

Lowly Fused Non-Fullerene Acceptors Towards Efficient Organic Solar Cells Enabled by Isomerization

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Electronic Supplementary Information

Abstract Two lowly fused non-fullerene acceptors (NFAs) with isomeric structures, named as BTP-out-4F and BTP-in-4F, were developed by tailoring the fused 7-ring central core of Y6 into a lowly fused 5-ring linked with two octyloxythiophene bridges. BTP-out-4F with octyloxy side chains away from the central core exhibited large steric hindrance that restrained the rotational freedom between the thiophene bridge and end group but maintained free rotation between the central core and the thiophene bridge. In contrast, BTP-in-4F with octyloxy side chains close to the central core had much lower rotation freedom due to the non-covalent S...O interactions locked the central core, thiophene bridge and end group simultaneously, making BTP-in-4F have higher molecular crystallinity. On the other hand, the optical properties, energy levels and the blend morphology properties were significantly influenced, leading to distinctive photovoltaic performances. BTP-out-4F formed favorable energy level alignment and morphology when matching with PBDB-T donor, thus its device realized a much higher PCE of 13.32%, which was over 13 times than that of BTP-in-4F based device (PCE=0.97%).

Keywords Polymer solar cells; Nonfullerene acceptors; Lowly fused; Structural isomerization; Confirmation lock

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INTRODUCTION

Organic solar cells (OSCs) based on polymer donors and non-fullerene acceptors (NFAs) have attracted widespread attentions and achieved unprecedented development recently.^[1–11] Especially, the explosive development of fused-ring electron acceptors (FREAs) processing an A-DA'D-A structure along with broad and strong absorption, tunable energy level as well as regulable morphology, such as Y6,^[12] BTP-4CI,^[13] BTP-eC9,^[14] L8-BO,^[15] BTP-FTh,^[16] etc., have boosted the power conversion efficiency (PCE) reaching 19%.^[16,17] Currently, the mainstream research on this type of FREAs is to change the side chain group, central core and terminal unit, or to construct asymmetric molecules.^[18–26] While these changes do lead to improved device performance, however, the complexity of synthesis cannot be ignored, which is an important factor for commercial applications in the near future.

As the first-generation FREA, ITIC,^[27] which is composed of an A-D-A structure, shows very excellent optoelectronic properties, enabling the PCE to easily exceed the 10% benchmark.

By tailoring the fused 7-ring core of ITIC into lowly fused 5-ring core and alkylthiophene bridge, a lowly fused A- π -D- π -A type FREA of IEIC was developed, which did not sacrifice the broad absorption range but significantly impact the energy levels.^[28] Replacing the alkyl side chains with alkoxy side chains on the thiophene bridges, the newly developed IEICO exhibited largely narrowed optical bandgap (E_g^{opt}) from 1.50 eV to 1.34 eV.^[29] The largely narrowed E_g^{opt} could be ascribed to the enhanced electron donating ability and the non-covalent S...O interactions locked the rotation of thiophene bridges, offering high intramolecular rigidity and planarity similar to a fused 9-ring core. Therefore, relatively high photovoltaic performance can also be obtained by tailoring complex fused-ring molecules into easily synthesized and lowly fused molecules.^[30–32] By introducing noncovalent interactions, these lowly fused molecules could also maintain high coplanarity and charge transport properties.^[33–37]

In addition, structural isomerization has also attracted wide attention in developing highly efficient NFAs.^[38,39] The structural isomerization could be applied to the central cores, side chains, π bridge and end groups of NFAs.^[38–42] Absolutely, structural isomerization is a promising strategy to tune the electronic structure, optical properties, energy levels, molecular stacking behavior, and charge transport properties.^[42] Most recently, we flanked 5,5-bis(4-hexylphenyl)-5H-

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dithieno[3,2-*b*:2',3'-*d*]pyran (DTP) to the 2,5-difluorophenylene central core with two different orientations to develop non-fused-ring electron acceptors (NFERAs).^[42] which made excellent use of configuration lock and structural isomerization effects, resulting in significant changes in the optical properties, electrochemical properties and molecular stacking properties of NFERAs that associated with photovoltaic properties.^[42] A further research of the combination of conformation lock and structure isomerization effects on the overall properties of the NFAs would provide an in-depth understanding on the structure-property relationship for guiding new NFA design and further improving the performances of OSCs.

Herein, we report the development of two novel lowly fused NFAs with isomeric structures, named as BTP-out-4F and BTP-in-4F, by tailoring the fused 7-ring based on central core of Y6 into a lowly fused 5-ring linked with two alkoxythiophene bridges (Scheme 1a). The main difference between the two isomeric acceptors was the position of the octyloxy side chains relative to the central core or not. BTP-out-4F with octyloxy side chains away from the central core exhibits large steric hindrance, restraining the rotational freedom between the thiophene bridge and end group and maintaining free rotation between the central core and the thiophene bridge. In contrast, BTP-in-4F with octyloxy side chains close to the

central core has much lower rotation freedom due to the non-covalent S...O interactions locked with the central core, thiophene bridge and end group simultaneously, making BTP-in-4F have higher molecular crystallinity. On the other hand, the optical properties, energy levels and the blend morphology characters were significantly influenced, leading to distinctive photovoltaic performances. BTP-out-4F formed favorable energy level alignment and blend morphology, when matching with PBDB-T donor, thus realizing a much higher PCE of 13.32%, which was over 13 times than that of BTP-in-4F based devices (PCE=0.97%).

