

Synergetic alkoxy side-chain and chlorine-contained end group strategy toward high performance ultra-narrow bandgap small molecule acceptors

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Abstract

Ultra-narrow bandgap (ultra-NBG) small molecule acceptors (SMAs) show great potential in organic solar cells (OSCs) due to the extend-ed near-infrared (NIR) absorption. In this work, a synergetic alkoxy side-chain and chlorine-contained end group strategy is employed to achieve A-DA'D-A type ultra-NBG SMAs by introducing alkoxy chains with oxygen atom at the second position into the thiophene β posi-tion as well as replacing the F atoms with Cl atoms in the end group. As a result, the heptacyclic BZO-4F shows a redshifted absorption onset (960 nm) than Y11 (932 nm) without oxygen atoms in the side chains. Then, the fluorinated end groups are substituted with the chlorinated ones to synthesize BZO-4Cl. The absorption onset of BZO-4Cl is further redshifted to 990 nm, corresponding to an optical ultra-NBG of 1.25 eV. When blending with the polymer donor PBDB-T, the binary devices based on PBDB-T: BZO-4F and PBDB-T: BZO-4Cl delivers power conversion efficiencies (PCEs) over 12%. Furthermore, ternary devices with the addition of BZ4F-O-1 into PBDB-T: BZO-4Cl system achieve the optimal PCE of 15.51%. This work proposes a synergetic alkoxy side-chain and chlorine-contained end group strategy to achieve A-DA'D-A type ultra-NBG SMAs, which is important for future molecular design.

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Synergetic alkoxy side-chain and chlorine-contained end group strategy toward high performance ultra-narrow bandgap small molecule acceptors

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Comprehensive Summary

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Keywords

Organic solar cells | A-DA'D-A type small molecule acceptors | Ultra-narrow bandgap | Alkoxy side chains |

Background and Originality Content

Organic solar cells (OSCs) have made continuous progress in recent years due to the breakthrough in organic semiconducting materials^[1-11]. Especially, the emerging A-DAD-A type small molecule acceptors (SMAs), Y6 and its analogs^[2, 12], promote the efficiency of OSCs to 15%-20% through the modification of the fused DAD backbone, electron-withdrawing end groups and side chains^[13-30]. Meanwhile, some A-DAD-A acceptors with ultra-narrow bandgap (ultra-NBG) have been reported to realize high J_{SC} for high-performance tandem or semi-transparent OSCs^[31-36]. Extending the fused backbone and modulating the push-pull effects of molecules are the general methods to narrow the molecular optical bandgap (E_g^{opt})^[16, 37-40]. And the molecular absorption onset could even be redshifted to exceeding 1000 nm^[31, 36]. However, the synthetic cost is increased due to the increased synthetic complexity and reduced yield.

Side-chain engineering is one of the simplest methods to subtly tune the molecular properties and device performance, which can effectively reduce the synthetic difficulty and cost^[21, 41-42]. Particularly, the side chains with functional heteroatoms could regulate the intra/intermolecular interactions due to the electronegativity and conjugative/ inductive effects, therefore having the potential in modulating the molecular packing and absorption properties. For instance, alkoxy chains are widely used in electron-donating materials for broadening the absorption spectra^[43-45]. However, alkoxy substituents on the SMAs usually cause abnormal blue-shifted absorption^[46-47].

In our most recent work, two efficient A-DA'D-A type pentacyclic acceptors, BZ4F-O-2 and BZ4F-O-3, have been reported by moving the oxygen atoms in the alkoxy side chains to the second or third position for the first time^[48]. Through the simple side-chain engineering strategy, the molecular absorption is obviously redshifted. And the BZ4F-O-3 achieves one of the highest J_{SC} s among the binary OSCs based on the pentacyclic acceptors. Therefore, it is significant to extend the strategy into heptacyclic acceptors for high-performance ultra-NBG SMAs with excellent J_{SC} .

