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Regio-Regular Polymer Acceptors Enabled by Determined Fluorination on End Groups for All-Polymer Solar Cells with 15.2 % Efficiency

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Abstract: Polymerization sites of small molecule acceptors (SMAs) play vital roles in determining device performance of all-polymer solar cells (all-PSCs). Different from our recent work about fluoro- and bromo- co-modified end group of IC-FBr (a mixture of IC-FBr1 and IC-FBr2), in this paper, we synthesized and purified two regiospecific fluoro- and bromosubstituted end groups (IC-FBr-o & IC-FBr-m), which were then employed to construct two regio-regular polymer acceptors named PYF-T-o and PYF-T-m, respectively. In comparison with its isomeric counterparts named PYF-T-m with different conjugated coupling sites, PYF-T-o exhibits stronger and bathochromic absorption to achieve better photon harvesting. Meanwhile, PYF-T-o adopts more ordered inter-chain packing and suitable phase separation after blending with the donor polymer PM6, which resulted in suppressed charge recombination and efficient charge transport. Strikingly, we observed a dramatic performance difference between the two isomeric polymer acceptors PYF-T-o and PYF-T-m. While devices based on PM6:PYF-T-o can yield power conversion efficiency (PCE) of 15.2%, devices based on PM6:PYF-T-m only show poor efficiencies of 1.4%. This work demonstrates the success of configuration-unique fluorinated end groups in designing

high-performance regular polymer acceptors, which provides
guidelines towards developing all-PSCs with better efficiencies.

Introduction

Solution-processed polymer solar cells (PSCs) have been developed as a sustainable technology for solar energy harvesting, which attract significant research attention owing to their outstanding advantages of mechanical flexibility, low cost, light weight and facile large-area fabrication.^[1-7] Recently, the bulk-heterojunction (BHJ) PSCs based on polymer donors and small molecule acceptors (SMAs) have progressed rapidly with impressive power conversion efficiencies (PCEs) exceeding 17%, due to the in-depth investigations on efficient photovoltaic materials, device optimization and interfacial engineering.^[8-17] Different from SMA-based PSCs, all-polymer solar cells (all-PSCs), which comprise conjugated polymers as both electron donors and acceptors, provide extra merits of excellent morphological stability, remarkable mechanical flexibility and suitability for industrial fabrication (e.g., roll-to-roll printing).^[18-26] However, the major bottleneck that limits the development of all-PSCs is currently the

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lack of high-performance polymer acceptors with superior photovoltaic properties.

Conventional all-PSCs typically employ the polymer acceptors based on naphthalene diimide, perylene diimide, bithiophene imide derivatives or $B \leftarrow N$ bridge bipyridine moieties (Figure S1), but these polymer acceptors suffer from several inherent drawbacks including narrow absorption range, deficient absorptivity, low-lying energy levels and excessive crystallinity, which limit the further improvement of their PCEs.^[27-31] Regarding these issues, Li and co-workers first proposed an effective approach by adopting SMAs as the acceptor units to construct high-performance donor-acceptor (D-A) polymer acceptors,^[32] which significantly improves the PCEs of all-PSCs owing to the higher absorption coefficient, broader photon response range and better complementary spectra with donor polymers in multiple cases.^[33-35] Subsequently, encouraged by the rapid progress of Y-series SMAs, the efficiencies of all-PSCs consisting of a novel polymer acceptor, PY-T, have been optimized to over 13 %.^[36,37] These results demonstrate that SMA-polymerization is an effective approach, but most research has concentrated on the modifications of the D units and the side chains of the SMAs as the comonomers (Figure S2).^[38-41] Fluorination on polymer chain is an effective method to enhance the photon harvesting ability and aggregation property. Recently, we reported that by implementing a polymer acceptor called PYF-T (Figure 1) with fluorinated end groups on the SMA sub-units, a remarkably enhanced PCE of 14.1 % can be achieved.^[42,43] However, one of the intrinsic disadvantages of this type of polymer acceptors lies in the uncertain configurations of the polymer chains (i.e., random polymers), as the SMA sub-units of these polymer acceptors are the mixture of several constitutional isomers. The origin of this phenomenon is that the terminal groups used to end-cap the SMA sub-units and provide crosscoupling sites are generally asymmetric with the bromine atoms locating at different positions. Historically, the regularity of polymer chains has been thoroughly investigated and emphasized in order to endow the materials with better solid-state packing, synthetic repeatability and less energy disorder, eventually leading to enhanced device performance.^[10,13,22,44-47] Considering these issues, the development of terminal groups with the determined substitution positions of fluorine and bromine atoms for regiospecific SMA subunits and thus regular polymer acceptors would provide more intuitive insights into interchain packing,^[48,49] which can further improve the performance of all-PSCs.