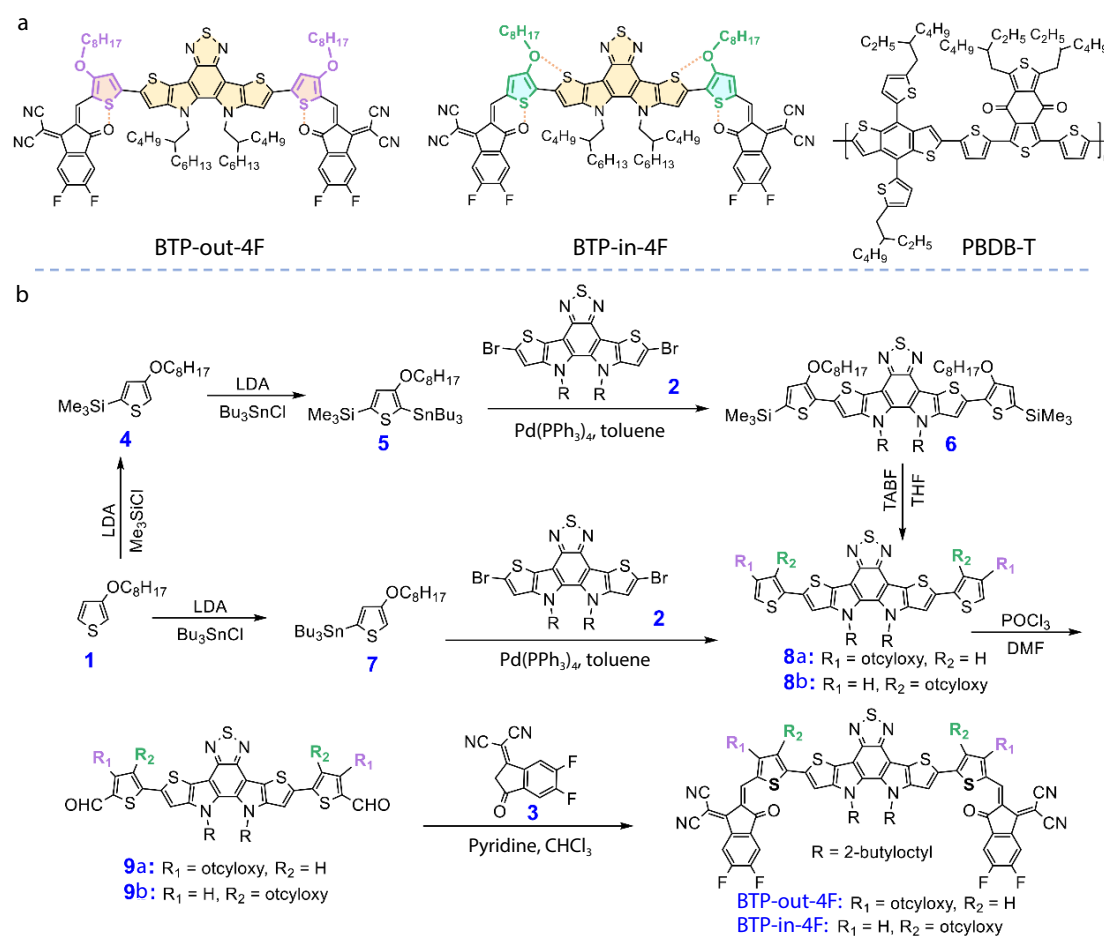
EXPERIMENTAL

The experimental details are shown in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Materials Synthesis and Characterizations

The synthetic routes of the two isomeric NFAs are shown in Scheme 1(b). Compound **1** was lithiated and subsequently quenched with tributyltin chloride to afford compound **7**. Stille coupling of compound **7** and compound **2** with the catalyst of tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄]



Scheme 1 (a) The chemical structures of BTP-out-4F, BTP-in-4F and PBDB-T; (b) Synthetic routes to BTP-out-4F and BTP-in-4F.

in toluene solution afforded **8a**. Compound **5** was obtained by the reaction of compound **1** with lithium diisopropylamide (LDA) and trimethylchlorosilane, followed by reaction with LDA and trimethyltin chloride. Compound **8b** was obtained by Stille coupling of compound **2** with compound **5** followed by removing of silane protecting groups. The target BTP-out-4F and BTP-in-4F were synthesized by dialdehyde reaction of compounds **8a** or **8b** followed by Knoevenagel condensation with compound **3**, respectively. The detailed synthetic routes and structure characterizations can be found in ESI. The two acceptors exhibit good solubility in common solvents, such as tetrahydrofuran (THF), dichloromethane (DCM), chloroform (CF) and chlorobenzene (CB). According to the results from thermogravimetric analysis (TGA), the decomposition temperature (T_d , 5% weight loss) are 313 °C for BTP-out-4F and 343 °C for BTP-in-4F, respectively, suggesting their excellent thermal stability (Fig. S1a, in ESI). Differential scanning calorimetry (DSC) were performed to analyze the solid-state thermal transitions (Fig. S1b, in ESI). Melting temperature (T_m) of 266 °C was observed for BTP-out-4F. Interestingly, we observed an endothermic peak at 208 °C and an exothermic peak at 220 °C for BTP-in-4F, which could be attributed to crystal transformation. When rising the temperature, a sharper endothermic peak at 269 °C could be observed for BTP-in-4F. The sharper endothermic peak at higher temperature demonstrated the higher crystallinity of BTP-in-4F than BTP-out-4F.

Optical Properties and Energy Levels

The Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption of BTP-out-4F and BTP-in-4F in dilute chloroform solutions and thin films were measured to investigate the isomerization effect on the optical properties. As shown in Fig. 1(a), BTP-out-4F has a main absorption in the range of 600–825 nm and an absorption peak at 738 nm with a maximum extinction coefficient (ϵ) of $1.5 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in CF solution. Compared with BTP-out-4F, BTP-in-4F shows a significantly redshifted absorption over 100 nm with a main absorption range of 650–1000 nm and absorption peak of 848 nm ($\epsilon = 1.1 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). The somewhat temperature-dependent absorption in CF may arise from the conformation lock effect formed by the non-covalent S...O interactions, which can be weakened by elevating the solution temperature (Fig. S2 in ESI). From solution to film state, both the two acceptors show obvious red shift absorption (~80 nm) with the absorption peak of 816 nm for BTP-out-4F and 931 nm for BTP-in-4F, respectively, implying their intensified molecular packing in film state (Fig. 1b). The E_g^{opt} was estimated to be 1.34 eV for BTP-out-4F, which is comparable to that of Y6 acceptor (1.33 eV).^[12] In contrast, an ultra-narrow E_g^{opt} of 1.07 eV was obtained for BTP-in-4F, which indicated the strong intramolecular charge transport (ICT) between the central core and the end group of BTP-in-4F. PBDB-T has a main absorption in the range of 450–700 nm, which is well complementary with these NFAs.

