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Alkyl-Chain Engineering and Synergistic Annealing Enable Enhanced Performance in Non-Fullerene Organic Solar Cells

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Abstract

Molecular design and synthesis of non-fullerene acceptors are critical for the advancement of organic solar cells (OSCs). In this study, a new series of acceptor - donor- acceptor (A - D - A)-type non-fullerene acceptors incorporating an oxindole-based π -bridge- denoted WH7, WH11, and WH17, each bearing distinct branched alkyl side chains- has been developed for bulk-heterojunction OSCs. These side-chain substituents enable fine tuning of the morphology of the corresponding polymer blends. In preliminary device optimisation, OSCs exhibited power conversion efficiencies (PCEs) of 5.83% for WH7 with an octylindoline side chain, 5.33% for WH11 with a (2-ethylhexyl)indoline side group, and 4.26% for WH17 with a butylindoline side group. Upon application of appropriate solvent vapour annealing (SVA), particularly SVA followed by thermal annealing (TA), the device performance was significantly enhanced. Notably, an optimised film morphology yielded a maximum PCE of 8.21% with a high fill factor (FF) of 0.65 for the non-fullerene acceptor WH7 bearing octyl side chains. By employing the space-charge limited current (SCLC) model to test charge transport and utilizing atomic force microscopy (AFM) to examine morphology, we determined that solvent treatment enhances performance through increased and more balanced charge transport, as well as the development of smoother, compact surface morphologies. These factors contribute to the enhancement of short-circuit current density (J_{sc}) and FF. This study provides a compelling example of how side-chain engineering can be used to adjust molecular packing, charge transport, and blend morphology of acceptors. Additionally, solvent treatment presents a straightforward and effective approach to improving the efficiency of OSCs.

Keywords

branched alkyl chain, non-fullerene acceptor, solvent vapor annealing, organic solar cells, side-chain engineering

1.Introduction

Bulk-heterojunction (BHJ) solar cells, formed from a blend of electron-donating π -conjugated polymers and electron-accepting organic semiconductors, have received enormous academic and industrial enthusiasm, because of promising advantages such as light weight, mechanical flexibility, and solution-processed production.^{1,2} The efficiency of OSCs has now been enhanced by more than 20% through fundamental understanding, new materials synthesis, and device architecture innovation.³⁻⁶ For p-type semiconductors, conjugated polymers have been well developed and played a key role in the PSC

applications for many years.^{7,8} To improve the photovoltaic performance of OSCs, a variety of n-type semiconductors with different fused-ring structures have been designed and synthesized.^{9,10} Typically, fused-ring nonfullerene molecular acceptors consist of a central core, two terminal acceptor units, and side chains.^{11,12} In general, the backbone units have a big influence on the optical and electrical properties of non-fullerene molecular acceptors.^{13,14}