In this study, we report our further endeavors to enhance the PCE of all-PSCs up to 15.2% by designing regio-regular and fluorinated polymer acceptors. We successfully synthesized two new isomeric end groups with determined substitution positions of fluorine and bromine, named IC-FBr-o and IC-FBr-m (i.e., ortho- and meta-positions of the two halogen atoms). These end groups have different cross-coupling sites, leading to two configurationally unique comonomers and regular polymer acceptors (PYF-T-o & PYF-T-m, Figure 1). The design principle is to decrease the conformational disorder of the previous PYF-T-based acceptor. It is anticipated that reducing the number of configurational isomers of the polymer can enhance the interchain packing, and thus charge transport. In this way, we investigated the isomeric effects on the optoelectronic properties and photovoltaic performance of the polymer acceptors. PYF-T-o, which couples with thiophene units at the ortho-positions of fluorine on the end group moieties, shows a stronger intramolecular charge transfer (ICT) effect relative to PYF-T-m coupling at the meta-positions. This is revealed by theoretical calculations that PYF-T-o shows better conjugation along the polymer backbone and thus a bathochromic absorption. When blend-



Figure 1. The chemical structures of PYF-T, IC-FBr, IC-FBr-o, IC-FBr-m, PYF-T-o and PYF-T-m.

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ing with the donor polymer PM6, the PYF-T-o-based devices showed both enhanced open-circuit voltage (V_{OC} , 0.901 V) and fill factor (FF, 72.4%) compared with the PYF-T-based ones (14.0%), thus a higher PCE of 15.2%, which is among the best efficiencies for reported all-PSCs (Table S1). Surprisingly, the PM6:PYF-T-m device presented an extremely low performance of 1.40%, which results from deficient exciton dissociation, poor charge mobility and severe charge recombination. Morphological studies elucidated that the higher performance of the PYF-T-o-based devices originated from the stronger interchain packing and more suitable phase separation. Based on these findings, we further investigate the adaptability of the PM6:PYF-T-o in large-scale manufacture that a decent PCE of 13% was maintained in 1-cm² device through blade-coating method. Our work sheds light on the structure-performance relationships of the fluorine-substituted Y-series polymer acceptors and highlights the importance of the design of regular polymer acceptors for efficient all-PSCs.

Results and Discussion

The key to constructing regular fluorinated polymer acceptors based on Y-series SMAs is to synthesize the terminal groups with determined positions of fluorine and bromine atoms. As we know, terminal groups are strong nucleophiles that would even condense itself during column chromatography, so that it is a typical method to purify the isomeric terminal groups through recrystallization.^[47] Where-

as, it is a different story for the dihalogenated terminal groups, because the similar dipole moments between the isomers lead to comparable solubility in different solvents, hindering the separation of IC-FBr isomers by the previous method. Therefore, we intuitively design synthetic routes that can yield only one regiospecific product of dihalogenated terminal groups. The synthetic routes to IC-FBr-o and IC-FBr-m are illustrated in Scheme 1.^[50,51] By introducing the fluorine atom adjacent to one of the carbonyl groups of the precursor, the following condensation reaction will only occur at the other carbonyl group with less steric hindrance, resulting in configuration-unique terminal group moieties and the corresponding SMA comonomers (Y-OD-FBr-o and Y-OD-FBrm). Notably, the synthetic routes of these two regiospecific terminal groups are even easier and more efficient compared to that of the previous IC-FBr containing regio-isomers. Finally, Y-OD-FBr-o or Y-OD-FBr-m was copolymerized with 2,5-bis(trimethylstannyl)thiophene, generating two novel Y-series polymer acceptors, PYF-T-o and PYF-T-m, with different cross-coupling sites between the thiophene units and the terminal group moieties. Structure characterizations including ¹H NMR, ¹³C NMR and mass spectra of all the intermediate compounds are summarized in the Supporting Information. Both polymer acceptors can dissolve well in common organic solvents, such as chloroform and chlorobenzene. High-temperature gel permeation chromatography measurements (GPC, Table 1) showed that all polymer acceptors possess comparable molecular weights. The thermal decomposition temperature (T_d) of PYF-T, PYF-T-o and PYF-T-m are 337 °C, 330 °C and 343 °C, respectively, obtained