Cyclic voltammetry (CV) measurements were conducted to

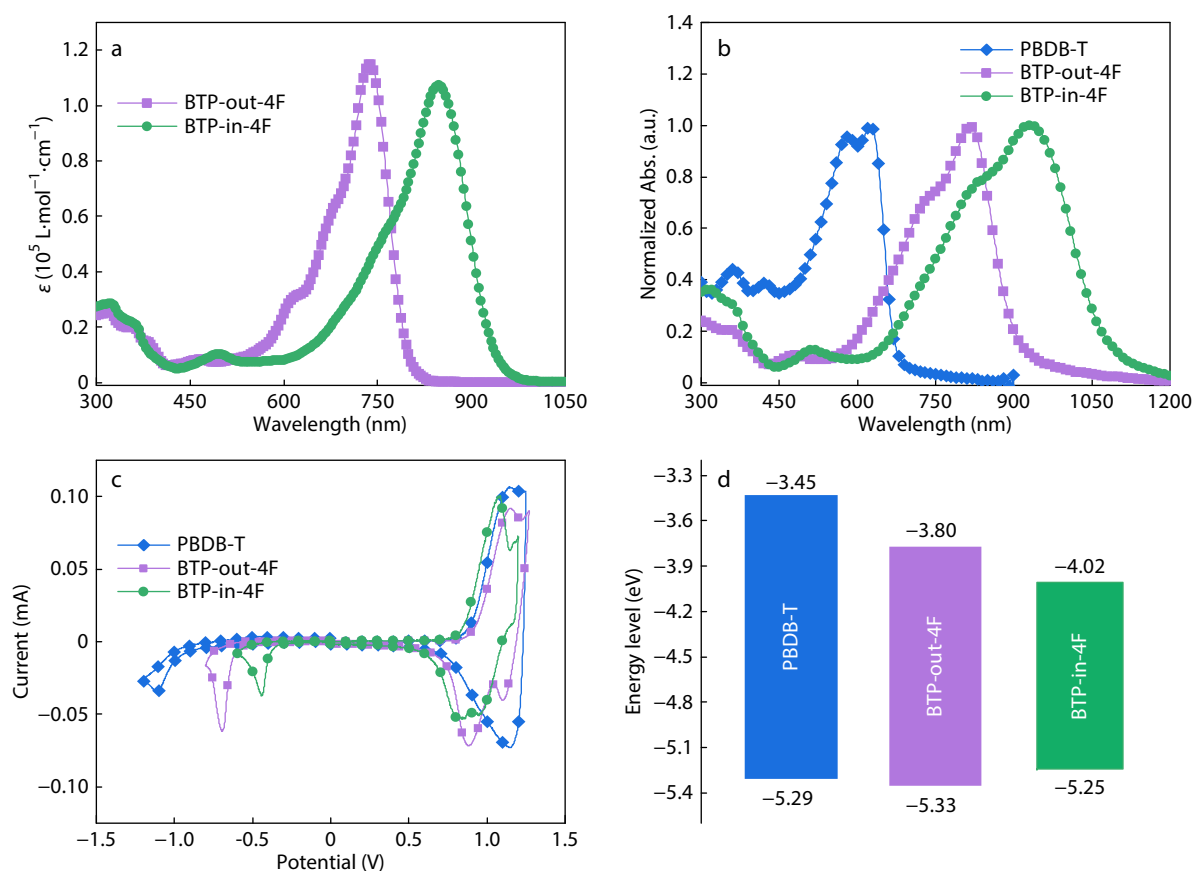


Fig. 1 UV-Vis-NIR spectra of SMAs in (a) chloroform solutions and (b) film state. (c) CV curves of PBDB-T and the SMAs. (d) The energy diagram of PBDB-T and the SMAs.

investigate the isomerization effect on the energy levels (Fig. 1c). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level are estimated to be -5.33 and -3.80 eV for BTP-out-4F, respectively, corresponding to an electrochemical band gap (E_g^{CV}) of 1.53 eV (Fig. 1d). Compared to BTP-out-4F, BTP-in-4F exhibits a higher HOMO of -5.25 eV but a lower LUMO of -4.02 eV, corresponding to a narrower E_g^{CV} of 1.23 eV. The energy levels of PBDB-T donor were also measured for comparison. The HOMO/LUMO of $-5.29/-3.45$ eV for PBDB-T could match well with BTP-out-4F, the minimal HOMO offset ($\Delta_{\text{HOMO}} = 0.04$ eV) was expected to obtain high open circuit voltage (V_{oc}) with low energy loss (E_{loss}). However, the HOMO of PBDB-T was even lower than that of BTP-in-4F, the unfavorable energy level alignment might lead to inefficient exciton dissociation in the resulting devices (*vide infra*).

The isomerization effect on the molecular geometry and electronic properties was investigated by density functional theory (DFT) simulation at the B3LYP/6-31G level. All the long alkyl groups were replaced with methyl groups to simplify the calculation process. These two NFAs exhibit very similar steric hindrance between the central core and thiophene bridges (Fig. 2a). In spite of that, the rotation freedom of the two thiophene bridges relative to the central core of BTP-in-4F was largely restrained due to the conformational lock formed by the non-covalent S $\cdots$ O interactions (Scheme 1). A large steric hindrance between the thiophene bridges and the end

groups of BTP-out-4F induced by the octyloxy side chains, which restrained the rotation of the end groups (Fig. 2b). On the other hand, the non-covalent S $\cdots$ O interactions between the thiophene bridges and the end groups also limited the rotation of the end groups of both molecules. As can be seen, all the π -conjugated species in BTP-in-4F were totally locked into a planar conformation, which is favorable for more compact molecular packing and electron delocalization. The HOMO orbitals were mainly distributed along the central core and thiophene bridges, while the LUMO orbitals were delocalized the whole backbones of these NFAs (Fig. 2c). The HOMO/LUMO levels were calculated to be $-5.39/-3.38$ eV for BTP-out-4F and $-5.16/-3.50$ eV for BTP-in-4F, respectively. The variation trends were consistent with the results from UV-Vis-NIR and CV measurements. The results also indicated that the minimal change by structure isomerization could result in huge impact on the optical and energy levels of NFAs.

Photovoltaic Properties

To investigate the photovoltaic properties of these NFAs, OSCs were fabricated and evaluated with a conventional device structure of indium tin oxide (ITO)/poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PBDB-T:NFA/PNDIT-F3N/Ag. PBDB-T:NFA solution was prepared with a D:A ratio of 1:1.2 by weight and a total concentration of $17.6 \text{ mg}\cdot\text{mL}^{-1}$ in chloroform (CF). The detailed device fabrication procedure was presented in ESI.

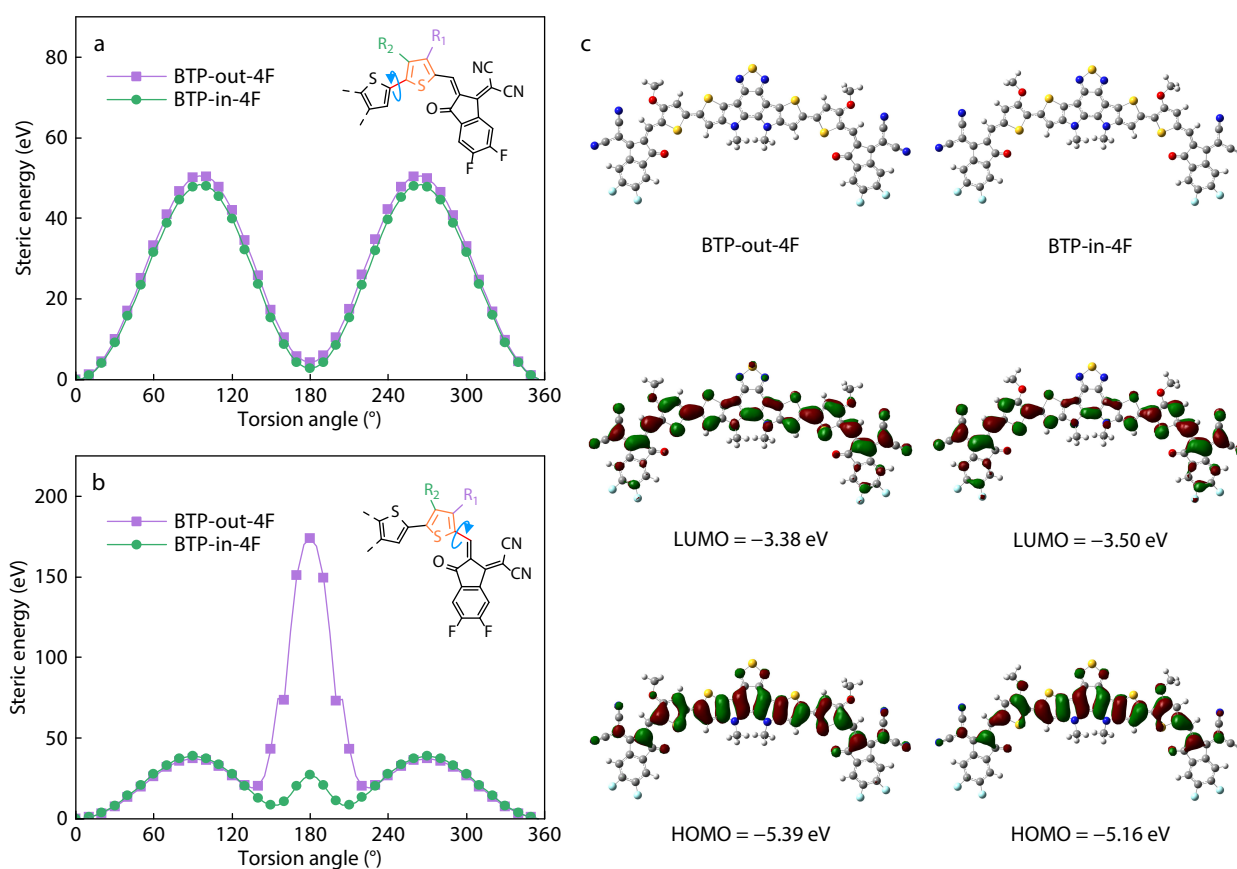


Fig. 2 The rotary steric energy plots between (a) the central core and thiophene bridges, and (b) the thiophene bridges and the end groups. (c) Optimized molecular geometry and frontier molecular orbitals of the NFAs.