Accordingly, we insert oxygen atoms into the second position of the side chains on our reported heptacyclic acceptor (Y11^[49]) to synthesize BZO-4F. As predicted, BZO-4F shows a redshifted absorption onset of 960 nm than that of Y11 (932 nm, Figure S1). By replacing the fluorine atoms on the end groups with chlorine atoms, BZO-4Cl is obtained with a further redshifted absorption onset of 990 nm. Choosing the low-cost polymer PBDB-T as the donor, both the PBDB-T: BZO-4F and PBDB-T: BZO-4Cl-based devices exhibit a moderate photovoltaic efficiency of ~12.4% with a poor V_{OC} . However, the J_{SC} of the PBDB-T: BZO-4Cl based device is increased due to the redshifted absorption. To further optimize the energy level arrangement, light absorption and blend morphology, BZ4F-O-1 with high lowest unoccupied molecular orbital (LUMO) level and complementary absorption is introduced as a third component into the PBDB-T: BZO-4Cl blend. As a result, the PBDB-T: BZ4F-O-1: BZO-4Cl-based device achieves a higher PCE of 15.51% with the simultaneously boosted V_{OC} of 0.77 V, J_{SC} of 27.85 mA cm⁻² and FF of 0.71. As far as we know, this is the best efficiencies of single-junction OSCs based on PBDB-T and SMAs. This work highlights the importance of a synergetic alkoxy side-chain and chlorine-contained end group strategy to synthesize heptacyclic A-DA'D-A type ultra-NBG SMAs for high-performance OSCs.

Results and Discussion

Figure 1a shows the chemical structures of PBDB-T, BZ4F-O-1, BZO-4F and BZO-4Cl. PBDB-T is purchased from Solarmer Materials Inc., BZ4F-O-1 is synthesized according to our previous work. The synthetic

procedures of two new acceptors, BZO-4F and BZO-4Cl are shown in Scheme S1 in the supporting information (SI). Alkoxy-substituted thieno[3,2-b]thiophene unit (compound 4) is one of the key intermediates that is synthesized through three-step reactions, including Bouveault aldehyde synthesis, reduction reaction by sodium borohydride and Williamson reaction. Subsequently, BZO-4F and BZO-4Cl are obtained by the similar synthetic method of BZ4F-O-1. Chemical structures of the intermediate molecules and target SMAs are determined by nuclear magnetic resonance hydrogen and carbon spectra (^1H and ^{13}C NMR) and mass spectra (MS), as shown in Figures S12-S24. BZO-4F and BZO-4Cl have good solubility in common processing solvents, *eg.*, chloroform, chlorobenzene and toluene at room temperature. Thermogravimetric analysis (TGA) is employed to evaluate the thermal stability of the two acceptors, displayed in Figure S2. BZO-4F and BZO-4Cl exhibit high decomposition temperatures of 305 °C and 296°C (T_d , 5% weight loss), respectively, revealing their good thermal stability.

The ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra of BZO-4F and BZO-4Cl in chloroform solution are displayed in Figure S3. BZO-4F shows an optical absorption region in 670-830 nm, while both the absorption peak and onset of BZO-4Cl are redshifted by ~20 nm. Similarly, in the film state, BZO-4Cl has a bathochromic absorption spectrum with an ultra-NBG of 1.25 eV, 30 nm redshift than that of BZO-4F (Figure 1b and Table 1). Electrochemical energy levels of BZO-4F and BZO-4Cl were investigated by cyclic voltammetry (CV) measurement. The CV curves are shown in Figure S4. The highest occupied molecular orbital (HOMO)/LUMO energy levels of BZO-4F and BZO-4Cl are calculated as -5.61/-3.92 eV and -5.69/-3.93 eV, respectively (Figure 1c and Table 1). The redshifted absorption from BZO-4F to BZO-4Cl could be attributed to the enhanced ICT effect and the π - π stacking caused by the chlorine atoms. Different from the generally lowered LUMO energy level of chlorinated SMA than that of the fluorinated one, BZO-4Cl has a similar LUMO level with BZO-4F. Therefore, the BZO-4Cl-based OSCs have the potential to achieve high J_{sc} without the sacrifice of V_{oc} .

Density functional theory (DFT) is employed to further explore the molecular conformation and energy levels of BZO-4F and BZO-4Cl at the B3LYP/6-31G* level. Undecyl and 2-ethylhexyl onto the thiophene/benzotriazole units are simplified with methyl groups, while the 2-ethylhexyl side chains onto the pyrrole units are retained to reflect the relatively true molecular conformation. The top/side view of BZO-4F and BZO-4Cl in Figure S5 illustrates a planar molecular conformation with a slightly twisted backbone that results from the steric hindrance of the side chains in the pyrrole units. The twisted structure is beneficial for limiting excessive aggregation. The HOMO/LUMO energy levels of BZO-4F and BZO-4Cl are calculated as -5.37/-3.45 eV and -5.43/-3.53 eV, respectively, which is consistent with the CV results. Besides, electrochemical energy levels of BZO-4F and BZO-4Cl in dilute chloroform solution further verify the theoretical calculation (Figure S6).