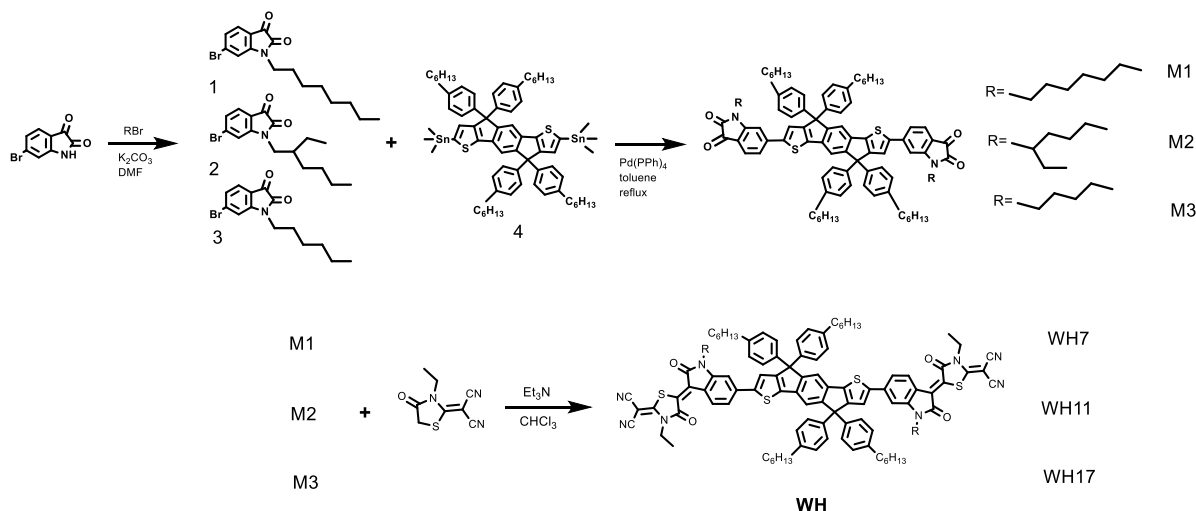
Side-chain engineering is another effective way to tune the energy levels of the acceptors and the morphology of their blend active layers for improving their photovoltaic performance.^{15,16} For example, by introducing branched alkyl chains at the β -position of thiophene moieties on a Y6-based dithienothiophen[3,2-b]-pyrrolobenzothiadiazole core, Li et al. developed a series of high-performance non-fullerene acceptors.¹⁷ This side-chain modification modulates molecular packing behavior, enhances structural order and charge transport in thin films, and delivers a PCE of 18.32% for single-junction organic solar cells. Similarly, Fei et al. modified the side chains of ITIC with alkyl groups to synthesize C8-ITIC. C8-ITIC exhibits a reduction in the optical band gap, higher absorptivity, and an increased propensity to crystallize, and the corresponding PBDB-T-based blend films achieve a high PCE of 12.4%.¹⁸ In addition, Yao et al. replaced the 2-ethylhexyl groups on the π -bridge of IEIC with alkoxy side chains to synthesize IEICO.¹⁹ IEICO possesses a substantially narrower optical band gap of 1.34 eV and exhibits strengthened molecular packing. As a result, IEICO-based devices deliver an improved PCE of 8.4% with higher J_{sc} and FF compared to IEIC-based counterparts. However, most side-chain engineering efforts have focused on the side chains attached to the central core, while little attention has been devoted to the side chains on the terminal groups.

Herein, we design and synthesize three small-molecule acceptors, WH7, WH11, and WH17, by introducing different branched alkyl side chains onto the terminal indoline units (octylindoline for WH7, (2-ethylhexyl) indoline for WH11, and butylindoline for WH17). These acceptors exhibit strong absorption in the range of 500 – 750 nm, enabling good complementary absorption with the PTzBI donor. When blended with PTzBI, the WH7:PTzBI, WH11:PTzBI, and WH17:PTzBI devices deliver relatively low PCEs of 6.64%, 6.21%, and 5.53%, respectively, primarily due to excessive phase separation. Remarkably, after chlorobenzene (CB) solvent vapor annealing, the device efficiencies are significantly enhanced, particularly for the WH7-based OSC, which achieves a PCE of 8.21%. Compared with CB-treated WH11:PTzBI device, the increased PCE in WH7:PTzBI could be attributed to the higher/more balanced charge transport, lower carrier recombination and improved morphology. This work highlights the significance of side-chain engineering and post-treatment for realizing high photovoltaic performance. Notably, the side chains anchored on terminal groups cannot be overlooked.

2. Materials And Methods

All reagents and materials were used as received without further purification, unless otherwise specified. Chlorobenzene, chloroform, acetone (analytical grade) and isopropanol (analytical grade) were purchased from Guangzhou Reagent Group. Molybdenum trioxide (MoO_3) was obtained from Sigma-Aldrich. Calcium (Ca) was supplied by Zhongnuo New Materials. PEDOT:PSS (Clevios-4083) was purchased from Hanfeng Group (Shanghai). ITO-coated glass substrates were provided by China Southern Glass Holding Group (Shenzhen). PFN-Br was synthesized and purified in our laboratory.

The device fabrication procedure was as follows: indium tin oxide (ITO) glass substrates were ultrasonically cleaned in deionized water and isopropanol for 30 min each, followed by plasma treatment of the ITO glass for 4 min. A PEDOT:PSS (CLEVIOS PVP AL 4083, 1.0 mg mL^{-1}) layer was then spin-coated onto the ITO at 3500 rpm for 30 s. The ITO glass was subsequently heated on a hot plate at 150°C for 15 min and then cooled to room temperature for later use. The polymer donor PTzBI and the non-fullerene acceptor WH were dissolved in chlorobenzene; after stirring the blend solution in a glovebox at 50°C until homogeneous, it was spin-coated onto the ITO glass. The resulting blend film, with a thickness of about 100 nm, was subjected to solvent vapor annealing in a glass Petri dish for 30 s, followed by thermal annealing on a hot plate at 120°C for 10 min. Finally, PFN-Br was spin-coated onto the blend film, and an approximately 100 nm thick silver layer was thermally evaporated onto the PFN-Br under a vacuum of 1×10^{-6} mbar.



