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# Side chain engineering investigation of non-fullerene acceptors for photovoltaic device with efficiency over 15%

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Side chain engineering plays a substantial role for high-performance organic solar cells (OSCs). Herein, a series of non-fullerene acceptor (NFA) molecules with A-D-A structures, TTC*n*-4F, with gradient substituent lengths of terminal side chains (T-SCs) on the molecular backbones have been designed and synthesized. The effects of T-SCs length, ranging from hydrogen atom to *n*-dodecyl, their optoelectronic properties, thin film molecular packing, blend film morphology, and overall photovoltaic performance have been systematically studied. The results show that among this series of molecules, TTC8-4F with *n*-octyl substituent, showed the best photovoltaic performance when applied with PM6 as the donor due to its favorable morphology, balanced charge mobility, effective exciton dissociation and less charge recombination. Based on this, its ternary device with F-Br as the secondary acceptor achieved a high PCE of 15.34% with the simultaneously enhanced  $V_{oc}$  of 0.938 V,  $J_{sc}$  of 22.66 mA cm<sup>-2</sup>, and FF of 72.15%. These results indicate that the engineering of T-SCs is an effective strategy for designing high-performance NFAs.

organic solar cells, non-fullerene acceptor, side chains

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# 1 Introduction

Among various photovoltaic technologies, organic solar cells (OSCs) have drawn great attention due to the advantages such as low cost, flexibility, light weight [1,2]. In recent years, studies on OSCs have made great progress, especially after the discovery of high-efficiency non-fullerene acceptors (NFAs) [3–8]. The power conversion efficiencies (PCEs) of state-of-the-art single-junction and tandem OPVs have exceeded 18% and 17%, respectively

[9,10]. Presently, NFAs with the acceptor-donor-acceptor (A-D-A) architecture have demonstrated great success owing to the easy control of absorptions, energy levels and molecular packings. In the past years, most efforts on the A-D-A acceptor design have been devoted to changing or modifying the conjugated lengths or fused rings of the molecular backbone D [11–22], and electron with drawing abilities of the end groups A [23–29]. Those strategies can effectively extend the absorption window and modulate energy levels and have significantly enhanced the corresponding devices performances. On the other hand, side chain engineering is also one of the effective strategies to improve the perfor-

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mance of OSCs. As early as in the fullerene era, lots of pioneering and excellent studies on polymer donor modification have proved that side chain engineering can efficiently tune the solubility, molecular orientation, charge transport property, and active layer morphology [2,30–32]. In fact, these perceptions could also work well for molecular design of NFAs.

For typical A-D-A acceptor molecules, the side chains attached on the molecular backbone D units are roughly defined here in three categories (Figure 1): (1)  $sp^3$  carbonbridged (including sp<sup>3</sup> carbon-oxygen-bridged) side chains (CB-SCs) [4,33-42]; (2) central side chains (C-SCs) [43-46]; (3) terminal side chains (T-SCs) [6,47,48]. The most commonly studied side chains are the CB-SCs (Figure 1(a)), which includes various alkylphenyl side chains, e.g., parahexylphenyl [4,33,41], and alkoxyl/alkylthio phenyl side chains [35,36]. The CB-SCs could effectively prevent the over aggregations of those A-D-A acceptors with large palanar backbones and significanly impove their solubilities. The C-SCs (Figure 1(b)) refer to the substituted groups attached on the central units of molecules with symmetry structures [43–46], such as alkyl, alkoxyl and alkylthienyl. Generally, C-SCs have much influence not only on the molecular energy levels, but also on the microscopic morphology.

In contrast to the above two types of side chains, T-SCs (Figure 1(c)), where the side chains are attached to the terminal position of the molecular backbones, have received less attention [47]. But, it is worth noting that T-SCs also have great influence on the properties and device performances of corresponding molecules. Although some molecules with T-SCs including the recent remarkable acceptor Y6 were reported and showed excellent device performances [6,48], few work has provided a systemic study and in-depth

investigation on the T-SCs. Therefore, a deep and thorough correlation of structure-property-performance of T-SCs is necessary and will give valuable guidelines for design of high performance NFAs.

