

15.51 % efficiency all-small-molecule organic solar cells achieved by symmetric thiazolyl substitution

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ABSTRACT

Two new small molecule donors of SW1 and SW2 are designed and synthesized by employing thiophene and thiazole substituents as the side groups of benzo[1,2-b:4,5-b']dithiophene central unit, respectively. Due to the more electron-withdrawing feature and enhanced intermolecular stacking of SW2 with respect to that of SW1, the all-small-molecule (ASM) organic solar cells (OSCs) based on SW2 afford a much better power conversion efficiency up to 15.51 %, along with both enlarged open-circuit voltage and fill factor. Further systematic investigation demonstrates that thiazole could act as an excellent building block to optimize the energy levels, molecular stacking as well as microscopic morphologies in ASM systems, leading to the highly efficient ASM-OSCs.

1. Introduction

Organic solar cells (OSCs) have attracted extensive attentions owing to their great advantages of high-throughput fabrication, flexibility and lightweight in the past decades [1–14]. The power conversion efficiencies (PCEs) have been brilliantly improved through both the design of light-harvesting materials [15–22] and device engineering [23–27]. Among them, the wise exploration of light-harvesting materials, including both the electron donors and acceptors, plays a dominant role in enhancing light absorption, controlling film morphology, and thus improving the PCEs of OSCs. Compared to the traditional electron acceptor of fullerene derivatives, non-fullerene acceptors (NFAs) overcome the fatal shortcomings of fullerene such as weak absorption in the visible region and non-tunable energy levels [21,22,28–34]. Up to now, the super-star NFA of Y6 based OSCs have achieved the remarkable PCEs approaching 19 % for single-junction [35] and over 20 % for tandem devices [36], exhibiting the huge potential for commercial applications in near future. In the current high-performance OSCs, the conjugated polymers have been widely employed as the donor parts in the donor/acceptor (D/A) blended films to reach the landmark PCEs. However, the application of polymer materials is significantly limited by

their intrinsic features of dispersive molecular weights and poor reproducibility, thereby leaving several great challenges for large-scale production of OSCs based on polymers. In another way, small molecule donors with well-defined structures could overcome the shortcomings of polymers and have emerged as the promising candidates for industrial production of OSCs.

Thus far, a great progress has been achieved by all-small-molecule (ASM) OSCs [37–43]. For instance, Ge's group has used BT-2F as the donor and N3 as the acceptor to achieve a good PCE of 15.39 % [43]. Lu's group prepared an ASM-OSC with 15.8 % PCE by employing L2 as small molecule donor [38]. Hou's group has achieved an efficient OSCs with 15.3% PCE by using a small molecule donor B1 [44], recently the PCE of B1 based OSCs further reached 17% benefitting from the elaborate devices engineering [39]. However, there is still a huge PCE gap between ASM based and polymer based OSCs, thus leaving a great space for further PCE improvement of ASM-OSCs.

Among the numerous small molecule donors, the benzo[1,2-b:4,5-b']dithiophene (BDT) unit has been widely used as the main building block in nearly all the high-performance systems because of its symmetric and planar conjugated structure [45,46]. In addition, the 4,8-positions of BDT unit could be conveniently functionalized with diverse side-groups

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to tune the electronic property and molecular geometries, thus affording lots of small molecule donors with different energy levels and intermolecular packing behaviors, such as DR3TSBDT [47], DR3TDOBBDT [48], PBDB-T-SF [49], BP-4F [50], DPP-E-BDT-T [51] and so on. When blending with the state-of-the-art NFA of Y6, the greatly upward highest occupied molecular orbital (HOMO) energy levels of above-mentioned small molecule donors with respect to that of Y6 will result in an extensive thermodynamic redundancy and thus limit the theoretical open-circuit voltage (V_{OC}) of resulting OSCs. Bearing this in mind, downshifting the HOMOs of small molecule donors to better match with Y6 should be an effective approach to achieve a higher V_{OC} in theory. Moreover, the small energy offset of HOMOs between small molecule donors and Y6 acceptors may give rise to the efficient hybridization between charge transfer states and local exciton states at the D/A interface, thus suppress the non-radiative recombination and further improve PCEs of OSCs [52]. Among all the efforts to downshift the HOMOs of small molecule donors by chemically structural optimizations, replacing or modifying the electron-rich thiophene side groups on 4,8-positions of BDT unit has been verified as a feasible strategy [38,44, 53–55].