Scheme 1. Synthetic routes to IC-FBr-o, IC-FBr-m, PYF-T-o and PYF-T-m.

Table 1: Molecular weight, optical and electrochemical properties of PYF-T, PYF-T-o and PYF-T-m.

	M _n (PDI) [kDa]	Average Monomer units	λ _{max,sol} [nm]	$\lambda_{ m max, film}$ [nm]	$lpha_{max,film}$ [cm $^{-1}$]	λ _{onset,film} [nm]	E _g ^[a] [eV]	LUMO/HOMO ^[b] [eV]
PYF-T	11.0 (2.22)	6.0	798	821	1.40×10 ⁵	900	1.38	-3.80/-5.71
PYF-T-0	11.1 (1.79)	6.0	800	824	1.45×10^{5}	896	1.38	-3.81/-5.73
PYF-T-m	10.5 (2.18)	5.7	758	805	1.36×10^{5}	880	1.41	-3.77/-5.73

[a] calculated from the absorption onset of the films. [b] estimated from the reduction/oxidation onset of the CV curves.

from thermogravimetric analysis (TGA, at 5% weight loss, Figure S3), which indicates that all these fluorinated polymer acceptors have comparable thermal stability for all-PSC fabrication.

The UV/Vis absorption spectra of PYF-T, PYF-T-o and PYF-T-m were obtained in both dilute solutions and thin-film states. In chloroform solution, PYF-T and PYF-T-o show comparable maximum absorption peaks ($\lambda_{max,sol}$) centered at 798 and 800 nm, respectively, while PYF-T-m exhibits an obviously hypochromic absorption peak centered at 758 nm (Figure 2a). In thin-film state, all fluorinated polymer acceptors exhibit bathochromic absorption relative to their solution states, showing the maximum absorption peaks ($\lambda_{max,film}$) at 821 nm, 824 nm and 805 nm for PYF-T, PYF-T-o and PYF-Tm, respectively. The corresponding optical band gaps (E_g) of PYF-T, PYF-T-o and PYF-T-m in film state are 1.38, 1.38 and 1.41 eV, determined from their absorption onsets of 900, 896 and 880 nm, respectively (Figure 2b). Besides, the absorption coefficients are measured to be $1.40 \times 10^5, 1.45 \times 10^5$ and 1.36×10^5 10^5 cm^{-1} for the PYF-T, PYF-T-*o* and PYF-T-*m* neat films, respectively. Consequently, all the polymer acceptors can form complementary absorptions when blended with PM6, covering the solar spectrum in the range of 300-900 nm (Figure S4). To reveal the relationship between absorption and conjugation, density-functional theory (DFT) calculations were carried out. As shown in Figure 2c, the hypochromic absorption of PYF-T-m is owing to the weaker conjugation between the thiophene comonomer and the end group moieties (Figure S5) and a smaller dipole moment (Figure 2d) that leads to the weakened ICT effect.^[52] Besides, the rising absorption peaks of PYF-T and PYF-T-o in the region of 450-550 nm can be attributed to the stronger transition dipole moment (e.g., HOMO \rightarrow LUMO + 3), which is also an indication of better orbital overlapping, namely better backbone conjugation. Such a phenomenon is not obvious for PYF-T-m (Figure S6), because the 5th-position-coupling thiophene can only conjugate with ketone and central backbone,