Based on the above consideration, in this work, we have designed and synthesized a series of NFAs. TTCn-4F. with gradient substituent lengths of T-SCs (Figure 2(a)). We have systematically studied the effect of the T-SCs size, ranging from hydrogen atom to n-dodecyl, on the molecular properties, photophysics, morphology, and photovoltaic performance. The OSCs performance of the TTCn-4F series is evaluated in blends with poly{[4,8-bis[5-(2-ethylhexyl)-4fluoro-2-thienyl]benzo[1,2-b:4,5-b]dithiophene-2,6-diyl]alt-[2,5-thiophenediyl[5,7-bis(2-ethylhexyl)-4,8-dioxo-4H,8H-benzo[1,2-c:4,5-c]dithiophene-1,3-diyl]]} (PM6) (Figure 2(a)) [49]. Among this series of NFAs, the highest PCE of 13.95% was achieved based on the n-octyl substituent TTC8-4F acceptor, with an open-circuit voltage  $(V_{oc})$ of 0.901 V, a short-circuit current density  $(J_{sc})$  of 22.36 mA cm<sup>-2</sup>, and a fill factor (FF) of 69.23%. The outstanding performance of PM6:TTC8-4F system was mainly due to more balanced hole/electron mobility, less charge recombination, and more favorable morphology. On the basis of the above binary system, we selected the acceptor F-Br that our group reported previously [50], as the third component to fabricate a ternary device. A high PCE of 15.34% was achieved for the optimized device due to the simultaneous improvement of the three photovoltaic parameters with  $V_{\rm oc}$  of 0.938 V,  $J_{\rm sc}$  of 22.66 mA cm<sup>-2</sup>, and FF of 72.15%.

## 2 Results and discussion

#### 2.1 Synthesis and DFT calculation

The synthesis details of TTCn-4F are provided in the Scheme



Figure 1 The three types of side chains attached on the representative molecular backbones of NFAs. (a)  $sp^3$  carbon-bridged side chains, CB-SCs; (b) central side chains, C-SCs; (c) terminal side chains, T-SCs. The chemical structures of end groups A are omitted for clarity (color online).



Figure 2 (a) Chemical structures of TTC*n*-4F and PM6; (b) normalized thin film optical absorption spectra of neat TTC*n*-4F (the maximum absorption peaks are shown in the inset for clarity); (c) LUMO/HOMO energy levels of TTC*n*-4F and PM6 (color online).

S1 (Supporting Information online). We utilized similar synthetic route to obtain the CBDT (4,4,10,10-tetrakis(4hexylphenyl)-4,10-dihydro-5,11-diocthylthieno[3',2':4,5]cyclopenta[1,2-b]thieno[2",3":3',4']cyclopenta[1',2':4,5]thieno [2,3-*f*][1]benzothiophene) analogue [43], named TTC0. Then the fused core was lithiated, and quenched with dimethylformamide (DMF) to afford TTC0-CHO. Followed by the Knoevenagel condensation of TTC0-CHO with 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malono-nitrile (DFIC), TTC0-4F was obtained as a dark-green solid. On this basis, we introduced a linear T-SC with gradient substituent lengths from n-ethyl to n-dodecyl. According to the number of carbon atoms in T-SCs, the newly derived series of NFAs were named as TTC2-4F, TTC4-4F, TTC6-4F, TTC8-4F, TTC10-4F, TTC12-4F, respectively (Figure 2(a)). All intermediates and final products were fully characterized as detailed in the supporting information. TTCn-4F all exhibit good solubility in common organic solvents, such as chloroform and chlorobenzene.

Density functional theory (DFT) calculation is used to evaluate the configuration and energy levels. As shown in Table S1 (Supporting Information online), all the acceptors possess planar skeletons, which are favorable for efficient intramolecular charge transfer (ICT). Compared with TTC0-4F, owing to the weak electron-donating T-SCs, the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) energy levels of TTC*n*-4F series acceptor are increased slightly by ~0.06 and ~0.08 eV, respectively.