Scheme 1. Synthetic Routes of WH7, WH11 and WH17

The synthetic routes of the three A-D-A acceptor WH7, WH11, and WH17 are depicted in Scheme 1, and their chemical structures are shown in Figure 1A. These three acceptors bear three distinct alkyl chains on the oxindole-based bridge. The detailed synthetic procedures are described in the Supporting Information. The center core intermediate 4 was prepared following a previously reported procedure.²⁰ Subsequently, 4 was subjected to Stille coupling with the bifunctional intermediates derived from bridge precursors 1, 2, and 3, yielding the corresponding intermediates M1, M2, and M3. These intermediates were then condensed with the 2-(3-ethyl-4-oxothiazolidin-2-ylidene) malononitrile terminal group to afford the target acceptor molecules.

The absorption spectra and electronic energy levels were analysed to preliminarily assess the influence of different substituents on the semiconductor properties of the acceptors. Figure 1B shows the UV-vis absorption spectra of WH7, WH11, and WH17 in solution. In dilute chlorobenzene, WH7 exhibits an absorption peak at 425 nm, assigned to the $\pi-\pi^*$ transition, and a peak at 655 nm, attributed to intramolecular charge transfer (ICT) from the central IDT donor unit to the two terminal acceptor units.^{20,21} For WH11, the $\pi-\pi^*$ transition peak locates at 425 nm while the ICT peak locates at 653 nm. All three acceptors display similar absorption profiles from 350 to 750 nm, with a principal absorption band around 650 nm and a weak shoulder at ≈ 425 nm. The absorption onsets of WH7, WH11, and WH17 are 752, 748, and 751 nm, respectively, corresponding to optical bandgaps of 1.64, 1.66, and 1.65 eV. Given that PTzBI is a typical wide-bandgap donor with a broad absorption range from 400 to 685 nm,²² these three acceptors are expected to afford a broader overall absorption window through complementary absorption with PTzBI.

The electronic energy levels of the acceptors are also critical parameters for their use in OSCs. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the acceptors were determined by cyclic voltammetry (CV) using Ag/AgCl as the reference electrode.²³ The cyclic voltammograms of the three acceptors are shown in Figure S1. The HOMO/LUMO energy levels ($E_{HOMO/LUMO}$) were calculated from the onset oxidation/reduction potentials according to $E_{HOMO/LUMO} = -e(E_{ox/red} + 4.35)$ eV,²⁴ where the redox potential of the ferrocene/ferrocenium (Fc/Fc⁺) couple is 0.45 V vs Ag/AgCl, and the energy level of Fc/Fc⁺ is taken as 4.8 eV under vacuum. The resulting $E_{HOMO/LUMO}$ values for WH7, WH11, and WH17 are -5.44/-3.99 eV, -5.46/-3.97 eV, and -5.42/-4.00 eV, respectively.

As shown in Figure 1C and Table 1, the $E_{HOMO/LUMO}$ levels of WH17 are -5.42/-4.00 eV, which exhibit the highest HOMO and lowest LUMO among three acceptors. The slightly upshifted E_{LUMO} of WH7 could be ascribed to the moderate steric hindrance of n-octyl side chains, which weakens intermolecular $\pi-\pi$ stacking and intramolecular charge transfer (ICT), thus lifting the LUMO energy level. As for the further upshifted E_{LUMO} and downshifted E_{HOMO} of WH11, we believe that the largest steric hindrance of branched

2-ethylhexyl side chains severely twists the dihedral angle between the central IDT core and terminal units, further suppressing ICT and intermolecular stacking. Such conformational distortion shortens the π -electron delocalization length on the IDT backbone, stabilizes the occupied HOMO orbital to a more negative value, and eliminates the electronic stabilization of LUMO simultaneously, resulting in the lowest E_{HOMO} (-5.46 eV) and highest E_{LUMO} (-3.97 eV) of WH11. The steric effect of N-alkyl substituents dominates intramolecular conjugation and intermolecular packing, triggering divergent shifts of HOMO and LUMO energy levels, which is consistent with the previously reported.²⁵

The $E_{\text{HOMO/LUMO}}$ levels of the PTzBI donor is located at -5.34/ -3.46 eV, respectively.²² The LUMO energy offset (ΔE_{LUMO}) between the three acceptors and PTzBI donor is 0.53, 0.51, and 0.54 eV for WH7, WH11, and WH17, respectively, and the HOMO energy offset (ΔE_{HOMO}) between the three acceptors and PTzBI donor is 0.1, 0.12, and 0.08 eV for WH7, WH11, and WH17, respectively. The acceptors afford rational level gradients with the donor PTzBI and could generate sufficient driving force for the photoexciton dissociation inside the BHJ.

