with the hydrogen or sulfur atoms (F^{...}H or F^{...}S), which can promote the molecular planarity and intermolecular assembly, and therefore the crystallinity without introducing any steric hindrance. This often leads to enhanced charge mobility of the polymers.^[36] Furthermore, fluorination can tune the polarity of the polymers and control the interfacial interaction with fullerenes, resulting in improved BHJ morphology with smaller phase domains and larger interfacial areas, thus increasing the exciton dissociation and enhancing J_{sc} and FF values.^[37] All these features are expected to improve PSC performance. However, as far as we know, current studies on the side-chain fluorination are all based on symmetric molecular

structures. Therefore, whether fluorination on asymmetric structure has the same effect mentioned above still needs to be further studied.

Herein, we designed and synthesized two novel D-A copolymers, named PIT_{Phf}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT, based on the indenothiophene donor unit and 4,7-di(thiophen-2-ethylhexyl)-5,6-difluoro-2,1,3-benzothiadiazole $(DT_{\rm ff}BT),$ а well-known acceptor unit. These two polymers feature asymmetric indenothiophene core with lower numbers of alkyl chains and different numbers of fluorine atoms (0 and 1) in the side chains of the donor units. The effect of the side-chain fluorination on the performance of the PSCs was investigated systematically. We found that, side chain fluorination has a remarkable impact on the properties of the polymers and the relative device performance. First, the fluorinated PIT_{Phf}-DT_{ff}BT polymer shows lower HOMO and LUMO levels, thus improving the Voc values (0.81 V for PIT_{Ph}-DT_{ff}BT device and 0.84 V for PIT_{Phf}-DT_{ff}BT device). In addition, fluorination is beneficial for enhancing charge mobility and promoting exciton dissociation with suppressed recombination process, thereby significantly improving both J_{sc} and FF values. Furthermore, compared with nonfluorinated PIT_{Ph}-DT_{ff}BT, the side-chain fluorination of PIT_{Phf}-DT_{ff}BT facilitates the formation of favorable BHJ morphology with small phase domains. As a result, the PIT_{Ph}-DT_{ff}BT cell exhibited moderate PCE of up to 5.68%, whereas the PIT_{Phf}-DT_{ff}BT cell yielded PCE as high as 7.03%.

Results and discussion

The two polymers were synthesized via Stille coupling reaction between the IT-based donor unit and the $DT_{ff}BT$ acceptor unit with $Pd_2(dba)_3/P(o-tol)_3$ as the catalyst. The synthetic routes to the monomers and the corresponding copolymers are showed in Scheme 1. Because of the asymmetry of IT structure, Stille coupling reaction could take place on two different sites. Thus, both the two polymers are random polymers. The resulting copolymers were precipitated in methanol and filtered off. The collected polymers were subjected to consecutive soxhlet extractions with methanol, acetone, n-hexane and chloroform in turn, and final the chloroform fractions were recovered. The copolymers are readily soluble in common organic solvents such as chloroform (CF), tetrahydrofuran (THF), toluene, and 1,2-dichlorobenzene (o-DCB). Gel permeation chromatography (GPC) analysis using THF as eluent at room temperature gave a number average molecular weight (Mn) of 67.5 kDa with a polydispersity index (PDI) of 2.29 for PIT_{Ph}-DT_{ff}BT and an Mn of 70.5 kDa with a PDI of 2.58 for PIT_{Phf}-DT_{ff}BT with respect to a polystyrene standard. Obviously, the differences between the two polymers in Mn and PDI are very small, which is beneficial for the comparative study on the effect of side-chain fluorination.



Scheme 1 Synthetic routes to the monomers and the corresponding copolymers.