#### 2.2 Opto-electronic properties

The optical absorption properties of TTC*n*-4F were studied in dilute solutions and on thin-films (Figure 2(b), Figure S1, and Table S2, Supporting Information online). TTC0-4F in solution shows an intense absorption from 600 to 800 nm, with a maximum peak located at 755 nm. After introducing T-SCs, compared with TTC0-4F, there is nearly no change of the maximum absorption peaks in solution for TTC*n*-4F (*n*=2–12). However, it is opposite in their solid film absorptions. The bigger the size of T-SC, the greater the blueshift of the maximum peak. For TTC12-4F, the maximum peak is blue-shifted by 17 nm, suggesting that T-SC could influence the molecular solid packing behavior.

Ultraviolet photoelectron spectroscopy (UPS) is an effective tool to evaluate the energy levels of photovoltaic materials. Figure S2(a–h) show the onset and cutoff regions of the TTC*n*-4F and PM6 films, respectively. The data of HOMO and LUMO energy levels are shown in Figure 2(c), and listed in Table S2. Compared with that of TTC0-4F (-5.65 eV), the HOMO energy levels of TTC*n*-4F (*n*=2–12) are increased by 0.05 eV, which is consistent with the DFT calculation results. The LUMO energy levels could be determined using the optical band-gap ( $E_g^{opt}$ ) and HOMO energy levels. TTC*n*-4F series exhibit a slight upward trend in LUMO energy with increasing lengths of the T-SCs.

#### 2.3 Photovoltaic properties

OSCs were fabricated utilizing an inverted architecture of ITO/ZnO/PFN-Br/PM6:TTC*n*-4F/MoO<sub>x</sub>/Ag. The photovoltaic parameters and J-V curves of the optimized devices are collected in Table 1 and Figure S3, respectively. Plots with error bars extracted from Table 1 are shown in Figure 3 (a, b). OSCs based on PM6:TTCn-4F blend films afford rising  $V_{\rm oc}$  values gradually from 0.817±0.004 to 0.903± 0.004 V, which is consistent with the upshifting LUMO energy levels as increasing in the size of T-SCs.  $J_{sc}$  values are continuously increased from 19.31±0.18 to 22.14±  $0.36 \text{ mA cm}^{-2}$  with increasing *n* lengths from 0 to 8, but decreased with n=12. And FFs have been maintained above 65% except TTC12-4F based device with a relatively low value of 61.77%. A champion device based on PM6:TTC8-4F delivers the highest PCE of 13.95%.

In order to understand the intrinsic reasons for the variation of photovoltaic parameters as discussed above, we selected four representatives, TTCn-4F (n=0, 4, 8, 12), for further characterizations. As shown in Figure S4, the absorption spectra of blend films of TTC4-4F, TTC8-4F, and TTC12-4F undergo a slightly redshift compared with that TTC0-4F, which exhibits an opposite trend in contrast to their neat films. This is consistent with the corresponding EQE re-

sponse changes for these molecules (Figure 3(c)). The results indicate that the molecular packing of TTCn-4F have changed after blending with polymer donor PM6, which will be discussed below.

#### 2.4 Charge carrier mobilities

The charge transport properties were investigated by the space charge limited current (SCLC) method using hole- and electron-only devices as shown in Figures S5(a, b), and Table 1. The hole mobilities decreased from  $5.14 \times 10^{-4}$  to  $4.73 \times 10^{-4}$ ,  $4.02 \times 10^{-4}$  and  $3.19 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, while the electron mobilities increased from  $2.82 \times 10^{-4}$  to  $3.50 \times 10^{-4}$ ,  $3.65 \times 10^{-4}$  and  $3.74 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> as acceptors varied from TTC0-4F to TTC4-4F, TTC8-4F, and TTC12-4F, respectively. For the case of TTC8-4F blend film, the most balanced carrier mobility ( $\mu_{\rm h}/\mu_{\rm e}$ , 1.10) is achieved, which is in agreement with the highest  $J_{\rm sc}$  of 22.14±0.36 mA cm<sup>-2</sup>, and FF of 69.37%±0.54% among these four acceptors based devices.