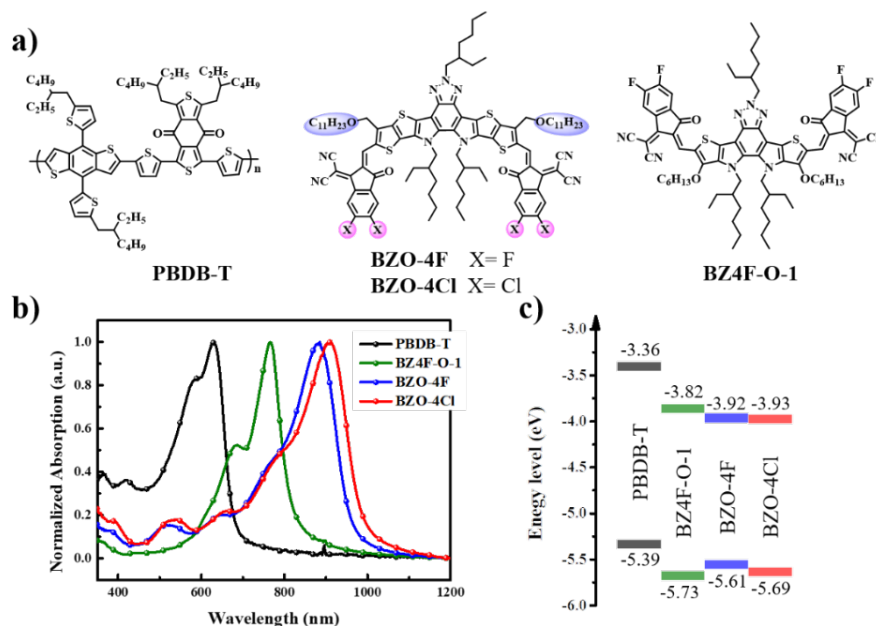


Figure 1. a) Chemical structures of PBDB-T, BZ4F-O-1, BZO-4F and BZO-4Cl; b) Normalized absorption spectra of PBDB-T, BZ4F-O-1, BZO-4F and BZO-4Cl in neat films; c) The energy levels alignment of PBDB-T, BZ4F-O-1, BZO-4F and BZO-4Cl.

Table 1. The optical absorption and electronic energy level properties of PBDB-T, BZ4F-O-1, BZO-4F and BZO-4Cl.

Acceptor	$\lambda_{\max}^a$ (nm)	λ_{onset}^a (nm)	$\lambda_{\max}^b$ (nm)	λ_{onset}^b (nm)	$E_g^{\text{opt } c)}$ (eV)	HOMO ^{d)} (eV)	HOMO ^{d)} (eV)	LUMO ^{d)} (eV)	LUMO ^{d)} (eV)
PBDB-T	620	666	631	679	1.83	1.83	-5.39	-5.39	-3.36
BZ4F-O-1	702	739	769	815	1.52	1.52	-5.73	-5.73	-3.82
BZO-4F	779	835	886	960	1.29	1.29	-5.61	-5.61	-3.92
BZO-4Cl	795	852	909	990	1.25	1.25	-5.69	-5.69	-3.93

^{a)}In chloroform solution; ^{b)}In neat film; ^{c)}Calculated from the formula: $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}^b$; ^{d)}By cyclic voltammetry (CV) measurement.

To investigate the photovoltaic performance of BZO-4F and BZO-4Cl, we fabricate two devices with a conventional structure of ITO/ PEDOT: PSS/ Donor: Acceptor /PDINN^[50]/ Ag. PBDB-T is selected as the polymer donor to blend with the acceptors because of the matched electrochemical energy levels and complementary optical absorption (Figures 1b and 1c). The device blend films adopt a bulk heterojunction (BHJ) structure with the optimized processing conditions such as donor/acceptor (D/A) concentration and weight ratio, additive ratio (chloronaphthalene, CN) and thermal annealing temperature/time (Table S1). As shown in the current density-voltage ($J - V$) graphs in Figure 2a, the BZO-4F-based binary device shows a moderate PCE of 12.42% with the V_{OC} of 0.73 V, J_{SC} of 26.44 mA cm⁻² and FF of 0.65. And the further charge generation, transport, recombination and morphology characterization are shown in Figures

S8-S10. By comparison, the BZO-4Cl-based binary device delivers a comparable efficiency of 12.48% with an improved J_{SC} of 26.86 mA cm^{-2} and a similar V_{OC} , which agrees with the absorption and energy level analysis. The photovoltaic parameters are summarized in Table 2. To further improve the photovoltaic performance limited by the poor V_{OC} and FF, a simple but efficient ternary strategy is considered. BZ4F-O-1, an alkoxy-substituted conjugated pentacyclic acceptor reported by our group is chosen as the third component into the PBDB-T: BZO-4Cl blend^[48]. BZ4F-O-1 has a strong light capture ability in 600-800 nm, which can compensate for the spectra gap between PBDB-T and BZO-4Cl (Figure 1b). Besides, the higher LUMO level of BZ4F-O-1 is favorable for the VOC. Furthermore, the introduction of BZ4F-O-1 might modulate the crystallinity and miscibility properties of the blend, thus improving the blend morphology.