while the 4th-position-coupling thiophene can conjugate with both malononitrile and central backbone, forming larger conjugation and resulting in bathochromic absorption (Figure S5f). Apart from absorption properties, the energy levels of the three polymer acceptors were then measured by cyclic voltammetry (CV, Figure 2e) in solid state using ferrocene/ ferrocenium (-4.80 eV) as the external standard. As illustrated in Figure 2 f, PYF-T-o demonstrated comparable HOMO/LUMO levels (-5.73/-3.81 eV) to PYF-T (-5.71/ -3.80 eV), while the LUMO level of PYF-T-*m* was slightly upshifted to -3.77 eV. The wider electrochemical band gap of PYF-T-m is consistent with its optical band gap, which may be due to the weaker conjugation along the polymer chains.^[53,54] Therefore, the cross-coupling sites of polymer acceptors indeed have great impacts on the conjugation and thus optoelectronic properties.

Conventional devices with the structure of ITO/PE-DOT:PSS/PM6:polymer acceptor/PNDIT-F3N/Ag were then fabricated to investigate the photovoltaic performances of all-PSCs based on the three fluorinated polymer acceptors. Figure 3a displays the current density versus voltage (J-V)curves of the PM6:PYF-T, PM6:PYF-T-o and PM6:PYF-T-m devices, and Table 2 summarizes the photovoltaic parameters of the three optimized all-PSCs. The PYF-T-based devices as the reference yielded a decent PCE of 14.0% with a $V_{\rm OC}$ of 0.891 V, a short-circuit current density (J_{SC}) of 23.1 mA cm⁻² and a FF of 68.0%, which is comparable to the previous report.^[42,43] The PYF-T-o-based all-PSCs produced a similar $V_{\rm OC}$ of 0.901 V, while the PYF-T-*m*-based ones generated a higher $V_{\rm OC}$ of 0.949 V that can be attributed to its higherlying LUMO level. Besides the enhancement in $V_{\rm OC}$, the PYF-T-o-based devices delivered a simultaneously improved $J_{\rm SC}$ of 23.3 mA cm⁻² and a FF of 72.4%, leading to a superior PCE of 15.2% relative to the PYF-T-based ones. It is notable that the J_{SC} and PCE of the PYF-T-o-based devices are among the highest values for the reported all-PSCs (Figure 3b,c). Despite the similar chemical compositions, PYF-T-m behaved



Figure 2. a) Normalized UV/Vis absorption spectra of PYF-T, PYF-T-*o* and PYF-T-*m* in dilute chloroform solution (concentration: 1.0×10^{-5} M). b) UV/Vis absorption spectra of PYF-T, PYF-T-*o* and PYF-T-*m* in thin films. c) Simulated absorption spectra of each repeating unit (PYF-T-1 and PYF-T-2 are two possible repeating units of PYF-T with different coupling sites) and d) dipole moments of half backbone of each repeating unit calculated at the B3LYP/6-31G (d, p) level. TT-IC-FT-1 and TT-IC-FT-2 refer to PYF-T, TT-IC-FT-*o* refers to PYF-T-*o* and TT-IC-FT-*m* refers to PYF-T, m. e) Cyclic Voltammetry curves of PYF-T, PYF-T-*o* and PYF-T-*m*. f) Architecture and energy alignment of the bulk heterojunction devices.

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Figure 3. a) *J*–V characteristic curves, b, c) the plot of PCE against V_{oc} and PCE against J_{sc} for all-PSCs reported previously with PCEs over 8% and in this study. d) EQE spectra. e) TR-PL decay spectra of the PYF-T, PYF-T-*o*, PYF-T-*m* neat films, and the PM6:PYF-T, PM6:PYF-T-*o* and PM6:PYF-T-*m* blend films. The pump wavelength and probe wavelengths are 750 nm and 850 nm, respectively. f) TPC and g) TPV measurements of the PM6:PYF-T, PM6:PYF-T-*o* and PM6:P

Table 2: Photovoltaic parameters of the solar cell devices based on PM6:PYF-T, PM6:PYF-T-*o* and PM6:PYF-T-*m* with the conventional architecture under the illumination of 100 mWcm⁻².