Thiazole is an electron-deficient heterocycle comparing to thiophene because of its typical imine ($C=N$) structure. Thereby, replacement of thiophene side group on 4,8-positions of BDT unit by thiazole will downshifts the HOMO energy levels of small molecule donors successfully and is expected to contribute to an enlarged V_{OC} for OSCs based on thiazole containing donors theoretically. Moreover, due to the highly similar backbones of thiophene and thiazole, almost the same geometries could be maintained for small molecule donors, which should be conducive to keeping the favorable molecular stacking models on the basis of high-performance systems. Although the great merits of thiazole have been expected, the lack of systematic study renders the effect of thiazole substitution still unclear in small molecule donor. Herein, we

designed and synthesized two small molecule donors of SW1 and SW2 with BDT as central donor core, alkyl chain substituted terthiophene as π bridge and 3-(2-ethylhexyl)-rhodanine as electron withdrawing terminals. The only difference of SW1 and SW2 focuses on the conjugated side groups on BDT, where SW1 possesses the alkyl-substituted thiophenes and SW2 has the 3-thiazole with the same substituent (Fig. 1a). Due to the relatively electron-withdrawing feature of thiazole, SW2 possesses the down-shifted HOMO compared with that of SW1, resulting in a higher V_{OC} for ASM-OSCs with SW2:Y6 blend as the active layer. Finally, a much better PCE of 15.51 % has been achieved by SW2:Y6 based device with respect to that of 12.90 % for SW1:Y6 based one, demonstrating thiazole as the excellent building block to optimize the energy levels, molecular stacking as well as microscopic morphologies in ASM systems.

2. Results and discussion

2.1. Synthesis and Characterizations

The chemical structures of SW1 and SW2 are shown in Fig. 1a and the detailed synthesis routes are presented in the Supporting Information (SI). Both SW1 and SW2 possess the good solubility in chloroform (CF) and chlorobenzene (CB), in favor of the solution processing during the following device fabrication. In order to investigate the optimal molecular geometries of SW1 and SW2, we carried out the density functional theory (DFT) calculations at the B3LYP/6–31 G* level. As illustrated in Fig. 1b, both SW1 and SW2 have the relatively planar skeletons with the dihedral angles between the BDT central core and the thienyl/thiazyl substituent as 54.75° and 55.84°, respectively, indicating the well-maintained configurations after thiazole substitution. Then, the electrochemical cyclic voltammetry (CV) was employed to discover the change of HOMO energy levels for SW1 and SW2 (Fig. S1).