First of all, the photovoltaic performance of PBDB-T: BZ4F-O-1 based binary device is studied. As shown in Figure 2a and Table 2, the PBDB-T: BZ4F-O-1 device shows a PCE of 10.48% with a V_{OC} of 0.774V, J_{SC} of 19.36 mA cm^{-2} and FF of 0.70. The V_{OC} and FF are much higher than that of the PBDB-T: BZO-4Cl binary devices. When BZ4F-O-1 is introduced to the PBDB-T: BZO-4Cl binary system, the PBDB-T: BZ4F-O-1: BZO-4Cl based ternary device achieved an optimal PCE of 15.51% with the V_{OC} , J_{SC} and FF simultaneously improved (Figure S7 and Table S2). The PCE- J_{SC} statistics of the PBDB-T-based OSCs are shown in Figure 2d and Table S3. As far as we know, this is the best value for single-junction OSCs based on the PBDB-T donor and SMAs.

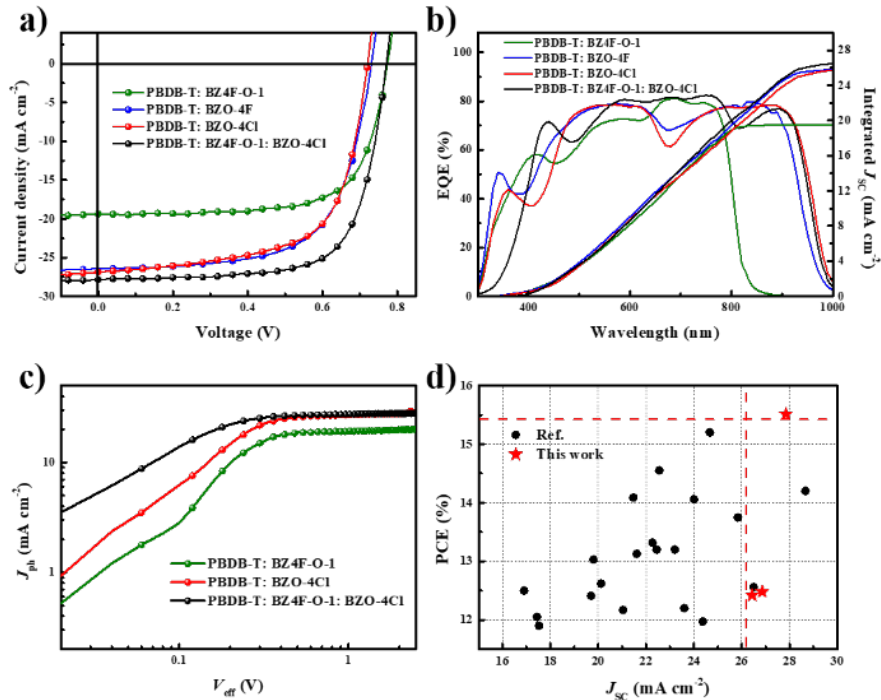


Figure 2. a) Current density-Voltage ($J - V$) curves; b) Corresponding EQE spectra; c) J_{ph} versus V_{eff} curves of the optimized binary and ternary OSCs; d) Statistics of PCE and corresponding J_{SC} values for single-junction OSCs based on PBDB-T and SMAs.

The integrated J_{SC} values of the PBDB-T: BZ4F-O-1, PBDB-T: BZO-4Cl and PBDB-T: BZ4F-O-1: BZO-4Cl based devices calculated from the external quantum efficiency (EQE) curves (Figure 2b) are 19.49, 25.80, and 26.50 mA cm^{-2} , respectively, which agree well with the measured J_{SC} s from $J - V$ curves within a deviation of 5%. The EQE spectra valley at the 560-780 nm range of the PBDB-T: BZO-4Cl blend was compensated by introducing BZ4F-O-1 as the third component, thus leading to a significantly integrated J_{SC} increase of 1.29 mA cm^{-2} (560-780 nm). Besides, the maximum EQE value is enhanced from 78.53% to

82.39%.

Table 2. The optimal photovoltaic parameters of the binary and ternary OSCs under 1 sun illumination.