Material combinations	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE (PCE _{avg}) [%]
PM6:PYF-T	0.891	23.1	68.0	14.0 (13.7±0.2)
PM6:PYF-T-o	0.901	23.3	72.4	15.2 (14.9±0.2)
PM6:PYF-T-m	0.949	4.60	32.7	1.40 (1.20 \pm 0.2)

Average values from 15 devices with the highest values shown in parentheses.

differently in photovoltaic devices in comparisons with PYF-T and PYT-F-*o*, yielding a much lower $J_{\rm SC}$ of 4.60 mA cm⁻², a drastically dropped FF of 32.7 %, and thus an inferior PCE of only 1.4%. To unveil the differences in J_{SC} among the three all-PSCs, the external quantum efficiency (EQE) spectra were recorded accordingly. As presented in Figure 3d, the PYF-T- and PYF-T-o-based devices display almost identical EQE edges and maximum EQE response approaching 80%. The PYF-T-o-based device exhibits slightly higher EQE values in the range of 400-500 and 650-820 nm, contributing to the enhanced $J_{\rm SC}$. Whereas, the photon response of the PYF-T-m-based device is much weaker and narrower with the EQE values of only 10-15%. As a result of the huge differences in photon response, the integrated J_{SC} calculated from the EQE spectra are 22.2, 22.6 and 4.40 mA cm⁻² for the PYF-T, PYF-T-o and PYF-T-m based all-PSCs, respectively, which match well with the values obtained from the J-Vcurves. The PYF-T-o with medium molecular weight exhibits better performance (Table S2), presenting a similar trend as the previous reported PYF-T based all-PSC.^[42]

To study the differences in charge dissociation process of the three all-PSCs, time-resolved photoluminescence (TRPL) technique was employed and the decay dynamics of both neat and blend films are shown in Figure 3e.[55] The photoluminescence decay dynamics of the three neat polymer acceptors are comparable with the lifetime of ≈ 0.36 ns. For the blend films, both the PM6:PYF-T and PM6:PYF-T-o blend films exhibited very fast charge dissociation (lifetime ≈ 0.09 ns). However, it is obvious that the PM6:PYF-T-m blend presented almost identical photoluminescence decay as the neat PYF-T-m, suggesting the very low extent of charge dissociation (lifetime ≈ 0.32 ns). This is further supported by the measurements of exciton dissociation probability P(E, T) that the PYF-T-*m*-based device showed a P(E, T) of only 74.2% (Figure S7 and Table S3). In contrast, the PYF-T- and PYF-To-based devices presented efficient charge dissociation with P(E, T) of 97.5% and 98.3% respectively, thus partially explaining the dramatically enhanced J_{SC} in PYF-T and PYF-T-o-based all-PSCs with stronger conjugated polymer acceptors.^[56]

Apart from the variations in $J_{\rm SC}$, it is also intriguing to reveal the reasons for the enormous differences in FF of the all-PSCs based on these fluorinated polymer acceptors from the perspective of charge extraction and recombination. Hence, transient photocurrent (TPC) and transient photovoltage (TPV) techniques were conducted for the three all-PSCs.^[57] First, we performed the TPC measurements under short circuit condition to evaluate the charge extraction capability of the three all-PSCs. As depicted in Figure 3 f, the photocurrent decay times of PM6:PYF-T, PM6:PYF-T-*o* and PM6:PYF-T-*m* are 0.39, 0.34 and 0.58 µs, respectively. Therefore, the PYF-T-*o*-based device exhibits a superior charge extraction capability, leading to a faster charge sweep-out. Furthermore, the charge carrier lifetimes were estimated by the TPV technique under open circuit condition. The extracted carrier lifetimes of PM6:PYF-T, PM6:PYF-T-*o* and PM6:PYF-T-*m* are 1.96, 4.58 and 1.48 µs, respectively (Figure 3 g). The longest carrier lifetime indicates the slowest recombination rate of the PM6:PYF-T-*o* device. In contrast, PYF-T-*m* based device suffers from severe charge recombination as well as poor charge extraction. These results are further evidenced by the light-intensity-dependent $J_{\rm SC}/V_{\rm OC}$ experiments of the three all-PSCs, where the PM6:PYF-T-*o* device expressed both effectively suppressed bimolecular and trap-assisted charge recombination (Figure S8) that guarantee a high FF.^[58,59]