In addition, the thermogravimetric analysis (TGA) curves of the three acceptors WH7, WH11, and WH17 are presented in Figure S2 of the Supporting Information, and their thermal decomposition temperatures (T_d , defined at 5% weight loss) are 379, 367, and 384 °C, respectively (see Table 1), indicating sufficient thermal stability for practical application in OSCs.

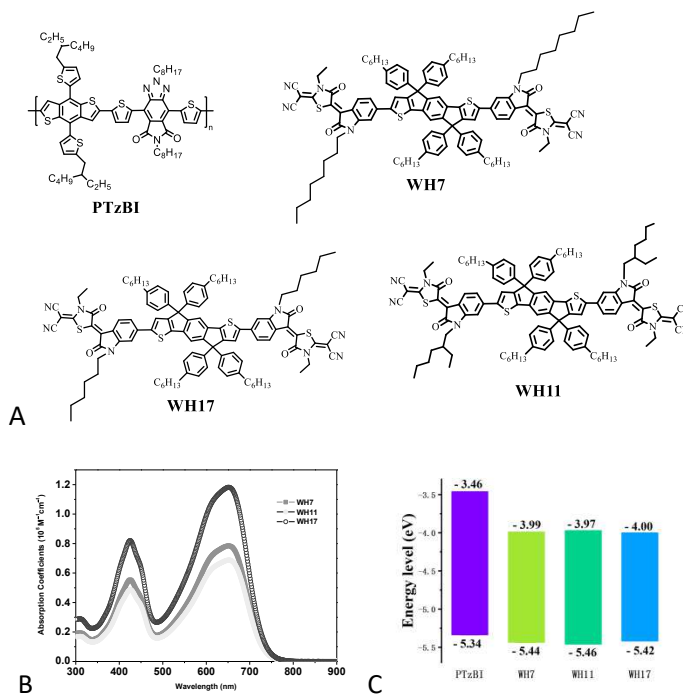


Figure 1. (A) Chemical structures of PTzBI and Non-Fullerene acceptors. (B) Absorption spectra of WH7, WH11 and WH17 in chlorobenzene form solutions. (C) Diagram of the HOMO and LUMO energy levels of PTzBI donor and Non-Fullerene acceptors.

Table 1. Physicochemical properties of WH7, WH11, and WH17.

acceptor	$\lambda_{\text{max}}^{\text{sol}}$ [nm]	$\lambda_{\text{onset}}^{\text{sol}}$ [nm]	$E_{\text{g}}^{\text{opt}}$ [eV] ^a	LUMO ^{CV} [eV]	HOMO ^{CV} [eV]	E_{g}^{CV} [eV]	T_d [°C]
WH7	655	752	1.64	-3.99	-5.44	1.45	379
WH11	653	748	1.66	-3.97	-5.46	1.49	367

WH17 ^b	650	751	1.65	-4.00	-5.42	1.42	384
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^a) Calculated from $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$.

The OSCs devices are fabricated with a conventional configuration of indium-tin-oxide (ITO) poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/ active layer (PTzBI:WH7, PTzBI:WH11 or PTzBI:WH17)/ poly(9,9-bis(3' -(N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene) dibromide) (PFN-Br)/ Ag (device area= 0.04 cm²) to investigate the influence of side-chain engineering on the photovoltaic properties. The optimized device conditions are described in the Supplementary Information (Figure S12, Table S1). Table 2 and Figure 2A show the optimal photovoltaic performances and current density-voltage (J-V) characteristics, respectively.

For the optimised OSC based on WH7 with an octylindoline side chain, a PCE of 8.21% is achieved, together with a V_{oc} of 0.79 V, a J_{sc} of 16.04 mA cm⁻², and a FF of 64.78%. The OSC employing WH11 with a (2-ethylhexyl)indoline alkyl chain exhibits a PCE of 7.16%, with a V_{oc} of 0.801 V, a J_{sc} of 16.15 mA cm⁻², and a FF of 55.31%. For the butylindoline-substituted WH17-based device, a PCE of 6.45% is obtained, accompanied by a V_{oc} of 0.766 V, a J_{sc} of 15.59 mA cm⁻², and a FF of 54.08%. These results demonstrate that variation in the terminal side chain exerts a pronounced influence on the photovoltaic performance of the acceptor materials, with the acceptor bearing the octylindoline side chain delivering superior device performance relative to those incorporating (2-ethylhexyl)indoline or butylindoline side chains.