For BTP-in-4F-based devices, an extremely low PCE of 0.97% was obtained because of the low V_{oc} of 0.610 V, J_{sc} of 4.21 mA·cm⁻² and fill factor (FF) of 37.74% (Fig. 3a and Table 1). One of the main reasons could be ascribed to the unfavorable energy level alignment between the donor and acceptor as discussed above. The mismatched energy level between PBDB-T and BTP-in-4F could be circumvented by using higher HOMO level donors, such as PBDTT-E-T (E_{HOMO} =5.09 eV).^[43] PBDTT-E-T could also realize a good complimentary absorption with BTP-in-4F (Fig. S4 in ESI), contributing to the significantly enhanced J_{sc} of 24.67 mA·cm⁻² and PCE of 10.17% (Fig. S5 and Table S1 in ESI). In contrast, BTP-out-4F could match well with PBDB-T, which enabled the simultaneously enhanced V_{oc} of 0.864 V, J_{sc} of 22.27 mA·cm⁻² and FF of 69.19%, delivering a significantly improved PCE of 13.32%. The enhanced V_{oc} was originated from the higher LUMO level of BTP-out-4F, and the significantly improved J_{sc} and FF could be attributed to the well-matched energy level for efficient exciton dissociation and charge transport. The higher J_{sc} of BTP-out-4F-based devices was further confirmed by external quantum efficiency (EQE) spectrum (Fig. 3b). Although BTP-

in-4F-based devices exhibited the photoresponse in a broad range from 300 nm to 1100 nm, the low EQE values (<20%) all over the whole absorption range led to a quite small calculated J_{sc} of 4.05 mA·cm⁻². On the other hand, the excellent photoresponse of BTP-out-4F-based devices from 300 to 900 nm contributed to the high calculated J_{sc} of 21.89 mA·cm⁻². The J_{sc} s calculated from the EQE spectra were close to those obtained from the current density-voltage (J - V) characteristics. The results indicated that the minimal change by side chain isomerization could have significant influence on the photovoltaic performance of the corresponding NFAs.

The charge transport properties of the blend films were investigated by using the space charge limited current (SCLC) method. The hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/PBDB-T:NFA/Au, and the electron-only devices were fabricated with a structure of ITO/ZnO/PBDB-T:NFA/PNDIT-F3N/Ag. The hole mobility (μ_h)/electron mobility (μ_e) values were estimated to be $5.27 \times 10^{-4}/4.05 \times 10^{-4}$ and $3.22 \times 10^{-4}/1.07 \times 10^{-4}$ cm²·V⁻¹·s⁻¹ for BTP-out-4F and BTP-in-4F, respectively. The higher and much more balanced μ_h/μ_e for BTP-out-4F based devices could contribute to more effi-

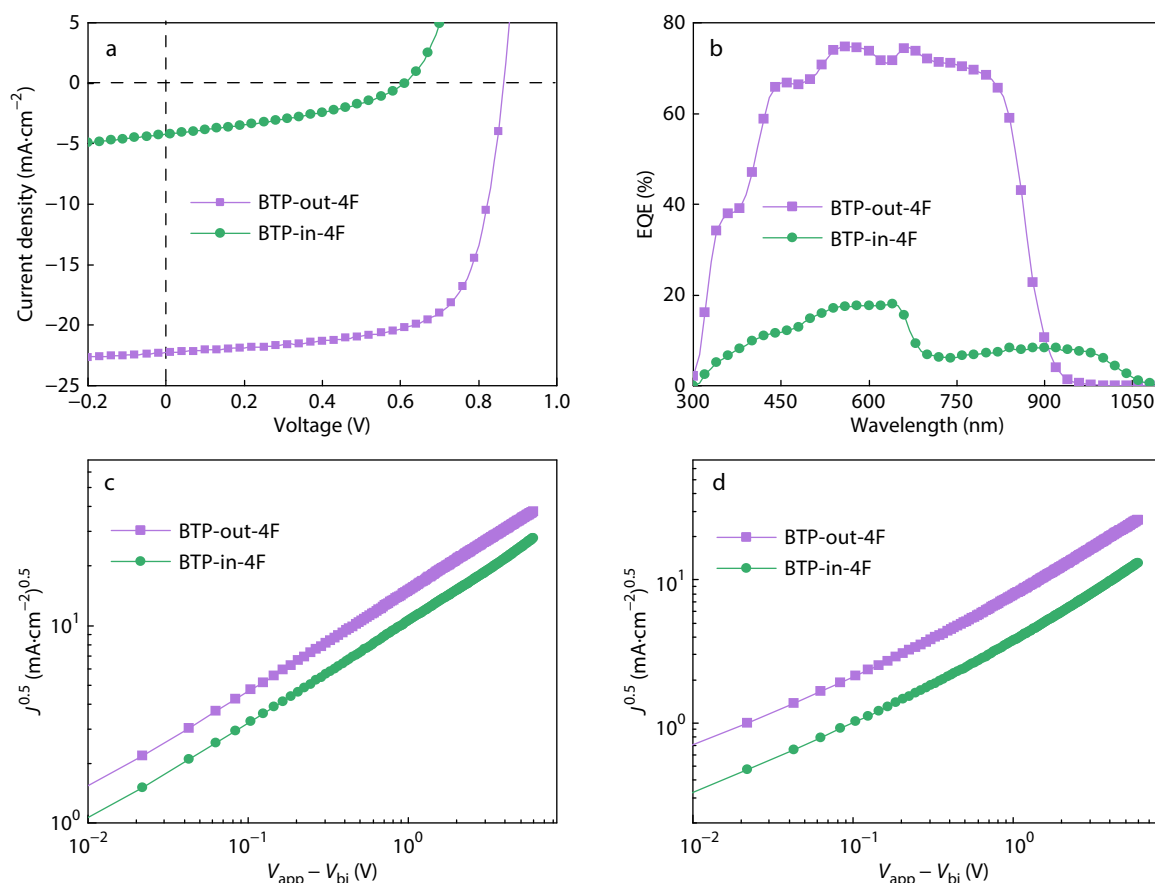


Fig. 3 (a) J - V curves and (b) EQE curves of NF-PSCs. $J^{0.5}$ - V curves of the (c) hole-only and (d) electron-only devices.

Table 1 Photovoltaic parameters of the OSCs based on BTP-out-4F and BTP-in-4F.

NFA	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	J_{sc}^a (mA·cm ⁻²)	FF (%)	PCE (%)
BTP-out-4F	0.864 (0.859±0.007) ^b	22.27 (21.91±0.28)	21.89	69.19 (68.59±0.47)	13.32 (12.91±0.27)
BTP-in-4F	0.610 (0.608±0.008)	4.21 (4.03±0.17)	4.05	37.74 (37.24±0.29)	0.97 (0.91±0.04)

^a The J_{sc} was calculated from EQE curves; ^b The average values with standard deviations were calculated from 10 individual devices.

cient charge transport, thus leading to higher J_{sc} and FF values.