Optical properties

Fig.1 (a) and (b) show the absorption spectra of PIT_{Ph}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT in chloroform solution and as thin films coated on quartz glass, and the relative optical data are summarized in Table 1. The absorption spectra in both the solution state and the thin film state exhibited dual absorption bands. In each spectrum, the absorption band in the 350-500 nm wavelength range could be assigned to the localized π - π * transition, whereas the relatively broad absorption in the 500-700 nm range can be attributed to the intramolecular charge transfer (ICT) between the acceptor units and donor units. In solution, PIT_{Ph}-DT_{ff}BT has an absorption maximum peak at 553 nm, while PIT_{Ph}-DT_{ff}BT is slightly blue shifted with a maximum at 548 nm. In thin film, the absorption peaks for PIT_{Ph}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT bathochoromically shift to 589 and 584 nm, respectively, indicative of some ordered structure and π - π stacking interactions in the film due to their coplanar backbones. The absorption onsets of PIT_{Ph}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT are at 721 and 713 nm in thin film, which correspond to optical bandgaps of 1.72 and 1.74 eV, respectively. It can be found that the spectrum of PIT_{Ph}-DT_{ff}BT is slightly blue-shifted in thin film compared with that of PIT_{Ph}-DT_{ff}BT, whether the absorption peak or onset, which may be due to the weak steric hindrance of F atom lead to the weakened π - π stacking effect of polymer backbone.^[42-44]

The similar blue shifts have been observed in some other fluorinated D-A polymer systems.^[40,45,46] Thus, the introduction of fluoroalkoxyphenyl side chains into indenothiophene unit will increase the band gap, which would favor its high V_{oc} in PSCs.



Fig.1 Normalized UV-vis absorption spectra of the polymers in chloroform solution (a) and in thin film (b).

|--|

	Experimental						Calculated			
Polymer	λ_{max}^{sol}	$\lambda_{max}^{\qquad film}$	$\lambda_{edge}^{\qquad film}$	$E_{ m g}^{ m opt}$	НОМО	LUMO	$E_{ m g}^{\ m e}$	HOMO	LUMO	$E_{\rm g}^{\ \rm c}$
	(nm)	(nm)	(nm)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
PIT_{Ph} - $DT_{ff}BT$	416,553	426,589	721	1.72	-5.28	-3.50	1.78	-4.92	-2.71	2.21
PIT _{Phf} -DT _{ff} BT	418,548	424,584	713	1.74	-5.38	-3.52	1.86	-5.00	-2.77	2.23

Electrochemical properties

As we know, energy level matching of donor and acceptor materials is an important factor to achieve high-performance PSCs. Cyclic voltammetry (CV) was performed to measure the HOMO energy level (E_{HOMO}) and LUMO energy level (E_{LUMO}) of the polymers. The measured cyclic voltammograms curves are illustrated in Fig.S1, and the results are summarized in Table 1. The onset oxidation/reduction potentials (E_{ox}/E_{red}) of the polymers, as shown in Fig.S1, are 0.57/-1.21 V vs. Ag/Ag⁺ for the alkoxyphenyl chain substituted PIT_{Ph}-DT_{ff}BT and 0.67/-1.19 V vs Ag/Ag⁺ for the fluoroalkoxyphenyl chain substituted PIT_{Ph}-DT_{ff}BT. The E_{HOMO}/E_{LUMO} levels of PIT_{Ph}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT are calculated to be -5.28/-3.50 eV and -5.38/-3.52 eV, respectively, according to the equations: $E_{HOMO/LUMO}$ =-e ($E_{ox/red}$ +4.71) (eV). The E_{HOMO} of PIT_{Ph}-DT_{ff}BT is 0.10 eV deeper than that of PIT_{Ph}-DT_{ff}BT, which will benefit for higher V_{oc} of the PSCs with the polymer as donor. Comparing to the alkoxyphenyl substitute, fluoroalkoxyphenyl substitute lowered the HOMO level of the D-A copolymer. Moreover, the change of E_{LUMO} is not very obvious. This is probably because the F atom is located on the donor unit, which would have great influence on the E_{HOMO} and little effect on the E_{LUMO} . Notably, the HOMO energy offset (ΔE_{HOMO}) and LUMO energy offset (ΔE_{LUMO}) between the two polymers

and $PC_{71}BM$ are both larger than the empirical threshold of 0.3 eV for effective exciton dissociation to overcome the binding energy of the excitons.