Relative to the photovoltaic performance of devices without solvent vapour annealing, the enhanced PCE of the PTzBI:WH11-based devices after solvent vapour annealing arises primarily from the increased FF (see Figure S12A and Table 2). Following solvent vapour annealing, the FF of the WH11-based OSC increases from 51.71% to 56.01%, which can be attributed to improved molecular packing. For the PTzBI:WH17 device subjected only to thermal annealing, a relatively low PCE of 5.53% is obtained; this value increases to 6.03%, with a V_{oc} of 0.76 V, a J_{sc} of 15.19 mA cm⁻², and a FF of 52.01%, after CB-based solvent vapour annealing. This improvement is ascribed to the ability of CB to diffuse into the active layer during volatilization, thereby optimizing blend-film morphology and molecular stacking through blend reorganization. Interestingly, for the WH7-based OSC, the enhanced PCE after solvent vapour annealing results from increases in both FF and J_{sc} , with FF rising from 55.57% to 63.28% and J_{sc} increasing from 15.39 to 16.00 mA cm⁻². The higher FF is likely associated with improved active-layer morphology, whereas the increased J_{sc} can be attributed to reduced charge recombination in the solvent vapour-annealed blend film due to its more favourable morphology.

Table 2. The photovoltaic performances of PTzBI:WH7, PTzBI:WH11, and PTzBI:WH17 solar cells with ratio of 1:1.5. All data were obtained under illumination of AM 1.5G (100 mW cm⁻²) light source.

D:A	Conditions	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%) ^a	PCE _{max} (%)	J_{sc} (mA/cm ²) ^b
PTzBI:WH7	TA	0.78	15.39	55.57	6.64	6.99	15.2
PTzBI:WH7	SVA+TA	0.79	16.00	63.28	8.02	8.21	15.5
PTzBI:WH11	TA	0.79	15.27	51.71	6.21	6.52	14.5
PTzBI:WH11	SVA+TA	0.80	15.39	56.01	6.85	7.16	15.2
PTzBI:WH17	TA	0.76	14.46	50.44	5.53	5.85	15.0

PTzBI:WH17	SVA+TA	0.76	15.19	52.01	6.03	6.45	14.7
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^a Statistical data obtained over 10 devices;

^b The J_{sc} calculated from external quantum efficiency (EQE) curves.

The external quantum efficiency (EQE) spectra of the corresponding devices are presented in Figure S3A. The close similarity of the EQE spectra for the three devices indicates that both the PTzBI donor and the WH acceptor contribute to the photocurrent. In comparison with the EQE spectra of the WH11- and WH17-based devices, the EQE spectrum of the WH7-based OSC exhibits an enhanced photoresponse in the 450–650 nm region, leading to a higher J_{sc} in its photovoltaic performance. As shown in Figure S3B, the SVA-optimised devices display almost identical spectral ranges of photocurrent response from 300 to 850 nm, while the response intensity differs markedly. In particular, the SVA-treated WH7- and WH11-based devices show higher EQE response intensities than their corresponding as-cast counterparts in the range of 450–650 nm, demonstrating that CB treatment effectively promotes charge generation and transport in the active layer and consequently yields a substantially higher J_{sc} . The J_{sc} values of the PTzBI:WH7, PTzBI:WH11 and PTzBI:WH17 devices under CB annealing conditions integrated from the EQE spectra are 15.5 mA cm^{-2} , 15.2 mA cm^{-2} and 14.7 mA cm^{-2} , respectively, which are consistent well with the current densities acquired from J–V curves (within 5% error). Figure 2(B) shows the EQE curve corresponding to the maximum efficiency of the solar cell under optimal optimization conditions. The maximum EQE response intensity of CB-treated PTzBI:WH7 device is 72.93%, a bit higher than that (69.07%) generated from CB-treated PTzBI:WH11 device. The reported PTzBI is a donor with a medium bandgap. The EQE of the PTzBI:WH7 solar cell is > 40% in the range of 325–375 nm. In contrast, the EQE of the PTzBI:WH11 solar cell is < 35% in this range. The PTzBI:WH7 solar cell has a higher photoelectric conversion efficiency than the PTzBI:WH11 solar cell, which confirms the effect of different side chains on the photoelectric performance of the material-based BHJ solar cell. This may be attributed to the better molecular packing between PTzBI and WH7.