Besides charge recombination, we characterized the hole (μ_h) and electron (μ_e) mobility of the three all-PSCs by the space-charge-limit current (SCLC, Figure S9) method. In this study, the hole- and electron-only devices were fabricated with the structures of ITO/PEDOT:PSS/active layer/MoO₃/ Al and ITO/ZnO/active layer/PNDIT-F3N/Ag, respectively.^[60] As tabulated in Table S4, the measured μ_h and μ_e of PM6:PYF-T-o are 8.4×10^{-4} and 7.8×10^{-4} cm²V⁻¹s⁻¹ respectively, which are higher than those of PM6:PYF-T ($\mu_h = 7.3 \times$ $10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $\mu_e = 6.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). However, PM6:PYF-T-m exhibits a much poorer charge mobilities $(\mu_h = 1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \ \mu_e = 2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$. In addition, the more balance μ_h/μ_e value of PM6:PYF-T-*o* is also beneficial for charge extraction and collection, thereby the better FF of the devices. Overall, these results illuminate the reduced charge recombination and excellent charge mobility in the PM6:PYF-T-o blend, which may be attributed to the better conjugation along the polymer backbone and the more ordered interchain-packing that facilitate three-dimensional charge transport in the BHJ.

Grazing incidence wide-angle X-ray scattering (GI-WAXS) experiments were conducted to investigate the morphology features in the pristine and blend films.^[61] The two-dimensional GIWAXS patterns are shown in Figure 4a, and Figure 4b,c display the corresponding one-dimensional sector-averaged ($\pm 10^{\circ}$) scattering profiles in the in-plane and

out-of-plane directions. The (010) peaks of the pristine PYF-T, PYF-T-*o* and PYF-T-*m* films appeared at $q_z = 1.65, 1.64$ and 1.67 Å⁻¹, demonstrating the π - π stacking distances ($d_{\pi,\pi}$) of 3.82, 3.84 and 3.77 Å, respectively. However, PYF-T-m shows a smaller (010) coherence length of 17 Å than those of PYF-T (19 Å) and PYF-T-o (19 Å), indicative of a slightly poor interchain packing of PYF-T-m. Besides, Figure 4b desplays that the higher scattering peaks of PYF-T and PYF-T-o at 0.3 $Å^{-1}$ and 0.6 Å^{-1} in the in-plane (001) direction represent the backbone peak (001) and (002), which suggest better polymer packing in the horizontal direction of the substrate and explain the better charge transport properties of these two materials. After blending with PM6, all three blends exhibit predominant face-on orientation with the π - π stacking peaks located at 1.68 Å⁻¹,1.70 Å⁻¹, 1.70 Å⁻¹ with the coherence lengths of 19, 26 and 26 Å for PM6:PYF-T, PM6:PYF-T-o and PM6:PYF-T-*m*, respectively. The almost identical π - π stacking distances may be due to the fact that the blend film morphology is mostly dominated by PM6 ($q_z = 1.72 \text{ Å}^{-1}, d_{\pi}$ $_{\pi}$ = 3.65 Å, Table S5). Nevertheless, the scattering volume normalized integrated intensity of PM6:PYF-T-m is indeed lower than the other two blends, which could explicate the inferior carrier mobility of the device. In this way, it can be concluded that the ordered fluorinated backbone with better conjugation leads to more compact interchain packing and thus the enhanced charge transport of the devices.

Moreover, we performed atomic force microscopy (AFM, Figure 5a) to characterize the surface morphology of the three blends. The height images show that all the blends form compatible surface morphology with suitable root-mean-square roughness (1.01 nm for PM6:PYF-T, 0.891 nm for PM6:PYF-T-*o* and 1.05 nm for PM6:PYF-T-*m*, respectively). In addition, from the phase images, it is clearly observed that the PM6:PYF-T-*o* and PM6:PYF-T-*m* blends exhibit obviously fiber-like surface morphology, which is not observed from the PM6:PYF-T one. This could originate from the more ordered polymer chain packing induced by the regular backbone of PYF-T-*o* and PYF-T-*m*. To provide more indepth understanding about the huge differences among the three blends, grazing-incidence small-angle X-ray scattering



Figure 4. a) 2D GIWAXS patterns of pure PYF-T, PYF-T-*o* and PYF-T-*m* films and PM6:PYF-T, PM6:PYF-T-*o* and PM6:PYF-T-*m* blend films. The corresponding 1D GIWAXS line-cuts of the in-plane and out-of-plane directions of b) neat films and c) blend films.