Theoretical calculation

To demonstrate the optimal molecular geometry and electronic properties, theoretical calculations were performed by using density functional theory (DFT) B3LYP with 6-31 G(d, p) basic set. To simplify the calculations, we investigated monomer model (the number of repeat units is one) of each polymer. At the same time, all of the alkoxy side chains were replaced by methoxy groups to save the calculation time. Fig.2 shows the frontier molecular orbitals, the corresponding LUMO and HOMO levels, and the calculated dipole moments of PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT. As can be observed, the HOMO wave functions are distributed entirely over the planar conjugated backbone, while the LUMO wave functions are mainly concentrated on the benzothiadiazole acceptor units. These images revealed the well-designed D-A structures and ICT behaviors of the two polymers. For PIT_{Ph}-DT_{ff}BT, the calculated HOMO, LUMO and Eg are -4.92, -2.71, and 2.21 eV, respectively, while for PIT_{Phf}-DT_{ff}BT, the calculated HOMO, LUMO and Eg are -5.00, -2.77 and 2.23 eV, respectively. The calculated HOMO level of PIT_{Phf}-DT_{ff}BT is 0.08 eV lower than that of PIT_{Ph}-DT_{ff}BT, which is consistent with the CV results. Though the LUMO difference between the two polymers is 0.06 eV from theoretical calculation, which is bigger than that of 0.02 eV from CV method, considering the calculation error, it still suggests that the influence of fluorine substitute on the energy level is mainly manifested on the HOMO level because fluoroalkoxyphenyl substitute is located on the donor unit. The difference of calculated E_g is also consistent with that of E_g^{opt} and E_g^{e} . Furthermore, the dipole moments (μ_g) calculated by DFT are 2.27 D and 2.45 D for PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT, respectively. The higher μ_g of PIT_{Phf}-DT_{ff}BT indicates that introducing a fluorine atom to the side chain of donor unit can improve the molecular polarizability, further enhance the molecular interaction. Some reports have mentioned that a repeating polymer unit with a high dipole moment might exert a considerable influence over the molecular assembly and the consequent morphology in film state.^[17] Especially, such unit might produce abundant donor-acceptor interfaces, thereby resulting in the suppression of charge recombination in bulk heterojunction PSCs. Therefore, the PIT_{Phf}-DT_{ff}BT polymer with a higher dipole moment is expected to produce a PSC device with higher J_{sc} and FF than PIT_{Ph}-DT_{ff}BT.



µg=2.27D

μ_o=2.45D

Fig.2 Theoretical calculated frontier molecular orbital and the dipole moment, obtained from density functional theory (DFT) calculations on the polymers with a chain length n=1 at the B3LYP/6-31 G(d,p) basic set.

Photovoltaic properties

To investigate the effect of fluorine atom on the photovoltaic properties, the PSC devices comprising of the polymer PIT_{Phf}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT as the donors and PC₇₁BM as the acceptor were fabricated with the configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/PDINO/Al, where PEDOT:PSS and PDINO are the abbreviations of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) and perylene diimide (PDI) derivative. Chloroform is used as the processing solvent and the optimized weight ratios for both two polymer blend systems are 1:1.2. To further optimize the morphology of the blend films and thus the photovoltaic performance, we adopted thermal annealing process and additive DPE (diphenyl ether) treatment to obtain the optimal devices. The optimal annealing temperature and time are at 120 \Box for 2 min. All the photovoltaic measurements were carried out under AM 1.5G illumination at an intensity of 100 mW cm⁻². Fig.3 shows the current density–voltage (J-V) curves of the PSC devices based on the two polymers. The short-circuit currents (J_{sc}), open-circuit voltages (V_{oc}), fill factors (FF) and PCEs of these PSCs are summarized in Table 2. As shown in Table 2, the as-cast device based on