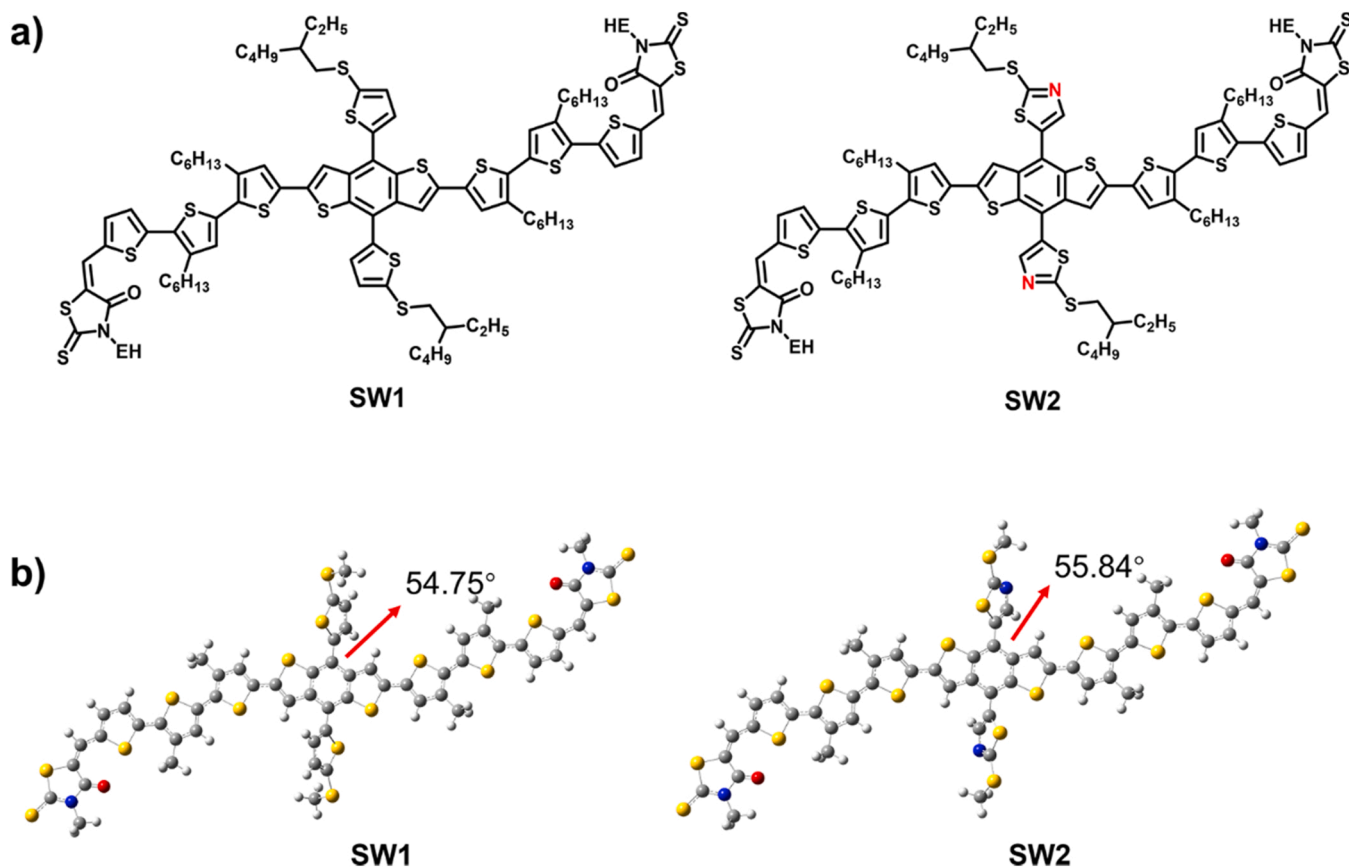


Fig. 1. a) Chemical structures of small molecule donors of SW1 and SW2. b) Optimized molecular geometries of SW1 and SW2 obtained from DFT calculations.

As shown in Fig. 2d and Table 1, the HOMO and LUMO energy levels of SW1 and SW2 are calculated to be -5.42 eV/ -3.43 eV and -5.47 eV/ -3.45 eV, respectively. These results are well consistent with the HOMO/LUMO of SW1 (-5.02 / -2.85 eV) and SW2 (-5.04 / -2.84 eV) derived from DFT calculations (Fig. S2). As it can be expected, SW2 with thiazole substitution affords a deeper HOMO energy level than that of SW1 with thiophene substitution. The downshifted HOMO of SW2 could lead to a larger V_{OC} of OSCs when blending with the same NFA of Y6 as we discussed above. Thereafter, the UV-vis absorption spectra of SW1 and SW2 in solutions and thin film states were recorded in Fig. 2a and b, demonstrating that the light-harvesting ability can be greatly affected by the substitution of thiazole. With the thiazole introduction, the absorptions in both solution and film of SW2 blue-shifted by ~ 10 nm in comparison with that of SW1. In addition, the onset absorptions of SW1 and SW2 can be estimated as 689 and 684 nm, respectively, corresponding to the optical bandgaps (E_g) of 1.79 eV for SW1 and 1.81 eV for SW2. The enlarged optical bandgap of SW2 can be ascribed to the significantly downshifted HOMO caused by the substitution of electron-withdrawing thiazole unit. The tendency of optical bandgaps is in good agreement with the results derived from CV measurements, which were 1.99 eV for SW1 and 2.01 eV for SW2. Note that both SW1 and SW2 display a strong absorption from 450 to 650 nm, being complementary with the narrow bandgap NFA of Y6.