Morphology Studies

The isomerization effect on the molecular packing was studied by grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements (Fig. 4). It was interesting that totally different molecular packing behaviors of the two NFAs were observed both in pristine and blend films. BTP-out-4F shows an obvious edge-on packing, the (100) diffraction of BTP-out-4F was mainly located in the out-of-plane direction with $q_z=3.88 \text{ nm}^{-1}$, corresponding to the lamellar stacking distance (d_l) of 16.2 Å. On the other hand, the (010) diffraction was mainly located in the in-plane direction with $q_{xy}=17.9 \text{ nm}^{-1}$, corresponding to the π - π stacking distance (d_π) of 3.51 Å. In contrast, BTP-in-4F exhibits a profound face-on packing with the (100) peak at $q_{xy}=3.38 \text{ nm}^{-1}$ ($d_l=18.6 \text{ Å}$) and (010) peak at $q_z=18.3 \text{ nm}^{-1}$ ($d_\pi=3.43 \text{ Å}$). The BTP-out-4F has more compact lamellar packing, while BTP-in-4F has more compact π - π stacking. Compared with the NFAs, the pristine PBDB-T film coexisted edge-on packing and face-on packing with a semicircle (100) peak at $q=2.99 \text{ nm}^{-1}$ ($d_l=21.0 \text{ Å}$) and (010) peak at $q=17.3 \text{ nm}^{-1}$ ($d_\pi=3.63 \text{ Å}$) preferred in the out-of-plane direction (Fig. S3 in ESI). In the blend films, the edge-on packing and face-on packing coexisted in PBDB-T:BTP-out-4F, while PBDB-T:BTP-in-4F preserved high ordered face-on packing. The face-on packing is considered to benefit the vertical charge transport, whereas the coexisted edge-on packing and face-on packing facilitated the three-dimensional (3D) charge transport throughout the active blend.

Atomic force microscopy (AFM) measurements were conducted to investigate the isomerization effect on the blend morphology (Fig. 5). PBDB-T:BTP-out-4F displayed a relatively

smooth topography with a small root mean square roughness (RMS) of 2.03 nm, in which fibrillar networks could be observed obviously. Such interpenetrating networks provide substantial D/A interfaces for exciton dissociation and highways for charge transport. The results explained the high J_{sc} and FF values obtained from BTP-out-4F-based devices. In contrast, a much coarser PBDB-T:BTP-in-4F film can be observed with a larger RMS of 4.70 nm, the more grain-like domains could hardly provide bicontinuous charge transport pathways, which explained the reason that PBDB-T:BTP-in-4F had lower charge carrier mobilities. The severe phase separation of PBDB-T:BTP-in-4F film could be ascribed to the excessive aggregation of BTP-in-4F induced by the conformation lock effect.

Charge Recombination Dynamics

To further explore the charge recombination processes, the J_{sc} and V_{oc} against the light intensity (P_{light}) of the NF-PSCs were investigated and plotted (Figs. 6a and 6b).^[44] As displays in Fig. 6(a), the relationship between J_{sc} and P_{light} could be defined as $J_{sc} \propto P_{light}^a$. The values were 0.99 and 0.81 for BTP-out-4F and BTP-in-4F, respectively, suggesting that the bimolecular recombination was efficiently suppressed for BTP-out-4F based device. Fig. 6(b) shows the relationship between P_{light} and V_{oc} , which was a linear correlation and the slope was denoted by kT/q . The slope values were calculated to be 1.22 kT/q and 1.68 kT/q for BTP-out-4F and BTP-in-4F, respectively, implying the less charge-trapped recombination occurred in BTP-out-4F based device. Moreover, the charge generation and extraction were also detected by photocurrent (J_{ph}) versus efficient voltage (V_{eff}) plots (Fig. 6c).^[44] The J_{ph} is defined as $J_L - J_D$, where J_L and J_D are the current densities under AM 1.5G illumination and

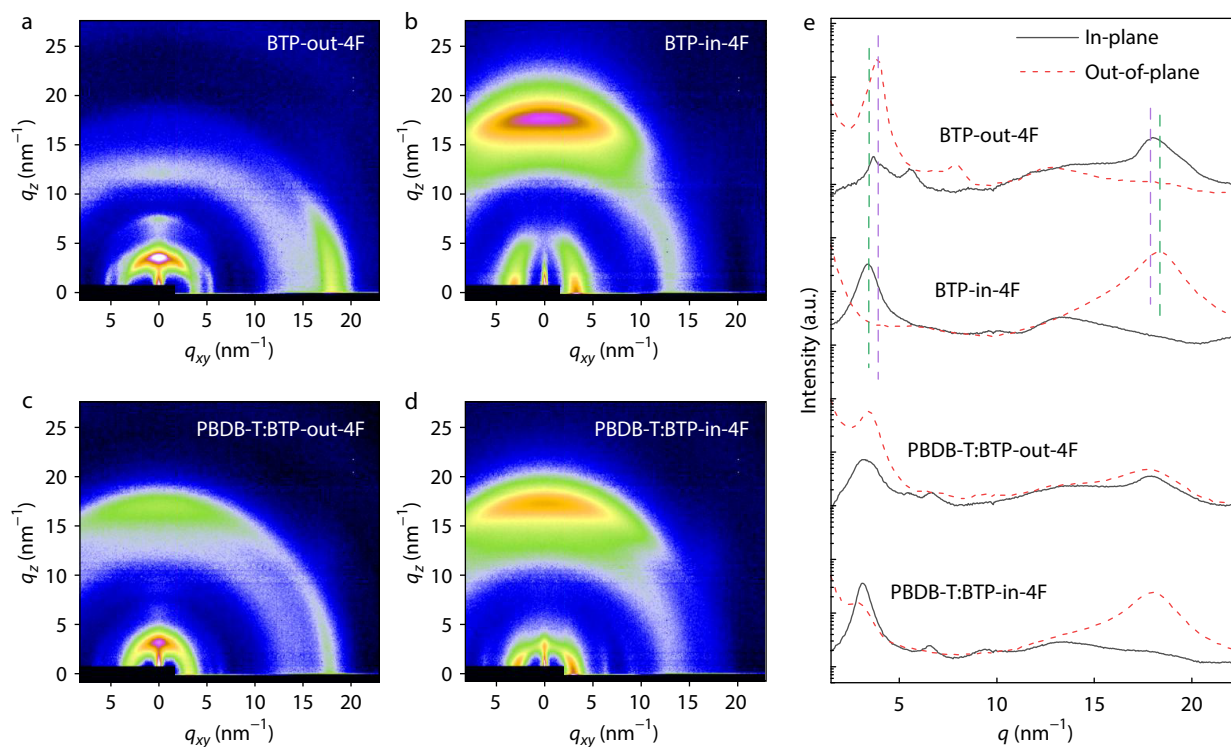


Fig. 4 (a–d) GIWAXS patterns of the pristine and blend films; (e) The corresponding in-plane and out-of-plane line-cuts.