PIT_{Ph}-DT_{ff}BT exhibits a V_{oc} of 0.81 V, J_{sc} of 10.66 mA cm⁻², and FF of 0.467, which yields the PCE of 4.06%. When the alkoxyphenyl is replaced by fluoroalkoxyphenyl, the PIT_{Phf}-DT_{ff}BT based as-cast device exhibits a relatively higher PCE of 5.56%, with a V_{oc} of 0.84 V, J_{sc} of 11.99 mA cm⁻², and FF of 0.549. As expected from the deeper E_{HOMO}, the cells based on PIT_{Phf}-DT_{ff}BT exhibit higher V_{oc} than the PIT_{Ph}-DT_{ff}BT. The J_{sc} and FF are increased significantly after the introduction of F atom. For the two polymers, the thermal annealing at 120 □ for 2 min dramatically improved the device performance. The PCE values of the PSCs based on PIT_{Phf}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT increased to 5.12% and 6.55%, respectively. The notably improved J_{sc} and FF account for the increased PCE values after thermal annealing. When DPE was incorporated into the active layer with the thermal annealing in the meantime, the corresponding PSC shows the highest efficiency of 5.68% with a J_{sc} of 13.21 mA cm⁻² and a FF of 0.533 for PIT_{Ph}-DT_{ff}BT. The adding of DPE further enhances the J_{sc} and FF values, resulting in even higher efficiencies for the two polymers.



Fig.3 Typical J-V characteristics of the PSCs based on (a) PIT_{Ph} - $DT_{ff}BT$ (1:1.2, w/w) and (b) PIT_{Phf} - $DT_{ff}BT$ (1:1.2, w/w) with (120 \Box) or without (none) thermal annealing at 120 \Box for 2 min and further additive DPE added with thermal annealing (120 \Box , 1% DPE), under the illumination of AM1.5G, 100 mW/cm².

Table 2. Photovoltaic performance parameters of the PSCs based on polymer/PC₇₁BM (1:1.2 w/w), under the illumination of AM1.5G, 100 mW/cm².

Polymer	Treatment	$V_{oc}(V)$	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^b (%)
PIT _{Ph} -DT _{ff} BT	none	0.81	10.66	46.7	4.06 (3.83±0.23)
	TA ^a	0.81	12.06	52.2	5.12 (4.94±0.18)
	TA ^a , 1%DPE	0.81	13.19	53.3	5.68 (5.53±0.15)
PIT _{Phf} -DT _{ff} BT	none	0.84	11.99	54.9	5.56 (5.36±0.20)
	TA^{a}	0.84	12.53	62.1	6.55 (6.29±0.26)
	TA ^a , 1%DPE	0.84	13.21	63.3	7.03 (6.90±0.13)

^a Thermal annealing at 120 \square for 2 min. ^b In parentheses are average values based on eight devices.

The optimal external quantum efficiency (EQE) curves of the two polymer devices are shown in

Fig.4. Both the two devices exhibited photo response ranging from 300 to 700 nm, suggesting that both the donor and acceptor contribute to EQE and thus the J_{sc} . Therein, the PIT_{Phf}-DT_{ff}BT blend showed a higher EQE value than the PIT_{Ph}-DT_{ff}BT blend, reaching a maximum value of 75% and over 70% across the range 350-650 nm. This result indicates the more highly efficient photoelectron conversion process in the PIT_{Phf}-DT_{ff}BT device, which is in consistent with the enhanced J_{sc} of PIT_{Phf}-DT_{ff}BT blend device. For the two polymers, both the J_{sc} values of the relative devices were in good agreement with the EQE spectra within an experimental error of 5%. The J_{sc} values calculated from the EQE spectra were 12.80 and 12.95 mA cm⁻² for the devices based on PIT_{Phf}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT, respectively, which are in good agreement with the J_{sc} values obtained from the J-V curves.



Fig.4 The EQE spectra of the PSCs based on polymer/PC₇₁BM blends with 1% DPE and thermal annealing at $120 \Box$ for 2 min.