Donor:Acceptor	V_{OC} (V)	$J_{SC}^{a)}$ (mA cm ⁻²)	FF (%)	PCE (%)	$\mu_h^{b)}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_e^{b)}$ (cm ² V ⁻¹ s ⁻¹)
PBDB-T: BZ4F-O-1	0.77	19.36 (19.49)	0.70	10.48	6.9×10^{-5}	6.6×10^{-5}
PBDB-T: BZO-4F	0.73	26.44 (25.80)	0.65	12.42	8.3×10^{-5}	1.54×10^{-4}
PBDB-T: BZO-4Cl	0.72	26.86 (25.80)	0.64	12.48	9.0×10^{-5}	1.51×10^{-4}
PBDB-T: BZ4F-O-1: BZO-4Cl	0.77	27.85 (26.50)	0.71	15.51	3.17×10^{-4}	4.20×10^{-4}

^{a)}The values in the bracket are integrated from EQE spectrum; ^{b)}Measured by space charge limited current (SCLC) method.

To further understand the exciton dissociation process of the binary and ternary devices, the photocurrent density (J_{ph}) versus effective applied voltage (V_{eff}) was measured (Figure 2c). J_{ph} is calculated by the formula of $J_{ph} = J_L - J_D$, where J_L and J_D are the photocurrent density in the light and in the dark. V_{eff} is calculated by the formula of $V_{eff} = V_o - V$. V_o denotes the voltage when the $J_{ph} = 0$, and V denotes the applied voltage. All the devices obtain their saturated photocurrent density (J_{sat}) when the $V_{eff} = 2V$. The exciton dissociation probability (P_{diss}) and charge collection efficiency (P_{coll}) are calculated from J_{ph}/J_{sat} and $J_{maxpower}/J_{sat}$ under the short-circuit condition and maximal power output point, respectively. The specific data are displayed at Table S4. All the devices showed high P_{diss} over 97% and P_{coll} over 81%. And the ternary device achieves the highest P_{diss} of 98.2% and P_{coll} of 84.4%, indicating the effective exciton dissociation and charge collection processes.

The hole and electron mobilities (μ_h and μ_e) are measured by the space charge-limited current (SCLC) method for investigating the charge transport of the blend films (Figures 3a and 3b). As a result, the μ_h / μ_e values of PBDB-T: BZ4F-O-1, PBDB-T: BZO-4Cl and PBDB-T: BZ4F-O-1: BZO-4Cl based devices are $6.9 \times 10^{-5} / 6.6 \times 10^{-5}$, $9.0 \times 10^{-5} / 1.51 \times 10^{-4}$ and $3.17 \times 10^{-4} / 4.20 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (Table 2 and Table S5). The less balanced charge transport of the PBDB-T: BZO-4Cl blend leads to a poor FF of 0.64. However, the ternary blend achieves both the increased μ_h / μ_e values and a more balanced charge transport, therefore, the J_{SC} and FF are simultaneously improved.

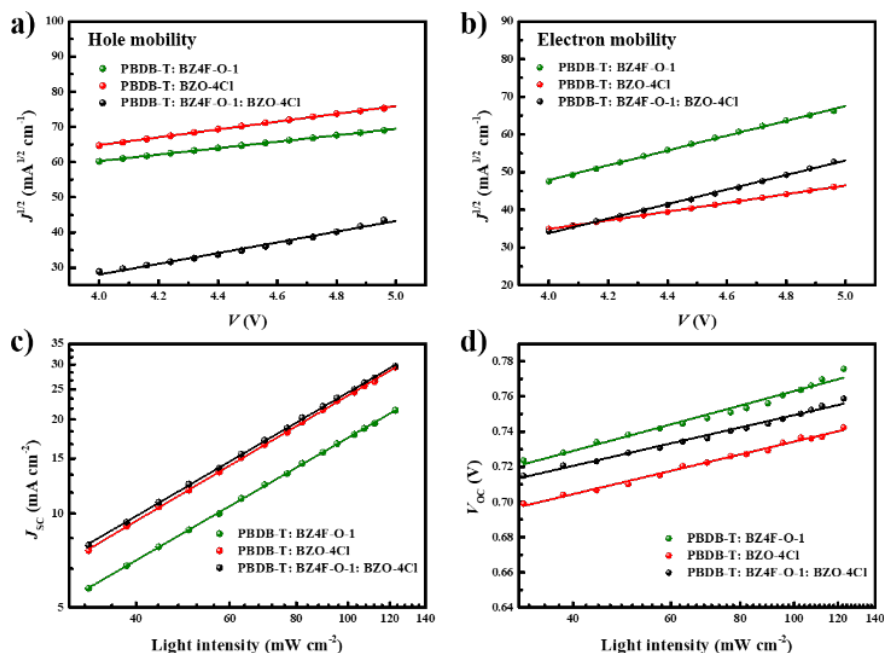


Figure 3. a) Hole mobility; b) Electron mobility; c) J_{SC} versus light intensity; d) V_{OC} versus light intensity of the optimized binary and ternary OSCs.