# 2.5 Recombination losses and collection of mobile charges

To gain deeper insight into the size of T-SCs on the electrical properties, we also studied the recombination mechanism by measuring the  $J_{sc}$  and  $V_{oc}$  plots as a function of light intensities (P) from 100 to 6 mW cm<sup>-2</sup>, as shown in Figure 3(d, e). At short-circuit, the recombination loss is described using the power law dependence of  $J_{sc} \propto P^{\alpha}$ . The values of  $\alpha$  are 0.95, 0.97, 0.99, and 0.97, as acceptors varied from TTCO-4F to TTC4-4F, TTC8-4F, and TTC12-4F, respectively (Figure 3(d)). The closer  $\alpha$  value to unity, the weaker bimolecular recombination during sweep-out. It indicates that the bimolecular recombination is reduced at short-circuit for the acceptors with large size of T-SCs, which is consistent with higher  $J_{sc}$  above 22.00 mA cm<sup>-2</sup> for TTC8-4F and TTC12-4F blend films. Under the open-circuit condition, the recombination mechanism can be reflected by the formula  $V_{\rm oc}$  $\propto nk_{\rm B}T/(q\ln P)$ , where  $k_{\rm B}$ , T, and q are the Boltzmann con-

 Table 1
 Summary of device parameters of PM6:TTCn-4F solar cells

Active layer	$V_{\rm oc} ({\rm V})^{\rm a)}$	$J_{\rm sc}~({\rm mA~cm}^{-2})^{\rm a)}$	calc. $J_{\rm sc}$ (mA cm <sup>-2</sup> ) <sup>b)</sup>	FF (%) <sup>a)</sup>	PCE (%) <sup>a)</sup>	$(10^{-4} \operatorname{cm}^{\mu_h/\mu_e} \operatorname{V}^{-1} \operatorname{s}^{-1})$
PM6:TTC0-4F	0.806 (0.817 ±0.004)	19.49 (19.31±0.18)	18.73	67.39 (67.58±0.46)	10.59 (10.53±0.04)	5.14/2.82
PM6:TTC2-4F	0.836 (0.838±0.003)	20.30 (20.00 ±0.17)	19.55	67.38 (68.02±0.37)	11.43 (11.39±0.03)	_
PM6:TTC4-4F	$0.883 (0.884 \pm 0.005)$	21.03 (20.96 ±0.16)	20.42	68.31 (67.90±0.59)	12.68 (12.57±0.08)	4.73/3.50
PM6:TTC6-4F	0.887 (0.890±0.003)	21.70 (21.65±0.20)	20.72	68.79 (68.39±0.50)	13.24 (13.17±0.05)	-
PM6:TTC8-4F	0.901 (0.895±0.005)	22.36 (22.14±0.36)	21.61	69.23 (69.37±0.54)	13.95 (13.72±0.19)	4.02/3.65
PM6:TTC10-4F	0.896 (0.899±0.004)	22.61 (22.16±0.44)	21.57	65.16 (65.53±1.02)	13.20 (13.05±0.09)	-
PM6:TTC12-4F	0.909 (0.903±0.004)	22.32 (21.91±0.43)	21.65	61.77 (62.71±0.98)	12.53 (12.40±0.12)	3.19/3.74

a) The average values in parentheses were obtained from 20 devices; b) the  $J_{sc}$  values integrated from EQE spectra.



Figure 3 Plots of (a)  $V_{oc}$ ,  $J_{sc}$ , (b) FF and PCE vs. the length of T-SCs ranging from 0 to 12; (c) EQE responses; light-intensity dependence of (d)  $J_{sc}$  and (e)  $V_{oc}$  obtained from the OSCs based on PM6:TTCn-4F (n=0, 4, 8, 12) (color online).

stant, absolute temperature, and the elementary charge, respectively. The values of n are 1.20, 1.15, 1.08, and 1.12 for TTC0-4F, TTC4-4F, TTC8-4F, and TTC12-4F, respectively, indicating additional trap-assisted recombination involved. Especially for the TTC8-4F system, the n value of 1.08 is close to the unit, which means that trap-assisted recombination is effectively suppressed and bimolecular recombination should be the dominate mechanism under the open-circuit condition.