To further understand the additive DPE and thermal annealing effect on the device performance, the bulk transport properties of the polymer/PC₇₁BM blends were investigated using the space charge-limited current (SCLC) method with the hole only device (ITO/PEDOT:PSS/active layer/Au) and electron only device (ITO/ZnO/active layer/PDINO/Al). The plots of $J^{1/2}$ vs (V_{appl}-V_{bi}) characteristics for the devices are showed in Fig.S2, and the results are summarized in Table 3. The hole (μ_h)/electron (μ_e) mobilities of the PIT_{Ph}-DT_{ff}BT/PC₇₁BM films are calculated to be 0.15 for the as-cast film, 0.29 for the annealed film and 0.33 for the annealed film with DPE. The hole (μ_h) /electron (μ_e) mobilities of the PIT_{Phf}-DT_{ff}BT/PC₇₁BM films are calculated to be 0.18 for the as-cast film, 0.36 for the annealed film and 0.37 for the annealed film with DPE. Apparently, after thermal annealing, charge mobilities are increased for some extent, and further enhanced by adding the additive DPE. Meanwhile, more balanced hole and electron mobilities (μ_b/μ_e) are also observed with thermal annealing and additive DPE. These observations are consistent with the corresponding PCE changes shown in Tabel 1. Around two or three times higher and more balanced hole and electron mobilities of the polymer blends with thermal annealing and DPE compared to the as-cast blends is one of the reasons for the enhanced J_{sc} of the corresponding devices. In addition, for the two polymers, in comparison with the charge carrier mobilities of as-cast, thermal annealed or annealed with DPE devices, it can be found that the devices based on the fluoroalkoxyphenyl substituted copolymers (PIT_{Phf}-DT_{ff}BT) demonstrated higher and more balanced hole and electron mobilities, which should be one reason for their higher J_{sc} and PCE values.

Polymer	Treatment	$\mu_h [cm^2 V^{-1} s^{-1}]$	$\mu_{e} \ [cm^{2}V^{-1} \ s^{-1}]$	μ_h/μ_e
PIT_{Ph} - $DT_{ff}BT$	none	0.34×10^{-4}	2.26×10^{-4}	0.15
	TA^{a}	1.14×10^{-4}	3.95×10^{-4}	0.29
	TA ^a , 1%DPE	2.47×10^{-4}	7.38×10^{-4}	0.33
PIT_{Phf} - $DT_{ff}BT$	none	0.52×10^{-4}	2.84×10^{-4}	0.18
	TA^{a}	1.84×10^{-4}	5.18×10^{-4}	0.36
	TA ^a , 1%DPE	3.37×10^{-4}	9.21×10 ⁻⁴	0.37

Tabel 3 Hole and electron mobilities of PIT_{Ph} - $DT_{ff}BT$ and PIT_{Phf} - $DT_{ff}BT$ blends measured via the SCLC method

^a Thermal annealing at $120 \square$ for 2 min.

To gain deeper insight into the charge generation and dissociation behavior, the photocurrent density (J_{ph}) as a function of effective applied voltage (V_{eff}) were measured for the two polymer devices. $J_{ph}=J_L-J_D$, where J_L is the current density under illumination and J_D is the current density in the dark. $V_{eff}=V_0-V_a$, where V_a is the applied voltage and V_0 is the voltage at which J_{ph} is zero. As shown in Fig.5, when V_{eff} arrives at ~2V, J_{ph} values for both devices reach saturation (J_{sat}), suggesting that charge recombination is minimized at higher voltage due to the high internal electric field in the devices. The charge dissociation efficiency can be evaluated by using J_{ph}/J_{sat} ratio. Under the short-circuit and maximal power output conditions, the J_{ph}/J_{sat} values of PIT_{Phf}-DT_{ff}BT are 91.6%, 64.1% for the as-cast device, 92.6%, 64.8% for the device with thermal annealing, and 93.8%, 68.6% for the device with additive DPE and thermal annealing, respectively. The increased J_{ph}/J_{sat} values indicate that the thermal annealing and additive DPE treated devices exhibited higher exciton dissociation and more efficient charge collection efficiency compared to the as-cast device. In addition, the J_{ph}/J_{sat} values of PIT_{Ph}-DT_{ff}BT are 93.2%, 60.5% for the device with additive DPE and thermal annealing, which are smaller than those of PIT_{Phf} -DT_{ff}BT. The results indicate that the change in the structure of fluoroalkoxyphenyl substitute can improve the charge dissociation and collection as well.