The dependences of J_{SC} and V_{OC} on light intensity (P_{light}) of the binary and ternary devices are shown in Figure 3c, 3d and Table S6 to evaluate the charge recombination. The relationship between J_{SC} and P_{light} can be described by $J_{SC} \propto P_{light}^\alpha$. All the α values of the devices are approaching 1, indicating negligible bimolecular recombination in the devices. Meanwhile, $V_{OC} \propto \ln(P_{light})$ is used to define the correlation between V_{OC} and P_{light} , where k is the Boltzmann constant, T is the Kelvin temperature, and e is the elemental charge. Generally, if the slope is close to kT/e , the dominant recombination mechanism is bimolecular recombination. If not, the mechanism is a complex recombination process. The slopes of the $V_{OC} - \ln(P_{light})$ curves of the PBDB-T: BZ4F-O-1, PBDB-T: BZO-4Cl and PBDB-T: BZ4F-O-1: BZO-4Cl devices are $1.48kT/q$, $1.30kT/q$ and $1.26kT/q$, respectively. The above results demonstrate that the ternary device possesses a more suppressed charge recombination.

Active layer morphology has great effects on the exciton dissociation, charge transport and recombination process, thus the photovoltaic performance of the resulting OSCs. Differential scanning calorimetry (DSC) is employed to understand the miscibility of the donor and acceptor materials (Figure S11). In the heating process, BZ4F-O-1 and BZO-4Cl exhibit their endothermic peaks at 240.4 °C and 215.9 °C, respectively. The BZ4F-O-1: BZO-4Cl (1: 1, w/w) mixture shows a medium value of melting temperature at 223.4°C, while the melting peaks of neat BZ4F-O-1 and BZO-4Cl are disappeared, suggesting good miscibility between BZ4F-O-1 and BZO-4Cl^[51].

Atomic force microscopy (AFM) is employed to investigate the surface morphology of the devices based on PBDB-T: BZ4F-O-1, PBDB-T: BZO-4Cl and PBDB-T: BZ4F-O-1: BZO-4Cl blends. The AFM images are shown in Figure 4. The phase images present obvious fiber-like interpenetrating morphology. According to the height images, all the blend films have uniform surfaces with the root-mean-square (RMS) roughness of 1.510, 0.967 and 0.972 nm. PBDB-T: BZO-4Cl film possesses the lowest RMS value. When the BZ4F-O-1 is introduced to the PBDB-T: BZO-4Cl binary system, the RMS value of the ternary film is slightly increased. It is evident that the crystallinity and miscibility of the blend might be finely improved, favoring the charge dissociation and transport. In addition, transmission electron microscopy (TEM) patterns (Figure 4) also prove the uniform morphology of the binary and ternary blend films.