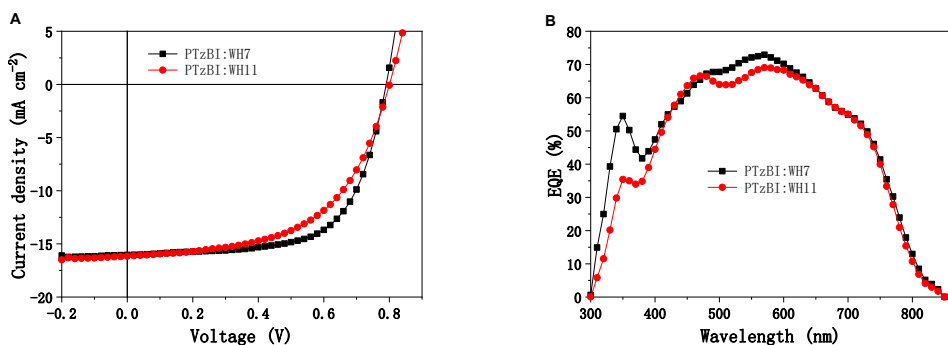


Figure 2. (A) J-V characteristics of the optimized OSCs based on the PTzBI and Non-Fullerene acceptors, under the illumination of AM1.5G, 100 mW/cm². (B) EQE spectra of the corresponding devices.

To better understand exciton dissociation and charge collection processes, the photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) was plotted, as shown in Figure S4A. The J_{ph} is defined as the difference between J_L and J_D ($J_{ph} = J_L - J_D$), where J_L and J_D are the current densities under illumination and in the dark, respectively. The effective voltage is given by $V_{eff} = V_0 - V_{bias}$, where V_0 is the voltage at which $J_{ph} = 0$ and V_{bias} is the applied bias voltage.²⁶ At high V_{eff} (greater than 2 V), all photogenerated electron–hole pairs are assumed to dissociate into free carriers and be efficiently collected at the electrodes, such that J_{ph} reaches a saturated value (J_{sat}). In this regime, the ratio J_{ph}/J_{sat} is positively correlated with the charge dissociation probability $P(E, T)$. It should be noted that

P(E,T) is discussed only for the CB-treated devices. Likewise, charge transport, recombination, and extraction behaviors are compared exclusively for CB-processed PTzBI:WH7 and PTzBI:WH11 devices. The J_{ph}/J_{sat} ratio for the PSCs based on PTzBI:WH7 and PTzBI:WH11 are calculated to be 0.962 and 0.939 under short-circuit conditions. The results show that the devices based on octylindoline-substituted WH7 hold higher efficiencies of the photogenerated exciton dissociation and charge collection than that based on (2-ethylhexyl) indoline alkyl-substituted WH11.

To explore the charge transport properties, the space charge limited current (SCLC) method is carried out to estimate both the hole and electron mobilities.²⁷ From Table 2, it is evident that strongly unbalanced charge transport occurs in PTzBI:WH11-based devices, with hole (μ_h) and electron (μ_e) mobilities of 2.40×10^{-4} and $3.30 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The poor electron mobility can be primarily attributed to the limited crystallinity of WH11, and the pronounced imbalance between μ_h and μ_e is expected to aggravate charge recombination within the device. By contrast, PTzBI:WH7-based OSCs exhibit not only higher μ_h/μ_e values of $1.74 \times 10^{-4}/4.03 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ but also more balanced charge transport, which can partially account for the enhanced J_{sc} and FF. Furthermore, PTzBI:WH11-based OSCs subjected to SVA were also characterized. The device treated with SVA displays high and relatively balanced charge transport, with μ_h/μ_e of $1.28 \times 10^{-4}/1.58 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, consistent with its improved FF. Encouragingly, both hole and electron mobilities in the PTzBI:WH7-based device were further enhanced simultaneously after SVA treatment. The μ_h/μ_e reached $3.49 \times 10^{-4}/1.75 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an outstanding μ_e/μ_h value, thus resulting in the most competitive J_{sc} and FF as well as PCEs between the two OSCs.

Table 2. The electron mobility μ_e and hole mobility μ_h of the corresponding devices.