Fig.5 Photocurrent density versus effective voltage $(J_{ph}-V_{eff})$ characteristics for devices based on $PIT_{Ph}-DT_{ff}BT$ and $PIT_{Phf}-DT_{ff}BT$ blends.

To further probe the charge recombination behavior in the devices, which is one of the most important factors influencing the FF values of PSCs, the light-intensity (P) dependence of current density (J_{sc}) was then measured. The relationship between J_{sc} and P can be represented by the power-law equation $J_{sc} \propto P^{\alpha}$, where α would be unity (α =1), when the bimolecular recombination can be negligible under short circuit condition. Fig.6 shows the log-log plot of J_{sc} as a function of the light intensity (P). As presented in Fig.6, the α value for the as-cast PIT_{Phf}-DT_{ff}BT blend is 0.94, which is higher than 0.92 for the as-cast PIT_{Ph}-DT_{ff}BT blend. This suggests that less bimolecular recombination occurred in the PIT_{Phf}-DT_{ff}BT blend, supporting its higher FF and PCE. Considering the significant impact of thermal annealing and additive DPE on the FF value, we chose the polymer PIT_{Phf}-DT_{ff}BT as the research object. The α values were measured as 0.96 for the device with thermal annealing and 0.97 for the device with thermal annealing and additive DPE. In contrast to as-cast PIT_{Phf}-DT_{ff}BT device, the devices via thermal annealing and further additive treatment possess higher FF values, implying reduced bimolecular recombination, leading ultimately to relatively higher FF values and consequently higher PCEs.



Fig.6 Double logarithmic polts of photocurrent density as a function of incident light intensity for devices based on PIT_{Ph} - $DT_{ff}BT$ and PIT_{Phf} - $DT_{ff}BT$ blends.

Grazing incident wide-angle X-ray scattering (GIWAXS) is further used to investigate the molecular packing and crystallinity of the blended PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT films with and without solvent additives and thermal annealing treatment. Fig.7 (a) and (b) shows the line-cuts of the blended PIT_{Phf}-DT_{ff}BT/PC₇₁BM films in the in-plane and out-of-plane directions, respectively, Fig.7 (c) and (d) shows the line-cuts of the blended PIT_{Ph}-DT_{ff}BT/PC₇₁BM films in the in-plane and out-plane directions, respectively. As shown in Fig.7, for all the blend films, the lamellar (100) peaks in the in-plane and out-of-plane directions could be observed. This indicates that the polymers have relatively strong lamellar molecular packing, which corresponds to the semi-crystalline nature of the copolymers. However, the stronger intensity of the (100) reflection in the out-of-plane profile than in the in-plane profile indicates that the lamellar packing of both PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT based polymers preferentially stacked out of the film plane (edge-on rich orientation), though with some randomness. For the additive-free PIT_{Phf}-DT_{ff}BT /PC₇₁BM film, the broad peak at q=1.32 Å⁻¹ is characteristic of PC₇₁BM aggregation, and the