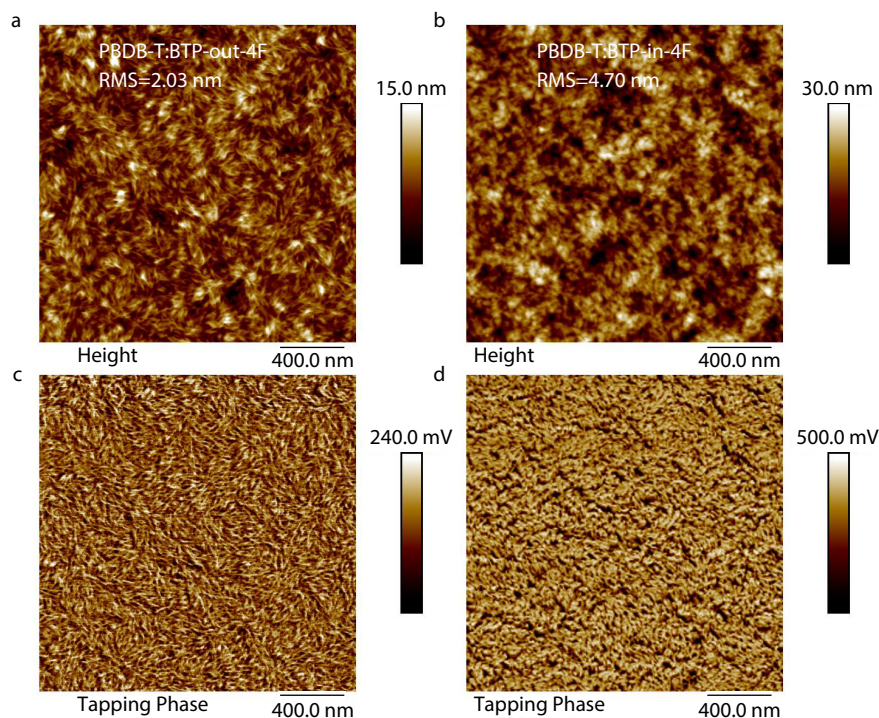


Fig. 5 AFM (a, b) height images and (c, d) phase images of the blend films.

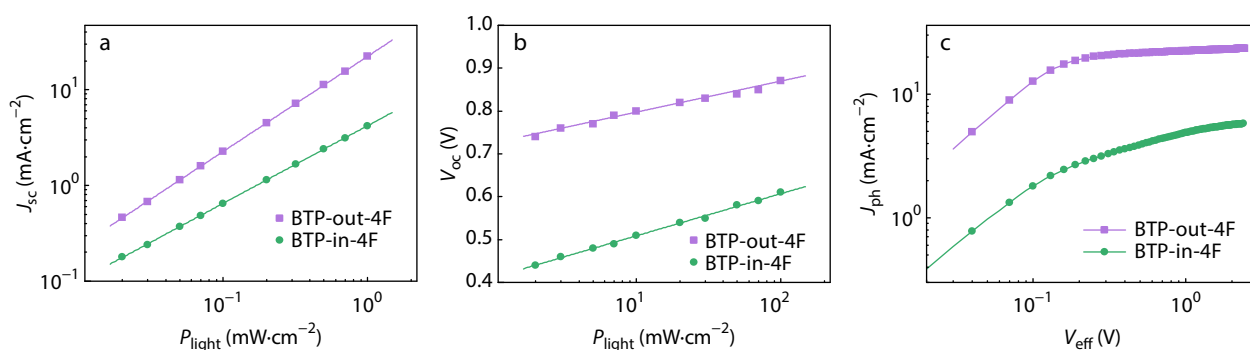


Fig. 6 (a) J_{sc} and (b) V_{oc} versus P_{light} plots of the NF-PSCs. (c) Photocurrent against effective voltage of the NF-PSCs.

dark, respectively, and V_{eff} is defined as $V_0 - V$ (where V_0 is the voltage at which $J_L = J_D$, respectively, and V is the applied voltage), the charge dissociation probability ($P(E,T)$) can be calculated by J_{ph}/J_{sat} ratios under short-circuit conditions, the $P(E,T)$ of 0.95 was observed in BTP-out-4F based device, which was higher than the corresponding device based on BTP-in-4F (0.73). Such higher excellent charge dissociation probability for BTP-out-4F device was the excellent explanation for its superior J_{sc} and FF values.

CONCLUSIONS

In conclusion, two lowly fused NFAs, named as BTP-out-4F and BTP-in-4F, were designed and synthesized by tailoring the fused 7-ring central core of Y6 into a lowly fused 5-ring with two octyloxythiophene bridges to form the isomeric structures. BTP-out-4F with octyloxy side chains away from the central core exhibits large steric hindrance, which restrains the rotational freedom between the thiophene bridge and end group but

maintains free rotation between the central core and the thiophene bridge. In contrast, BTP-in-4F with octyloxy side chains close to the central core has much lower rotation freedom due to the non-covalent S...O interactions locked with the central core, thiophene bridge and end group simultaneously, making BTP-in-4F have higher molecular crystallinity for excessive aggregation. BTP-in-4F exhibited largely enhanced ICT, leading to the ultra-narrow E_g^{opt} of 1.07 eV and upshifted HOMO of -5.25 eV. Such high HOMO level made BTP-in-4F could not form favorable energy alignment with PBDB-T, resulting in inferior PCE of 0.97% with a low J_{sc} of 4.21 $\text{mA}\cdot\text{cm}^{-2}$. In contrast, the favorable energy alignment and suitable crystallinity of BTP-out-4F made it match well with PBDB-T, and form ideal blend morphology for charge separation and transport. As a result, a much higher PCE of 13.32% was obtained with significantly improved J_{sc} of 22.27 $\text{mA}\cdot\text{cm}^{-2}$, V_{oc} of 0.864 V and FF of 69.19%. This work provides a good example of developing efficient lowly fused NFAs by the structural isomerization.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2751-z>.