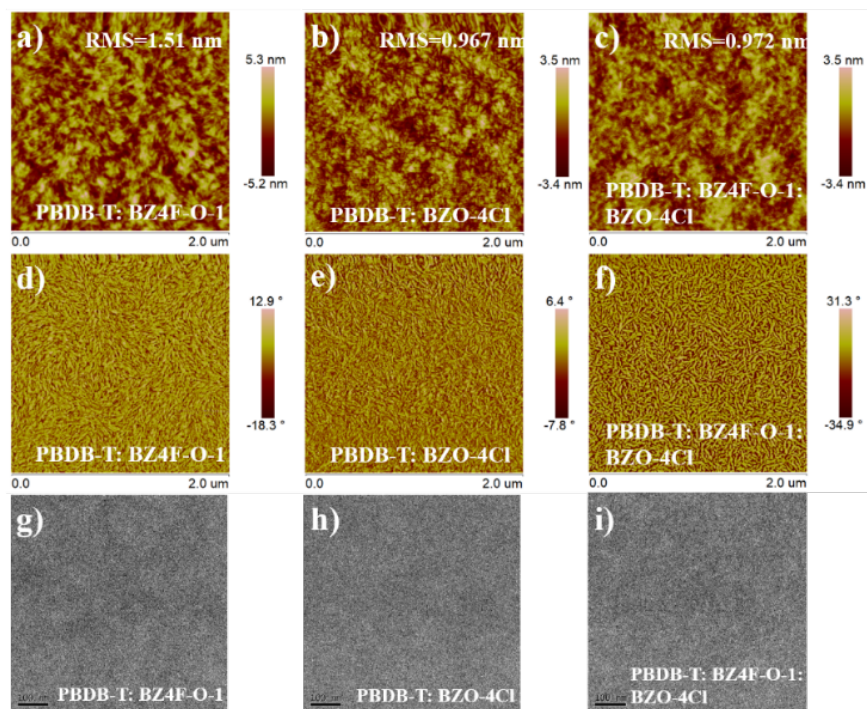


Figure 4. The AFM height images (2 $\mu\text{m} \times 2 \mu\text{m}$) of a) PBDB-T: BZ4F-O-1; b) PBDB-T: BZO-4Cl; c) PBDB-T: BZ4F-O-1: BZO-4Cl; The AFM phase images (2 $\mu\text{m} \times 2 \mu\text{m}$) of d) PBDB-T: BZ4F-O-1; e) PBDB-T: BZO-4Cl; f) PBDB-T: BZ4F-O-1: BZO-4Cl; The TEM images of g) PBDB-T: BZ4F-O-1; h) PBDB-T: BZO-4Cl; i) PBDB-T: BZ4F-O-1: BZO-4Cl

To further investigate the intermolecular stacking behavior of the neat and blend films, 2D-grazing incidence wide-angle X-ray scattering (GIWAXS) patterns and the corresponding 1D profiles are fully analyzed. As shown in Figures 5, S10 and Table S7, all the neat films of the acceptor materials show a strong (010) peak at $\sim 1.8 \text{ \AA}^{-1}$ in the out-of-plane (OOP) direction and (100) peak at $\sim 0.4 \text{ \AA}^{-1}$ in the in-plane (IP) direction, which indicates a predominant face-on orientation. The (010) peak is further studied to understand the π - π stacking properties. BZ4F-O-1 and BZO-4Cl show the π - π stacking distance (d -spacing) of 3.50 and 3.42 $\text{\AA}$ with the crystal coherence lengths (CCLs) of 22.5 and 27.0 $\text{\AA}$, respectively. BZO-4Cl presents a shorter d -spacing and longer CCL than that of BZ4F-O-1, thus a closer π - π stacking, which could be ascribed to the stronger intermolecular interaction. Compared with the neat films, the binary blends retain the favorable face-on orientation. PBDB-T: BZO-4Cl blend exhibits the closest d -spacing among the binary devices with the longest CCLs, which is favorable for charge transport and consistent with the higher J_{SC} . When BZ4F-O-1 is introduced into the PBDB-T: BZO-4Cl system, the d -spacing of the ternary blend is slightly increased and the CCL is meanwhile reduced, indicating the slightly reduced crystallinity. Combined with the suppressed recombination process and the improved charge transport (Figure 3), we can conclude that a proper (not that close) molecular π - π stacking is achieved in the ternary blends due to the introduction of BZ4F-O-1.

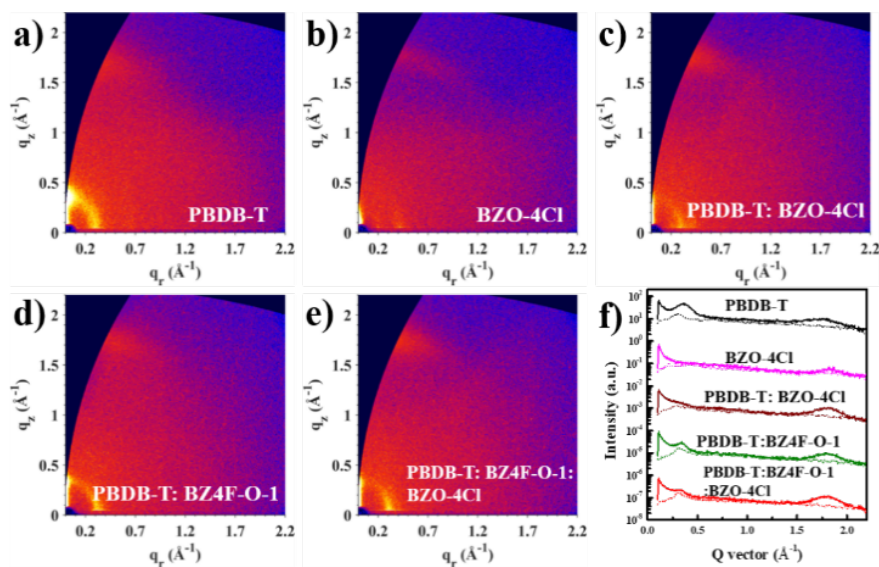


Figure 5. 2D-GIWAXS patterns of a) PBDB-T, b) BZO-4Cl, c) PBDB-T: BZO-4Cl, d) PBDB-T: BZ4F-O-1 and e) PBDB-T: BZ4F-O-1: BZO-4Cl films; f) In-plane (dashed) and out-of-plane (solid) GIWAXS curves of the corresponding 2D patterns.