To assess the potential effects of thiazole substitution on photovoltaic performance, the ASM-OSCs have been fabricated with a conventional architecture of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/ active layer (SW1:Y6 or SW2:Y6)/PDINO/Al (Fig. 2c). A general optimization of device fabricated conditions including D/A weight ratios, thermal annealing temperatures has been carried out carefully and the detailed photovoltaic parameters were presented in Table S1–S2. The $J-V$ characteristics of champion devices were plotted in Fig. 3a, and the corresponding photovoltaic parameters were summarized in Table 2. SW1 based devices afford a PCE of 12.90 % with a V_{OC} of 0.806 V, a J_{SC}

of 25.09 mA cm^{-2} , and an FF of 66.1 %. Replacing the thiophene group on BDT by an electron-deficient thiazole, SW2 based devices reach a higher V_{OC} up to 0.835 V, a much better FF of 74.0 % and a comparable J_{SC} of 25.10 mA cm^{-2} , leading to a significantly improved PCE up to 15.51 %. As we have discussed above, the downshifted HOMO of SW2 should mainly account for its higher V_{OC} of OSCs. In addition, a lower nonradiative recombination loss for SW2 based OSC can be also indicated by its relatively higher external electroluminescence yield (EQE_{EL}) [52] comparing to that of SW1 based one (Fig. S3 and Table S3), which agrees well with the higher V_{OC} of SW2 based OSCs. Note that the lower nonradiative recombination loss may be attributed to the smaller energy offset of HOMOs between SW2 and Y6 acceptors, which could result in the efficient hybridization between charge transfer and local exciton states at the D/A interface, thus suppress the non-radiative recombination [52]. Regarding to the significantly enlarged FF for SW2 based OSCs in comparison to that of SW1, the enhanced and more ordered molecular packing of SW2 caused by thiazole substitution and thus increased charge mobility should be taken into consideration, which will be discussed in detail below.

Fig. 3b displays the EQE curves of SW1 and SW2 based ASM-OSCs, demonstrating not only the strong photon to electron response in range of 450–900 nm, but also the similar maximum EQE over 85% for both devices. Then, the charge generation behavior in the optimal SW1:Y6 and SW2:Y6 systems were investigated. The plots of photocurrent (J_{ph}) versus effective applied voltage (V_{eff}) were presented in Fig. 3c. The charge dissociation probabilities can be estimated as 91.7% for SW1:Y6 and 96.9% for SW2:Y6 based devices, suggesting the more efficient exciton dissociation after thiazole substitution. Furthermore, the incident light intensity dependent $J-V$ response tests were implemented to shed light on the charge recombination and transport features. As illustrated in Fig S4, the relationship between J_{sc} and incident light intensity follows the power-law equation $J_{sc} \propto P^\alpha$ [56]. When the α value approaches unit, the bimolecular recombination in blended films can be neglected. Herein, the negligible bimolecular recombination for both