out-of-plane (010) π - π stacking peak located at q=1.78 Å⁻¹ (d-spacing of 3.53 Å) is attributed to face-on orientation of PIT_{Phf}-DT_{ff}BT. After thermal annealing treatment, the blend film shows a slight enhanced (010) π - π stacking peak located at q=1.81 Å⁻¹ (d-spacing of 3.47 Å). When DPE was used as a solvent additive, the corresponding film shows a (010) π - π stacking peak located at q=1.83 Å⁻¹ (d-spacing of 3.43 Å). At the same time, the out-of-plane (100) peak slightly enhanced, which is corresponding to the weakly increased in-plane (010) peak. Notably, the facial π - π stacking distances are decreased. Similarly, for the PIT_{Pb}-DT_{ff}BT/PC₇₁BM film, the location of out-of-plane (010) peak increases from 1.75 Å⁻¹ (d-spacing of 3.59 Å) to 1.77 Å⁻¹ (d-spacing of 3.55 Å) and then 1.79 Å⁻¹ (d-spacing of 3.51 Å) after thermal annealing treatment and further adding of additive DPE. The decreased π - π stacking distances and relatively strong face-on orientation for PIT_{Phf}-DT_{ff}BT/PC₇₁BM and PIT_{Ph}-DT_{ff}BT/PC₇₁BM film are beneficial to charge transport and reducing bimolecular recombination. As a result, the corresponding PSCs with thermal annealing treatment and DPE exhibit enhanced PCEs with increased J_{sc} and FF values. These results suggest that the thermal annealing and DPE additive treatment may help to crystallize PIT_{Phf}-DT_{ff}BT and PIT_{Ph}-DT_{ff}BT, which are beneficial for improving the solar cell performance. In addition, the out-of-plane (010) π - π stacking distances of PIT_{Phf}-DT_{ff}BT is shorter than that of PIT_{Ph}-DT_{ff}BT. This phenomenon indicates that the fluoroalkoxyphenyl substitute promotes the π - π stacking interaction, which can improve the inter-molecular exciton transfer. The tighter packing of PIT_{Phf}-DT_{ff}BT, associated well with its higher crystalline behavior of the blend film, corresponds well with the higher value of hole mobility and FF. These results suggest that the presence of large amounts of fluoroalkoxyphenyl substitutes contribute to highly ordered structure and effective charge transport, which are desirable for higher carrier mobility thereby higher photovoltaic efficiencies.



Fig.7 GIWAXS of PIT_{Phf} - $DT_{ff}BT$ blend film: (a) in-plane line-cuts, (b) out-of-plane line-cuts; and PIT_{Ph} - $DT_{ff}BT$ blend film: (c) in-plane line-cuts, (d) out-of-plane line-cuts.

In order to determine the effect of morphology of polymer/PC₇₁BM blend film on the device performance, atomic force microscopy (AFM) was performed. The surface morphology was recorded by tapping mode AFM and is illustrated in Fig.8. Among them, Fig.8 (a), (b) and (c) are of PIT_{Ph}-DT_{ff}BT/PC₇₁BM blend films; Fig.8 (d), (e) and (f) are of PIT_{Phf}-DT_{ff}BT/PC₇₁BM blend films. Fig.8 (a) and (d) are of casting films. Fig.8 (b) and (e) are of films after thermal annealing. Fig.8 (c) and (f) are of films both treated with 1% DPE and thermal annealing. From the AFM

images in Fig.8, it can be found that the casting polymer blends exhibit relatively large root-mean-square (RMS) value of 3.73 nm for PIT_{Ph}-DT_{ff}BT and 2.97 nm for PIT_{Phf}-DT_{ff}BT due to the formation of large-sized aggregates. After thermal annealing, reduced surface roughness values of 2.48 and 2.35 nm are observed from the surface AFM images of PIT_{Ph}-DT_{ff}BT and PIT_{Phf} -DT_{ff}BT blends, respectively. Furthermore, both the addition of DPE and thermal annealing treated to the blends lead to improved morphology with the disappearance of relatively large-sized aggregations, especially for PIT_{Phf}-DT_{ff}BT blend with a fairly homogeneous surface in size and feature. The RMS values of PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT blends are reduced to 1.74 and 1.78 nm, respectively. As the morphology with small-scale phase separation is beneficial to efficient exciton diffusion, exciton separation, and charge transport, resulting in an increased Jsc and FF for the PSC devices, the post-treatment of thermal annealing and addition of DPE gradually reduce the phase separation size, therefore significantly improve the J_{sc} and FFs, further the PCEs of the two polymer based devices. These results seem to be directly linked to the above-observed dependency of PCEs on the application of various processing techniques, such as addition of DPE and thermal annealing. This morphology difference between the blend films with and without additive and thermal annealing is one of the main reasons for the photovoltaic performance variation of the two polymer based devices. What's more, the Rms values of PIT_{Phf}-DT_{ff}BT are smaller than those of PIT_{Ph}-DT_{ff}BT (except for the similar Rms values of Fig.8(c) and (f)), which is owing to the stronger inter-molecular interactions of fluoroalkoxyphenyl substitute in polymer PIT_{Phf}-DT_{ff}BT. Base on the stronger inter-molecular interactions, smaller phase separation size can be formed in PIT_{Phf}-DT_{ff}BT. This result may help to explain why PIT_{Phf}-DT_{ff}BT tends to obtain higher FFs and J_{sc} , and thus higher PCEs than PIT_{Ph}-DT_{ff}BT.