Figure 5. a) The AFM height (top) and phase (bottom) images, and b) the GISAXS intensity profiles and best fittings along the in-plane direction of the PM6:PYF-T, the PM6:PYF-T-*o* and the PM6:PYF-T-*m* blend film.

(GISAXS) experiments were conducted to study the phase segregation of these three material systems (Figure 5b).^[62] The intermixing domain spacings are determined to be 42.9, 33.9 and 63.5 nm for the PYF-T, PYF-T-o, and PYF-T-mbased blend, respectively. Furthermore, the domain sizes of the acceptor phase are calculated to be 18.7, 13.9, 24.2 nm, respectively. This is consistent with the trend in the exciton dissociation of the corresponding devices. The excessively large domain size of the PM6:PYF-T-m blend deviates from the ideal exciton diffusion length of 10-20 nm,^[63] while those of the other two blends lie in this range. Therefore, the PM6:PYF-T-m blend suffers from the oversized domain that limits the area of the D-A interface, which could be the major reason for the inferior exciton dissociation, poor carrier transportation and severe charge recombination of the devices as demonstrated above. In contrast, the smallest domain size of the PM6:PYF-T-o blend is more desirable for the exciton dissociation and thus beneficial for the following charge transport and suppressed charge recombination. We proposed that the weaker conjugated coupling site of PYF-Tm owns less steric hindrance in polymer chain which could lead to oversized domains in blend. Therefore, the balance between interchain packing and phase separation through ingenious chemical method is the key to achieving the high device performance of PM6:PYF-T-*o*.

The energy loss (E_{loss}) plays a crucial role in determining the efficiency limit of a solar cell, and the detailed energy losses were investigated for the three all-PSCs subsequently (Figure 6 and Table S6).^[64] Theoretically, E_{loss} for any types of solar cells contains three parts. The first part $\Delta E_1 \left(E_g - q V_{oc}^{SQ} \right)$ from the radiative recombination loss above $E_{\rm g}$ exists in all types of solar cells according to the detailed balance theory, and the three all-PSCs yielded almost identical ΔE_1 of 0.26 eV.^[65] The second part ΔE_2 (qV^{SQ}_{oc}-qV^{rad}_{oc}) from the radiative recombination loss depends on the absorption below Eg, and both PYF-T- and PYF-T-o-based devices show smaller ΔE_2 s of 0.03 and 0.04 eV, respectively, than that of PYF-T-m (0.06 eV). As for the third part ΔE_3 (the nonradiative recombination loss) is attained through the equation: $\Delta E_3 = -k T \ln(EQE_{EL})$. A small energy offset between donor and acceptor can effectively suppress the chargetransfer (CT) state recombination through the hybridization of the local excited (LE) state and the CT state, resulting in reduced non-radiative recombination loss.[66] Due to the smallest offset between PM6 and PYF-T-m, PM6:PYF-T-m was found to exhibit a smaller ΔE_3 of 0.20 eV relative to those of the other two devices (0.24 eV for PM6:PYF-T and 0.23 eV for PM6:PYF-T-o). According to these results, the total E_{loss} were determined to be 0.53, 0.52 and 0.52 eV for PM6:PYF-T, PM6:PYF-T-o and PM6:PYF-T-m, respectively. The slightly smaller $E_{\rm loss}$ s of the two devices based on regular polymer acceptors may be partially attributed to the decreased conformational disorder of polymer chains, leading to regular packing, less vibration states and reduced non-radiative recombination.