To explore the exciton dissociation and charge collection properties, the dependence of the photocurrent density  $(J_{ph})$ on effective voltage  $(V_{eff})$  were measured (Figure S6(a)). On this basis, the exciton dissociation probability  $(P_{diss}(E, T))$ can be reflected by normalizing  $J_{ph}$  with saturation  $J_{ph}(J_{ph,sat})$ ,  $J_{ph}/J_{ph,sat}$  (Figure S6(b)). Values of  $P_{diss}(E, T)$  for TTC0-4F, TTC4-4F, and TTC8-4F are continuously increased from 90% to 92%, and 94% under short-circuit, indicating more excitons dissociated into free carriers with the increasing length of T-SCs. In contrast,  $P_{diss}(E, T)$  value for TTC12-4F is decreased to 90%, indicating that excessive length of T-SCs is not beneficial to enhance the ability of charge dissociation and collection.

#### 2.6 Morphological properties

Essentially, changes in the solid-state optical absorptions, device parameters and charge transport properties should correspond to the difference in the molecular packing and crystallinity. To understand the reasons above and what the role T-SCs play, we carefully studied the morphology of neat and blend films using two-dimensional grazing incidence wide-angle X-ray scattering (2D-GIWAXS) measurements. 2D-GIWAXS patterns and line-cuts information for neat films are presented in Figures S7(a-e) and S6(f-j), respectively. The neat TTC0-4F film exhibits a lamellar (100) stacking along the in-plane (IP) direction at  $q_{xy}$ =0.35 Å<sup>-1</sup> as well as a strong  $\pi$ - $\pi$  (010) stacking peak in the out-of-plane (OOP) direction at  $q_z=1.81$  Å<sup>-1</sup> ( $d\sim3.47$  Å), indicating the predominant face-on orientation of TTC0-4F (Figure S7(af)). The diffraction pattern of TTC4-4F is similar to that of TTC0-4F. However, the crystal coherence length (CCL, calculated via Scherrer equation) of TTC4-4F is 21.5 Å, which is smaller than that of the TTC0-4F (23.6 Å) in the OOP direction. This confirms that the molecular packing becomes weak after introducing a T-SC in the neat film. With increasing the lengths, T-SCs, TTC8-4F and TTC12-4F show clear arcing diffractions, corresponding to the lamellar packings and no  $\pi$ - $\pi$  stacking diffractions and thus less crystallinities. The difference in the crystalline nature of TTC0-4F, TTC4-4F, TTC8-4F, and TTC12-4F in the neat film is consistent with their optical absorptions (Figure 2(b)).

2D-GIWAXS patterns and line-cuts information for blend films are presented in Figure 4(a–d) and (e–h), respectively. And the summary of the GIWAXS parameters for the blend films is listed in Table S3. For the blend film based on PM6: TTC0-4F, diffraction peaks could be assigned to the lamellar and  $\pi$ - $\pi$  stacking of PM6 at q=0.31 and 1.70 Å<sup>-1</sup>, respectively, which is almost identical to that of neat PM6 film. Surprisingly, the strong diffraction peaks of TTC0-4F in the neat film disappeared. This phenomenon indicates that the order packing of TTC0-4F is vulnerable to be disturbed when blended with PM6. In contrast, the blend films based on



Figure 4 (a-d) 2D-GIWAXD patterns, (e-h) line-cut profiles, and (i-l) TEM images for the blend films based on PM6:TTCn-4F (n=0, 4, 8, 12) (color online).

TTC*n*-4F (*n*>0), in which T-SCs are introduced, display completely different diffraction patterns. For the TTC4-4Fbased blend film, there exist two lamellar peaks in the IP direction at  $q_{xy}$ =0.31 and 0.36 Å<sup>-1</sup>, which can be assigned to the PM6 and TTC4-4F, respectively. In addition, two  $\pi$ - $\pi$ stacking peaks in the OOP direction are partially overlapped at  $q_z$ =1.71 Å<sup>-1</sup>, and the shoulder peak is located at 1.79 Å<sup>-1</sup> (d~3.50 Å) and assigned to TTC4-4F. Compared with TTC4-4F, intensities of lamellar packing and  $\pi$ - $\pi$  stacking peaks are stronger for the optimized TTC8-4F-based blend film. This indicates that the order of molecular packing in the thin film contributes to the more efficient charge transport and collection, and results in higher  $J_{sc}$ , FF, and PCE of the optimized TTC8-4F-based device. For the optimized TTC12-4F-based blend film,  $\pi$ - $\pi$  stacking peak of PM6 located at 1.71 Å<sup>-1</sup> turns into a shoulder peak, while the intensity of lamellar packing of PM6 in the IP direction is weaker than that for the case of TTC12-4F. Compared with the optimized TTC8-4F-based blend film, CCLs in the OOP direction are reduced from 22.1 to 17.2 Å for PM6, and increased from 38.2 (for TTC8-4F) to 49.2 Å for TTC12-4F, respectively. It is illustrated that strong self-aggregation of TTC12-4F may disturb the packing of PM6 in turn. Structural ordering of TTC*n*-4F in the blend film is further increased with the increasing size of T-SCs, which is consistent with the redshift optical absorption of blend films and the improved EQE response. On the basis of the above, we can draw the following conclusions. Firstly, the T-SCs could have some steric hindrance, based on the results of the ab-