PTzBI:Acceptor	Conditions	$\mu_h (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$	$\mu_e (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$	μ_h / μ_e
WH7	TA	1.74E-04	4.03E-07	432
WH7	SVA+TA	3.49E-04	1.75E-05	20
WH11	TA	2.40E-04	3.30E-07	727
WH11	SVA+TA	1.28E-04	1.58E-06	81

To gain deeper insight into the influence of the acceptor on photovoltaic performance, we measured the J_{sc} as a function of light intensity (P_{light}) to evaluate the charge recombination behaviour, as shown in Figure 3A. Charge recombination is a critical factor that can strongly affect both J_{sc} and the FF. In general, the relationship between J_{sc} and P_{light} follows $J_{sc} \propto P_{light}^\alpha$; ²⁸ when all photogenerated carriers are efficiently extracted at the electrodes and bimolecular recombination is negligible, the exponent α approaches 1. ²⁹ In our study, the α values for PTzBI:WH7- and PTzBI:WH11-based devices subjected to solvent vapour annealing (SVA) are 0.99 and 0.97, respectively. The higher α value, closer to unity, observed for the PTzBI:WH7-based device indicates weaker bimolecular recombination within its active layer. The relatively low bimolecular recombination losses observed in the optimized devices motivated us to examine another crucial recombination pathway, namely trap-assisted Shockley–Read–Hall (SRH) recombination. Trap-assisted SRH recombination can be evaluated from the dependence of the V_{oc} on the incident light intensity (P_{light}), which follows the relationship $V_{oc} \propto (nkT/q) \ln P_{light}$, where k , T , and q denote the Boltzmann constant, the absolute temperature, and the elementary charge, respectively. ³⁰ The slope of the V_{oc} versus $\ln P_{light}$ plot yields nkT/q , reflecting the competition between bimolecular and trap-assisted recombination. A slope approaching kT/q indicates that bimolecular recombination dominates under open-circuit conditions, whereas a slope close to $2kT/q$ suggests that trap-assisted recombination

is the predominant loss mechanism in the device. As shown in Figure 2B, for devices based on PTzBI:WH7 and PTzBI:WH11, the slopes of the fitted line of V_{oc} vs $\ln P_{light}$ are $1.45kT/q$ and $1.38kT/q$, respectively. It suggests that both bimolecular and trap assisted recombination happen in both devices at open circuit, the bimolecular recombination is the major in PTzBI:WH11 and PTzBI:WH7. Therefore, the J_{sc} and FF of PTzBI:WH7 are better, while the V_{oc} is smaller.

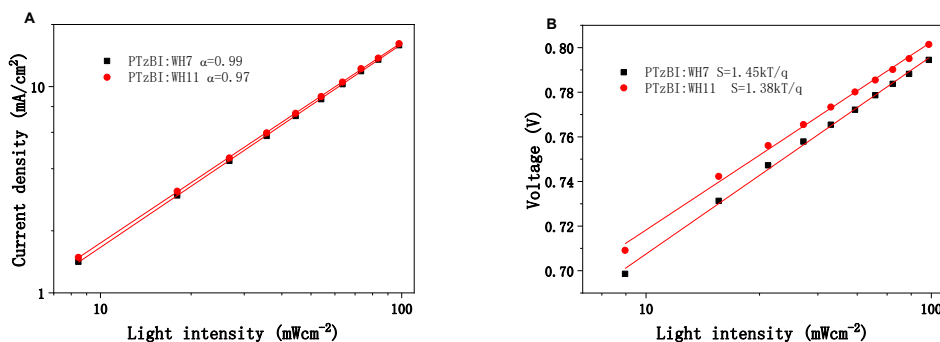


Figure 3. (A) Light intensity dependence of J_{sc} . (B) Light intensity dependence of V_{oc} of the corresponding devices.

Given that the morphology of the photoactive layer plays a critical role in determining the photovoltaic performance of PSCs, we directly investigated the surface morphology of the active layers with and without solvent exposure by tapping-mode atomic force microscopy (AFM). The corresponding AFM topography images are presented in Figure 4 and Figure S5 in the Supporting Information. As shown in Figure 4, the root-mean-square (RMS) roughness values are 2.86 and 5.26 nm for the solvent-vapour-annealed active layers of OSCs based on PTzBI:WH7 and PTzBI:WH11, respectively. In contrast, the AFM images of the blend films based on WH7 and WH11 without solvent-vapour treatment exhibit RMS roughness values of 3.1 and 6.9 nm, respectively. It implied that SVA can actually induce the reorganization of donor and acceptor. Although the 2-ethylhexyl group of WH11 is more sensitive to solvents than the octyl group of WH7, and the RMS is reduced by about 1.6 nm, the phase separation degree of the octyl group of WH7 based on the polymer donor is more reasonable. The phase diagram further reveals more information about uniformity and probe-surface interactions. We note that although both the PTzBI:WH7 film after SVA and the PTzBI:WH11 film after SVA are relatively smooth, the aggregates of the PTzBI:WH11 film are larger than those of the PTzBI:WH7 film. This discrepancy is most likely caused by the distinct dispersion degrees or molecular stacking modes of the branched C8 and linear C8 alkyl chains in the blend films. These results further confirm the origin of the enhanced J_{sc} and FF in the optimized WH7-based device.