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REFERENCES

- Hou, J. H.; Inganäs, O.; Friend, R. H.; Gao, F. Organic solar cells based on non-fullerene acceptors. *Nat. Mater.* **2018**, *17*, 119–128.
- Ma, L. J.; Zhang, S. Q.; Zhu, J. C.; Wang, J. W.; Ren, J. Z.; Zhang, J. Q.; Hou, J. H. Completely non-fused electron acceptor with 3D-interpenetrated crystalline structure enables efficient and stable organic solar cell. *Nat. Commun.* **2021**, *12*, 5093.
- Zhang, Y.; Liu, K.; Huang, J. M.; Xia, X. X.; Cao, J. P.; Zhao, G. M.; Fong, P. W. K.; Zhu, Y.; Yan, F.; Yang, Y.; Lu, X. H.; Li, G. Graded bulk-heterojunction enables 17% binary organic solar cells via nonhalogenated open air coating. *Nat. Commun.* **2021**, *12*, 4815.
- Lin, F.; Jiang, K.; Kaminsky, W.; Zhu, Z.; Jen, A. K. A non-fullerene acceptor with enhanced intermolecular π -core interaction for high-performance organic solar cells. *J. Am. Chem. Soc.* **2020**, *142*, 15246–15251.
- Ma, Y. L.; Zhang, M.; Wan, S.; Yin, P.; Wang, P. S.; Cai, D. D.; Liu, F.; Zheng, Q. D. Efficient organic solar cells from molecular orientation control of M-series acceptors. *Joule* **2021**, *5*, 197–209.
- Gasparini, N.; Paletti, S. H. K.; Bertrandie, J.; Cai, G. L.; Zhang, G. C.; Wadsworth, A.; Lu, X. H.; Yip, H. L.; McCulloch, I.; Baran, D. Exploiting ternary blends for improved photostability in high-efficiency organic solar cells. *ACS Energy Lett.* **2020**, *5*, 1371–1379.
- Li, S. X.; Zhan, L. L.; Jin, Y. Z.; Zhou, G. Q.; Lau, T. K.; Qin, R.; Shi, M. M.; Li, C. Z.; Zhu, H. M.; Lu, X. H.; Zhang, F. L.; Chen, H. Z. Asymmetric electron acceptors for high-efficiency and low-energy-loss organic photovoltaics. *Adv. Mater.* **2020**, *32*, 2001160.
- Meng, H.; Liao, C.; Deng, M.; Xu, X.; Yu, L.; Peng, Q. 18.77% Efficiency organic solar cells promoted by aqueous solution processed cobalt(II) acetate hole transporting layer. *Angew. Chem. Int. Ed.* **2021**, *60*, 22554–22561.
- Xu, X.; Yu, L.; Meng, H.; Dai, L.; Yan, H.; Li, R.; Peng, Q. Polymer solar cells with 18.74% efficiency: from bulk heterojunction to interdigitated bulk heterojunction. *Adv. Funct. Mater.* **2022**, *32*, 2108797.
- Tang, A.; Song, W.; Xiao, B.; Guo, J.; Min, J.; Ge, Z.; Zhang, J.; Wei, Z.; Zhou, E. Benzotriazole-based acceptor and donors, coupled with chlorination, achieve a high Voc of 1.24 V and an efficiency of 10.5% in fullerene-free organic solar cells. *Chem. Mater.* **2019**, *31*, 3941–3947.
- Wang, X.; Tang, A.; Yang, J.; Du, M.; Li, J.; Li, G.; Guo, Q.; Zhou, E. Tuning the intermolecular interaction of A2-A1-D-A1-A2 type non-fullerene acceptors by substituent engineering for organic solar cells with ultrahigh Voc of ~1.2 V. *Sci. China Chem.* **2020**, *63*, 1666–1674.
- Yuan, J.; Zhang, Y. Q.; Zhou, L. Y.; Zhang, G. C.; Yip, H. L.; Lau, T. K.; Lu, X. H.; Zhu, C.; Peng, H. J.; Johnson, P. A.; Leclerc, M.; Cao, Y.; Ulanski, J.; Li, Y. F.; Zou, Y. P. Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core. *Joule* **2019**, *3*, 1140–1151.
- Cui, Y.; Yao, H. F.; Zhang, J. Q.; Zhang, T.; Wang, Y. M.; Hong, L.; Xian, K. H.; Xu, B. W.; Zhang, S. Q.; Peng, J.; Wei, Z. X.; Gao, F.; Hou, J. H. Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages. *Nat. Commun.* **2019**, *10*, 2515.
- Cui, Y.; Yao, H. F.; Zhang, J. Q.; Xian, K. H.; Zhang, T.; Hong, L.; Wang, Y. M.; Xu, Y.; Ma, K. Q.; An, C. B.; He, C.; Wei, Z. X.; Gao, F.; Hou, J. H. Single-junction organic photovoltaic cells with approaching 18% efficiency. *Adv. Mater.* **2020**, *32*, 1908205.
- Li, C.; Zhou, J.; Song, J.; Xu, J.; Zhang, H.; Zhang, X.; Guo, J.; Zhu, L.; Wei, D.; Han, G.; Min, J.; Zhang, Y.; Xie, Z.; Yi, Y.; Yan, H.; Gao, F.; Liu, F.; Sun, Y. Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells. *Nat. Energy* **2021**, *6*, 605–613.
- Chong, K.; Xu, X.; Meng, H.; Xue, J.; Yu, L.; Ma, W.; Peng, Q. Realizing 19.05% efficiency polymer solar cells by progressively improving charge extraction and suppressing charge recombination. *Adv. Mater.* **2022**, *34*, 2109516.
- Cui, Y.; Xu, Y.; Yao, H.; Bi, P.; Hong, L.; Zhang, J.; Zu, Y.; Zhang, T.; Qin, J.; Ren, J.; Chen, Z.; He, C.; Hao, X.; Wei, Z.; Hou, J. Single-junction organic photovoltaic cell with 19% efficiency. *Adv. Mater.* **2021**, *33*, 2102420.
- Gao, W.; Fu, H. T.; Li, Y. X.; Lin, F.; Sun, R.; Wu, Z. A.; Wu, X.; Zhong, C.; Min, J.; Luo, J. D.; Woo, H. Y.; Zhu, Z. L.; Jen, A. K. Y. Asymmetric acceptors enabling organic solar cells to achieve an over 17% efficiency: conformation effects on regulating molecular properties and suppressing nonradiative energy loss. *Adv. Energy Mater.* **2021**, *11*, 2003177.
- Chen, Y. Z.; Ma, R. J.; Liu, T.; Xiao, Y. Q.; Kim, H. K.; Zhang, J. Q.; Ma, C.; Sun, H. L.; Bai, F. J.; Guo, X. G.; Wong, K. S.; Lu, X. H.; Yan, H. Side-chain engineering on Y-series acceptors with chlorinated end groups enables high-performance organic solar cells. *Adv. Energy Mater.* **2021**, *11*, 2003777.
- Zhang, Z. Z.; Li, Y. W.; Cai, G. L.; Zhang, Y. H.; Lu, X. H.; Lin, Y. Z. Selenium heterocyclic electron acceptor with small Urbach energy for as-cast high-performance organic solar cells. *J. Am. Chem. Soc.* **2020**, *142*, 18741–18745.
- Liu, W. Y.; Sun, S. M.; Zhou, L.; Cui, Y.; Zhang, W. K.; Hou, J. H.; Liu, F.; Xu, S. J.; Zhu, X. Z. Design of near-infrared nonfullerene acceptor with ultralow nonradiative voltage loss for high-performance semitransparent ternary organic solar cells. *Angew. Chem. Int. Ed.* **2022**, *61*, e202116111.
- Zhu, C.; Yuan, J.; Cai, F.; Meng, L.; Zhang, H.; Chen, H.; Li, J.; Qiu, B.; Peng, H.; Chen, S.; Hu, Y.; Yang, C.; Gao, F.; Zou, Y.; Li, Y. Tuning the electron-deficient core of a non-fullerene acceptor to achieve over 17% efficiency in a single-junction organic solar cell. *Energy Environ. Sci.* **2020**, *13*, 2459–2466.
- Xu, Y.; Yao, H. F.; Ma, L. J.; Hong, L.; Li, J. Y.; Liao, Q.; Zu, Y. F.; Wang, J. W.; Gao, M. Y.; Ye, L.; Hou, J. H. Tuning the hybridization of local exciton and charge-transfer states in highly efficient organic photovoltaic cells. *Angew. Chem.* **2020**, *59*, 9004–9010.