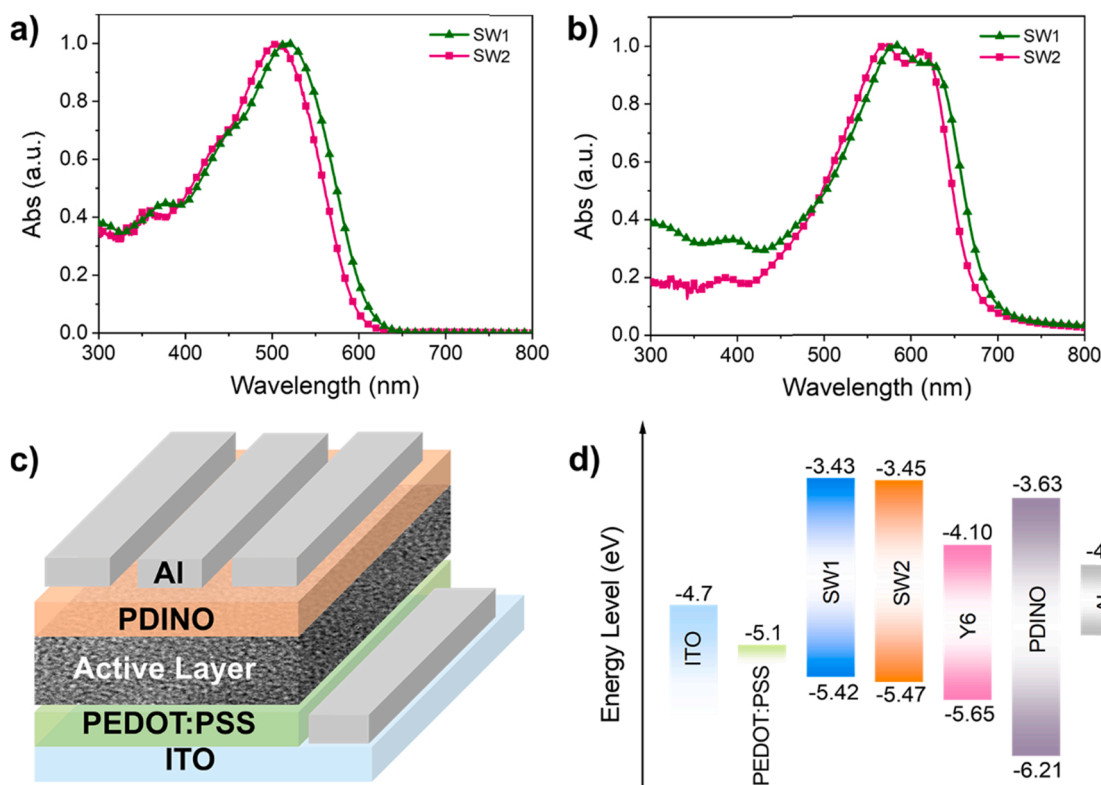


Fig. 2. a) Normalized absorption spectra of SW1 and SW2 in chloroform solutions. b) Normalized absorption spectra of as-cast films of SW1 and SW2. c) Device structure of SW1 and SW2 based OSCs. d) Energy levels diagram of each material in herein studied OSCs.

Table 1
Optical and Electrochemical Data of SW1 and SW2.

Comp.	$\lambda_{\max}^{\text{CF}}$ (nm)	$\lambda_{\max}^{\text{Film}}$ (nm)	HOMO ^{Film} (eV)	LUMO ^{Film} (eV)	E_g^{CV} (eV)	$\lambda_{\text{edge}}^{\text{Film}}$ (nm)	E_g^{OPT} (eV)
SW1	518	581, 620	− 5.42	− 3.43	1.99	689	1.79
SW2	506	572, 613	− 5.47	− 3.45	2.02	684	1.81