Fig.8 Topographic AFM images $(5\times5 \text{ um}^2)$ of the blend films of $\text{PIT}_{\text{Ph}}\text{-}\text{DT}_{\text{ff}}\text{BT}$ (a, b, c) and $\text{PIT}_{\text{Ph}}\text{-}\text{DT}_{\text{ff}}\text{BT}$ (d, e, f). Panels (a) and (d) are of as-cast films; (b) and (e) are of films with thermal annealing at 120 \Box for 2min; (c) and (f) are of films with additive DPE and thermal annealing at 120 \Box for 2min.

Conclusion

We synthesized two novel IT-based asymmetric polymers with nonfluorinated and fluorinated side chain, namely, PIT_{Ph}-DT_{ff}BT and PIT_{Phf}-DT_{ff}BT. The fluorination preferentially influences the HOMO of the polymer, resulting in deeper HOMO, slightly deeper LUMO, and slightly wider E_g for PIT_{Phf}-DT_{ff}BT relative to the nonfluorinated PIT_{Ph}-DT_{ff}BT counterpart. As expected from the deep HOMO level, V_{oc} of the PIT_{Phf}-DT_{ff}BT cell was improved to 0.84 V from 0.81 V of the PIT_{Ph}-DT_{ff}BT cell. The optimized PIT_{Ph}-DT_{ff}BT cell exhibited 5.68% PCE and lower J_{sc} and FF, whereas the PIT_{Phf}-DT_{ff}BT cell had a 7.03% PCE with higher J_{sc} and FF. The charge transport study revealed that higher and more balanced hole and electron mobilities of PIT_{Phr}-DT_{ff}BT should be one reason for the higher J_{sc}, which could also be evidenced by the increased charge dissociation efficiency of PIT_{Phf}-DT_{ff}BT relative to that of PIT_{Ph}-DT_{ff}BT. The bimolecular recombination study demonstrated that side-chain fluorination can decrease the recombination, and this was likely the cause of the higher FF of the PIT_{Phf}-DT_{ff}BT. The tighter π - π stacking and smaller phase domain of PIT_{Phf}-DT_{ff}BT were also be detected by GIWAXS and AFM measurements, these behaviors were well-correlated with the results mentioned above. Furthermore, thermal annealing and additive DPE are beneficial to gain high performance PSCs, associated with the great improvement on Jsc and FF. These findings and detailed studies provide an important guidance to tune and optimize the morphology and properties of indenothiphene-based copolymers.

Experimental Section

Experimental details and additional characterization data are included in the Supporting Information.

Acknowledgements

The 2D-GIXRD data were obtained at 1W1A, Beijing Synchrotron Radiation Facility. The authors gratefully acknowledge the assistance of scientists of the Diffuse X-ray Scattering Station during the experiments. The authors gratefully acknowledge the Chemcloud computing of the Beijing University of Chemical Technology for the theoretical calculation of molecular orbitals.

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Highlights

- 1. Two new D-A type asymmetric-indenothiophene-based polymers, PIT_{Ph} - $DT_{ff}BT$ and PIT_{Phf} - $DT_{ff}BT$ were obtained.
- 2. Side-chain fluorination in the asymmetric donor units has a remarkably positive impact.
- 3. PIT_{Phf}-DT_{ff}BT shows enhanced charge mobility, better crystallinity and surface morphology.