- 24 Tao, L. T.; Liu, X. H.; Deng, C. B.; Zhang, W. J.; Song, W. J. Highly efficient nonfullerene acceptor with sulfonyl-based ending groups. *ACS Appl. Mater. Interfaces* **2020**, *12*, 49659–49665.
- 25 Li, X. J.; Angunawela, I.; Chang, Y.; Zhou, J. D.; Huang, H.; Zhong, L.; Liebman, P. A.; Zhu, C. H.; Meng, L.; Xie, Z. Q.; Ade, H.; Yan, H.; Li, Y. F. Effect of the chlorine substitution position of the end-group on intermolecular interactions and photovoltaic performance of small molecule acceptors. *Energy Environ. Sci.* **2020**, *13*, 5028–5038.
- 26 Cheung, A. M. H.; Yu, H.; Luo, S. W.; Wang, Z.; Qi, Z. Y.; Zhou, W. T.; Arunagiri, L.; Chang, Y.; Yao, H. T.; Ade, H.; Yan, H. Incorporation of alkylthio side chains on benzothiadiazole-based non-fullerene acceptors enables high-performance organic solar cells with over 16% efficiency. *J. Mater. Chem. A* **2020**, *8*, 23239–23247.
- 27 Lin, Y.; Wang, J. Y.; Zhang, Z. G.; Bai, H. T.; Li, Y. F.; Zhu, D. B.; Zhan, X. W. An electron acceptor challenging fullerenes for efficient polymer solar cells. *Adv. Mater.* **2015**, *27*, 1170–1174.
- 28 Lin, Y. Z.; Zhang, Z. G.; Bai, H. T.; Wang, J. Y.; Yao, Y. H.; Li, Y. F.; Zhu, D. B.; Zhan, X. W. High-performance fullerene-free polymer solar cells with 6.31% efficiency. *Energy Environ. Sci.* **2015**, *8*, 610–616.
- 29 Yao, H. F.; Chen, Y.; Qin, Y. P.; Yu, R. N.; Cui, Y.; Yang, B.; Li, S. S.; Zhang, K.; Hou, J. H. Design and synthesis of a low bandgap small molecule acceptor for efficient polymer solar cells. *Adv. Mater.* **2016**, *28*, 8283–8287.
- 30 Wu, B.; Zhang, Y.; Tian, S.; Oh, J.; Yang, M.; Pan, L.; Yin, B.; Yang, C.; Duan, C.; Huang, F.; Cao, Y. Non-fused polymerized small molecular acceptors for efficient all-polymer solar cells. *Solar RRL* **2022**, *5*, 2101034.
- 31 Pang, S.; Zhou, X.; Zhang, S.; Tang, H.; Dhakal, S.; Gu, X.; Duan, C.; Huang, F.; Cao, Y. Nonfused nonfullerene acceptors with an A-D-A'-D-A framework and a benzothiadiazole core for high-performance organic solar cells. *ACS Appl. Mater. Interfaces* **2020**, *12*, 16531–16540.
- 32 Yang, M.; Wei, W.; Zhou, X.; Wang, Z.; Duan, C. Non-fused ring acceptors for organic solar cells. *Energy Mater.* **2021**, *1*, 100008.
- 33 Li, C. Q.; Zhang, X.; Yu, N.; Gu, X. B.; Qin, L. Q.; Wei, Y. N.; Liu, X. Z.; Zhang, J. Q.; Wei, Z. X.; Tang, Z.; Shi, Q. Q.; Huang, H. Simple nonfused-ring electron acceptors with noncovalently conformational locks for low-cost and high-performance organic solar cells enabled by end-group engineering. *Adv. Funct. Mater.* **2022**, *32*, 2108861.
- 34 Hou, R.; Li, M.; Ma, X. Q.; Huang, H.; Lu, H.; Jia, Q. Q.; Liu, Y. H.; Xu, X. J.; Li, H. B.; Bo, Z. S. Noncovalently fused-ring electron acceptors with C_{2v} symmetry for regulating the morphology of organic solar cells. *ACS Appl. Mater. Interfaces* **2020**, *12*, 46220–46230.
- 35 Li, S. X.; Zhan, L. L.; Zhao, W. C.; Zhang, S. H.; Ali, B.; Fu, Z. S.; Lau, T. K.; Lu, X. H.; Shi, M. M.; Li, C. Z.; Hou, J. H.; Chen, H. Z. Revealing the effects of molecular packing on the performances of polymer solar cells based on A-D-C-D-A type non-fullerene acceptors. *J. Mater. Chem. A* **2018**, *6*, 12132–12141.
- 36 Yu, Z. P.; Liu, Z. X.; Chen, F. X.; Qin, R.; Lau, T. K.; Yin, J. L.; Kong, X. Q.; Lu, X. H.; Shi, M. M.; Li, C. Z.; Chen, H. Simple non-fused electron acceptors for efficient and stable organic solar cells. *Nat. Commun.* **2019**, *10*, 2152.
- 37 Liu, Y. H.; Zhang, C. E.; Hao, D.; Zhang, Z.; Wu, L. L.; Li, M.; Feng, S. Y.; Xu, X. J.; Liu, F.; Chen, X. B.; Bo, Z. S. Enhancing the performance of organic solar cells by hierarchically supramolecular self-assembly of fused-ring electron acceptors. *Chem. Mater.* **2018**, *30*, 4307–4312.
- 38 Luo, Z. H.; Liu, T.; Yan, H.; Zou, Y.; Yang, C. L. Isomerization strategy of nonfullerene small-molecule acceptors for organic solar cells. *Adv. Funct. Mater.* **2020**, *30*, 2004477.
- 39 Wu, W. L.; Zhang, G. J.; Xu, X. P.; Wang, S. C.; Li, Y.; Peng, Q. Wide bandgap molecular acceptors with a truxene core for efficient nonfullerene polymer solar cells: linkage position on molecular configuration and photovoltaic properties. *Adv. Funct. Mater.* **2018**, *28*, 1707493.
- 40 Chai, G. D.; Chang, Y.; Zhang, J. Q.; Xu, X. P.; Yu, L. Y.; Zou, X. H.; Li, X. J.; Chen, Y. Z.; Luo, S. W.; Liu, B. B.; Bai, F. J.; Luo, Z. H.; Yu, H.; Liang, J. E.; Liu, T.; Wong, K. S.; Zhou, H.; Peng, Q.; Yan, H. Fine-tuning of side-chain orientations on nonfullerene acceptors enables organic solar cells with 17.7% efficiency. *Energy Environ. Sci.* **2021**, *14*, 3469–3479.
- 41 Chen, L.; Cao, C. C.; Lai, H. J.; Zhu, Y. L.; Pu, M. R.; Zheng, N.; He, F. End-group modifications with bromine and methyl in nonfullerene acceptors: the effect of isomerism. *ACS Appl. Mater. Interfaces* **2021**, *13*, 29737–29745.
- 42 Zhao, J.; Xu, X. P.; Yu, L. Y.; Li, R. P.; Li, Y.; Peng, Q. Highly efficient non-fused-ring electron acceptors enabled by the conformational lock and structural isomerization effects. *ACS Appl. Mater. Interfaces* **2021**, *13*, 25214–25223.
- 43 Huo, L.; Zhang, S.; Guo, X.; Xu, F.; Li, Y.; Hou, J. Replacing alkoxy groups with alkylthienyl groups: a feasible approach to improve the properties of photovoltaic polymers. *Angew. Chem. Int. Ed.* **2011**, *50*, 9697–9702.
- 44 Kyaw, A. K.; Wang, D. H.; Wynands, D.; Zhang, J.; Nguyen, T. Q.; Bazan, G. C.; Heeger, A. J. Improved light harvesting and improved efficiency by insertion of an optical spacer (ZnO) in solution-processed small-molecule solar cells. *Nano Lett.* **2013**, *13*, 3796–3801.