Conclusions

In conclusion, we employ a synergetic alkoxy side-chain and chlorine-contained end group strategy for ultra-NBG heptacyclic SMAs. And two A-DA'D-A type ultra-NBG acceptors, BZO-4F and BZO-4Cl are designed and synthesized with the E_g^{opt} of 1.29 eV and 1.25 eV, respectively. By blending with the polymer donor PBDB-T, the BZO-4Cl-based device shows a moderate PCE of 12.48% with a J_{SC} of 26.86 mA cm^{-2} , which is slightly higher than that of the BZO-4F-based device. However, the photovoltaic performance is limited by the low V_{OC} and FF. BZ4F-O-1 with a high LUMO level and a complementary absorption is considered to be introduced into the PBDB-T: BZO-4Cl system to construct ternary OSCs. As well investigated, the ternary blend materials possess good miscibility. Besides, the recombination process of the ternary device is suppressed and the charge transport is significantly improved. Furthermore, the molecular π - π stacking is also subtly controlled, leading to an optimal blend morphology. Consequently, the PBDB-T: BZ4F-O-1: BZO-4Cl-based ternary device achieves a high PCE of 15.51% with the simultaneously increased V_{OC} (0.77 V), J_{SC} (27.85 mA cm^{-2}) and FF (0.71). This work highlights a molecular strategy of altering the oxygen position along the side chains and chlorine-substitution for ultra-NBG acceptor, which is a potential alternative in semi-transparent OSCs.

Experimental

Synthesis of BZO-4F and BZO-4Cl: Under argon, compound 9 (0.14 g, 0.12 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.11 g, 0.48 mmol) were dissolved in chloroform (30 mL). Pyridine (1.5 mL) was added. After stirring at 65 °C overnight, the mixture was cooled to room temperature, the solution was concentrated under reduced pressure, and poured into methanol and filtered. The residue was purified in a silica gel column using petroleum ether/dichloromethane (1:1, v/v) as the eluent. BZO-4F was obtained as a dark blue solid (135 mg, 70% yield). BZO-4Cl was synthesized by the same method of BZO-4F.

Device fabrication: The optimized photovoltaic devices were fabricated with a conventional structure of Glass/ITO/PEDOT: PSS/ PBDB-T: acceptor/PDINN/Ag. Pre-patterned ITO coated glass substrates (Advanced Election Technology Co., Ltd) were washed with deionized water and isopropyl alcohol in an ultrasonic bath for 15 minutes. After blow-drying by high-purity nitrogen, all ITO substrates are cleaned

in the ultraviolet ozone cleaning system for 20 minutes. Subsequently, a thin layer of PEDOT: PSS (Xi'an Polymer Light Technology Corp 4083) was deposited through spin-coating on pre-cleaned ITO-coated glass at 4500 rpm for 30 s and dried subsequently at 150°C for 15 minutes in atmospheric air. Then the photovoltaic layers were spin-coated in a glovebox from a solution of PBDB-T: acceptors (14.5mg/mL with 0.1vol% CN with the PBDB-T: acceptors weight ratios of 1:1.2, PBDB-T: BZ4F-O-1: BZO-4Cl = 1: 0.6: 0.6) in CF. The optimal active layers were fabricated by spin-coating at about 3000 rpm for the 30s. Then the blend films were treated with thermal annealing at 100 °C for 10 min. After cooling to room temperature, a PDINN layer via a solution concentration of 1 mg/mL was deposited at the top of the active layer at a rate of 3000 rpm for 30 s. Finally, the top Ag electrode of 100 nm thickness was thermally evaporated through a mask onto the cathode buffer layer under a vacuum of 1.5×10^{-4} Pa.

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.2021xxxxx>.

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Author contributions

Yingping Zou and Qingya Wei conceived the idea and designed the acceptors. Qingya Wei synthesized the acceptor materials and tested the molecular optoelectronic properties. Songting Liang fabricated the organic solar cells and characterized the photovoltaic parameters. Qingya Wei and Songting Liang tested the AFM and TEM. BeiBei Qiu helped the theoretical calculations. Xinhui Lu and Yuang Fu supported the GIWAXS. Qingya Wei wrote the original draft, and all the authors including Jun Yuan, Wei Liu and Xiang Xu contributed to the data analysis and manuscript revision. Yingping Zou directed this project.

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