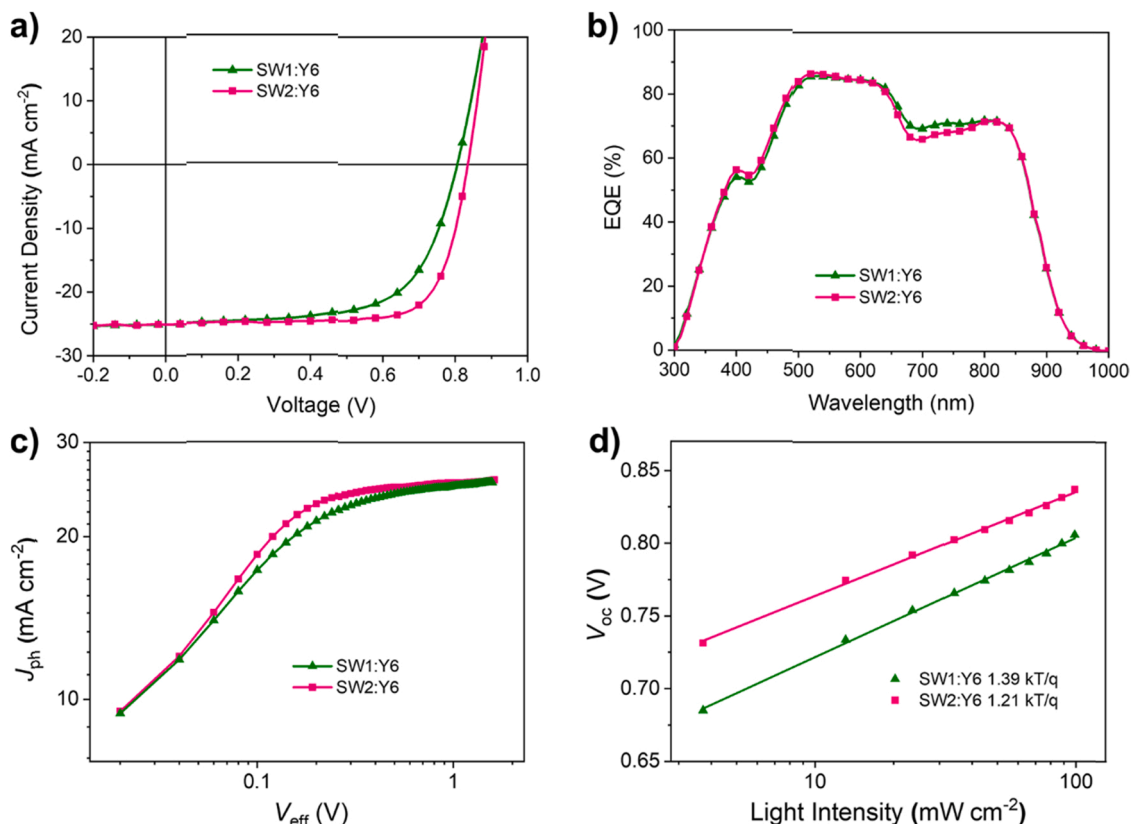


Fig. 3. a) *J*–*V* characteristics and b) EQE spectra of the best OSCs under illumination of an AM 1.5 G at 100 mW cm⁻². c) *J_{ph}* versus and *V_{eff}* characteristics. d) *V_{oc}* versus light intensity of the optimized devices.

Table 2
Photovoltaic Parameters of SW1 and SW2 based all-small-molecule OSCs under the illumination of AM 1.5 G (100 mW cm⁻²).

D:A	<i>V_{oc}</i> (V)	FF (%)	<i>J_{sc}</i> (mA cm ⁻²)	PCE ^a (%)
SW1:Y6 1:0.7	0.806	63.8	25.09	12.90 (12.72)
SW2:Y6 1:0.7	0.835	74.0	25.10	15.51 (15.21)

^a Statistical data obtained from at least 15 devices.

SW1:Y6 and SW2:Y6 based devices can be indicated by their similar and large α values of ~ 0.97 . Fig. 3d presented the plots of *V_{oc}* versus the intensity of incident light, which should follow the function of $V_{oc} \propto nkT/q(P)$ [56]. In the equation, *k*, *T* and *q* represent the Boltzmann's constant, temperature in Kelvin and basic charge, respectively. No trap assisted recombination can be recognized if the *n* value is limited to 1. Herein, the *n* value of SW2:Y6 based device is 1.21, slightly lower than that of 1.39 for SW1:Y6 based one, suggesting the less trap-assisted recombination centers in SW2:Y6 blend. Note that the decreased trap states for SW2:Y6 blend may be attributed to the more compact and ordered molecular packing caused by thiazole substitution discussed below.

The charge recombination and extraction kinetics in SW1:Y6 and SW2:Y6 based devices were also carried out by transient photovoltage (TPV) and transient photocurrent (TPC) characterizations (Fig. S5). The

carrier lifetimes (τ) under open-circuit conditions were determined to be 48.7 μ s for SW2:Y6 based device, slightly larger than its SW1:Y6 counterparts (43.2 μ s). This result agrees well with the reduced charge recombination indicated by the less trap-assisted recombination center of SW2:Y6 blend with respect to that of SW1:Y6 blend (Fig. 3d). The fierce competition between carrier sweep-out and recombination during the operation can be evaluated through the TPC measurements. The photocurrent decay lifetime of SW2:Y6 based device is 0.95 μ s, smaller than that of 1.23 μ s for SW1:Y6 based one, indicating the promotive charge extraction in SW2:Y6 blend. In addition, the hole and electron mobility of blended films have been evaluated and presented in Fig. S6 and Table S4. The SW2:Y6 blended film affords a hole mobility of 4.27×10^{-4} cm² V⁻¹ s⁻¹ and an electron mobility of 3.52×10^{-4} cm² V⁻¹ s⁻¹, whereas the SW1:Y6 blended film shows a hole mobility of 3.28×10^{-4} cm² V⁻¹ s⁻¹ and an electron mobility of 2.41×10^{-4} cm² V⁻¹ s⁻¹. As it can be observed that both SW1:Y6 and SW2:