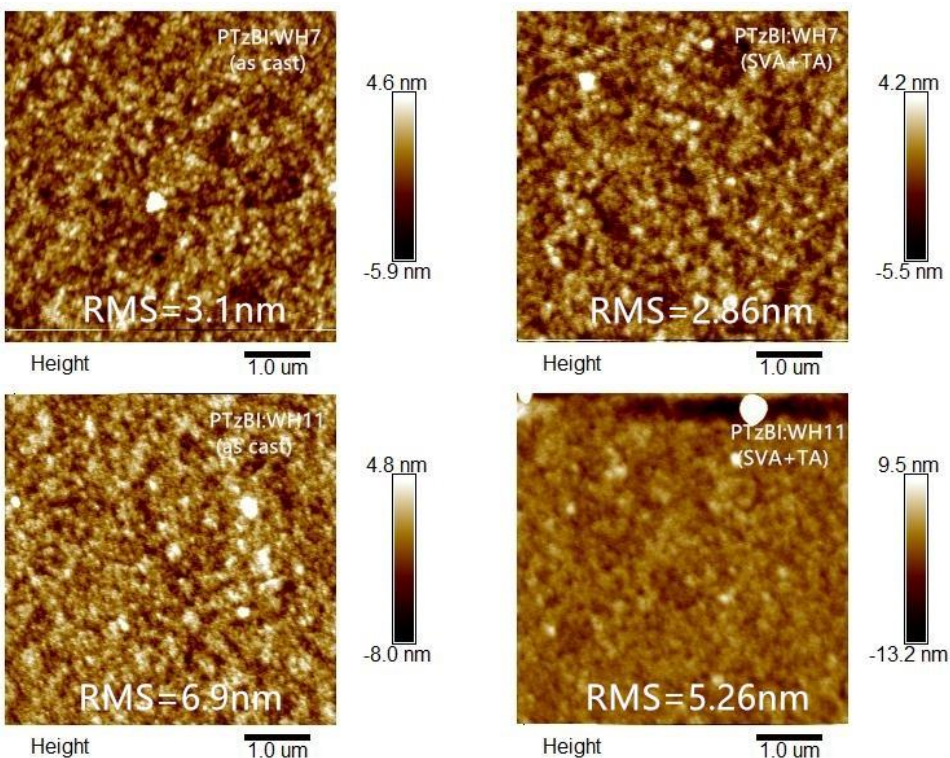


Figure 4. AFM height images of (A) PTzBI:WH7 (TA) , (B)PTzBI:WH7 (SVA+TA), (C) PTzBI:WH11 (TA) and (D)PTzBI:WH11 (SVA+TA);

4. Conclusion

In summary, We explored the alkyl side chain modification to rationally modulate the property of SMAs. Specifically, The change of chain-length on the terminal groups provided important parameters to tune energy levels, charge transport, and the morphology of the blended, which had significant impact on the device performance. The optimal PTzBI:WH7-based device delivered a FF of 56.33% and a high PCE of 6.99%, surpassing the best OSCs employing WH11 (6.52%) and WH17 (5.85%). Following solvent vapour annealing, the J_{sc} and FF of the OSCs were further slightly enhanced. The champion device achieved a state-of-the-art PCE of 8.21%, with a V_{oc} of 0.79 V, a J_{sc} of 16.04 mA cm⁻², and an excellent FF of 64.78%. Distinct from the many studies that mainly concentrate on tuning the side chains attached to the central core of SMAs, this work offers a new perspective on side-chain modulation by targeting the terminal groups of SMAs, which has largely been overlooked. This strategy provides an effective approach for regulating the morphology of SMAs. Thus, we anticipate that further efficiency gains can be realised through rational design of SMA side chains and careful matching with donor materials.

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315 **Author Contributions**

316 K. W. proposed the research and directed the study. J. H. and B. Z. synthesized and characterized the
317 acceptor materials. K. W. and J. H. helped with the device fabrication and characterization. K. W. prepared
318 the manuscript. All authors discussed the results and commented on the manuscript.

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321 **Declaration Of Interests**

322 The authors declare no competing interests.

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