Figure 6. Semi-logarithmic plots of normalized EL, measured EQE and EQE calculated by FTPS (EQE_{FTPS}) as a function of energy for devices based on a) PM6:PYF-T, b) PM6:PYF-T-*o* and c) PM6:PYF-T-*m*. The ratio of $\varphi_{EL}/\varphi_{bb}$ was used to plot the EQE in the low-energy regime (black line), where φ_{EL} and φ_{bb} represent the emitted photon flux and the room-temperature blackbody photon flux, respectively. Of note is that $\varphi_{EL}/\varphi_{bb}$ follows experimental EQE_{FTPS} faithfully at higher energies as expected from reciprocity. d) Schematic diagram for energy losses of PSCs according to the detailed balance theory. e) E_{loss} and its detailed three parts of ΔE_1 , ΔE_2 and ΔE_3 values of the three all-PSCs.

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As discussed in the introduction, all-PSCs are expected to exhibit robust morphology that is promising for large-scale manufacturing. Hence, we fabricated the 1.0 cm² devices of PM6:PYF-T-o by spin-coating as well as blade-coating (Figure 7 a) to further investigate the potential of PM6:PYF-T-o in scalable processing methods. Figure 7b depicted that the spin-coated device with an active area of 1.0 cm² shows a decreased PCE of 14.5% relative to the small-area device above (0.07 cm^2) . It is noted that this value is higher than the previous reports (12-13%) with similar active areas.^[67] Surprisingly, when blade-coated under ambient condition, the resulting devices showed very similar $V_{\rm OC}$ and $J_{\rm SC}$ to the spin-coated ones while a reasonably dropped FF of 63.4%, leading to a decent PCE of 13.0% for large-area all-PSCs. Therefore, these results highlight that the scalable processing of PM6:PYF-T-o have great potential in the large-scale production of highly efficient all-PSCs.



Figure 7. Schematics of the spin-coating and blade-coating processes, and the photograph of the 1-cm² device. d) The *J*–*V* curves of the spin-coated and blade-coated devices with a device area of a 1.0 cm².

Steady performance under long-term photo-irradiation should be ensured since exposure to light is inevitable during the device operation. As shown in Figure S10a, the PM6:PYF-T-o and PM6:PYF-T devices showed light-induced losses of ca. 20% and 25% after 250 hours irradiation, respectively, while the performance of PYF-T-m-based devices dropped by more than 30% over the same time period. The thermal stability of the devices was also tested (Figure S10b), where the PYF-T-o-based device demonstrated robust performance with $\approx 10\%$ decrease after 250-hour thermal aging at 80 °C. In contrast, the PYF-T- and PYF-T-mbased devices displayed decreased thermal stability, retaining 80% and 65% of their initial efficiencies under the same condition. Both stability experiments clearly demonstrate that the stability of the PYF-T-o-based devices is better than the other two systems, probably because of the denser intermolecular packing rising from fluorine-assisted interactions and stronger conjugation that stabilize the chemical structure and blend morphology.

Conclusion

In conclusion, we successfully synthesized two new isomeric end groups with determined substitution positions of fluorine and bromine, named IC-FBr-*o* and IC-FBr-*m*, which have different cross-coupling sites for polymerization. As a result, two configurationally unique comonomers and

the resultant regular polymer acceptors (PYF-T-o & PYF-Tm) were prepared and compared with a reported random polymer (PYF-T). Theoretical calculations indicated the better conjugation and the stronger ICT effect of PYF-T-o relative to the other two polymers. When blended with PM6, morphology studies revealed that the PM6:PYF-T-o blend formed ordered interchain packing and suitable fiber-like phase separation relative to the PM6:PYF-T one, while the PM6:PYF-T-m blend suffers from oversized phase segregation that leads to inferior exciton dissociation, slow charge transport and severe charge recombination. Consequently, the PM6:PYF-T-o all-PSC achieved the highest PCE of 15.2%, with a $V_{\rm OC}$ of 0.901 V and a remarkably enhanced $J_{\rm SC}$ of 23.3 mA cm⁻², which was superior to PM6:PYF-T (14.0%) and PM6:PYF-T-m (1.40%), and this is one of the highest efficiencies for all-PSCs. Our work demonstrates the structure-performance relationships of the fluorine-substituted Yseries polymer acceptors and paves the way towards regular fluorinated polymer acceptors for efficient all-PSCs.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: all-polymer solar cells \cdot fluorinated end group \cdot isomeric effect \cdot organic solar cells \cdot polymer acceptors

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