Figure 5 (a) *J-V* curves and (b) EQE responses of binary and ternary devices (color online).

sorptions and GIWAXS patterns of neat acceptors. Secondly, the molecular packing of acceptors possessing the T-SCs can be adjusted adaptively when blending with PM6, mainly induced by hydrophobic interaction originated from the flexible T-SCs. More importantly, the size of T-SCs can balance the influence of these two opposite aspects on molecular packing. Therefore, introducing T-SCs is an effective strategy to fine-tune the molecular packing, morphology of blend films, and device performance through regulating the size of T-SCs.

Microscopic morphologies of blend films were also characterized by transmission electron microscopy (TEM) (Figure 4(i-1)). As shown in Figure 4(i), the large aggregation of PM6 was presented clearly in the PM6:TTC0-4F blend films. which is consistent with the results of GIWAXS. The blend film based on PM6:TTC4-4F still yielded fibrous aggregates of PM6 (Figure 4(j)). However, the aggregates become thinner and shorter, which is consistent with the relatively weak  $\pi$ - $\pi$  stacking peak and smaller CCL of PM6. For the TTC8-4F-based blend film, more favorable phase separation and uniform morphology was formed, resulting from improved packing order of TTC8-4F (Figure 4(k)). For the PM6:TTC12-4F blend film, greater size of T-SCs can drive TTC12-4F to form over self-aggregates, and disrupt the packing order of PM6 indirectly (Figure 4(1)), resulting in a higher  $\mu_{\rm e}$  but decreased  $\mu_{\rm h}$  and FF.

#### 2.7 Ternary blend devices

Through the systematic study on the T-SCs, we screened the best acceptor, TTC8-4F, which showed a PCE of 13.95% when blended with PM6. Considering enhancing the optical absorption in the range of 650–750 nm, we selected F-Br (chemical structure of F-Br is presented in Figure S8), a NFA previously reported by our group, as the third component to fabricate ternary devices [50]. PM6:TTC8-4F:F-Br-based ternary devices were fabricated using the same conditions of the binary devices. The overall donor/acceptor weight ratio was kept at 1:1, while the ratio between TTC8-4F:F-Br was varied. The photovoltaic performance parameters and *J-V* 

curves of the best devices are collected in Table S4, Figure 5 (a), and Figure S9, respectively. After optimizing the ratio of the acceptors, PM6:TTC8-4F:F-Br (1:0.5:0.5) ternary device exhibit the best PCE of 15.34%, resulting from the simultaneously enhanced  $V_{\rm oc}$  of 0.938 V,  $J_{\rm sc}$  of 22.66 mA cm<sup>-2</sup>, and FF of 72.15%. The optimized ternary device exhibits high EQE response in the whole spectral range (Figure 5(b)), which benefits from complementary absorption spectra in the ternary blend film (Figure S10).

## 3 Conclusions

In summary, we have presented the synthesis of a series of NFAs, TTC*n*-4F, with gradient substituent lengths of T-SCs. It has been found that the size of T-SCs for these acceptors can influence the absorptions, energy levels, charge transport properties, and film morphologies, resulting in different photovoltaic performance. The device based on PM6:TTC8-4F, with *n*-octyl substituent, exhibited the best PCE of 13.95%. A ternary device using an acceptor F-Br as the third component achieved an outstanding PCE of 15.34%. This work has proved that T-SCs modulation is an effective strategy for the design of high-performance NFAs.

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Conflict of interest The authors declare no conflict of interest.

**Supporting information** The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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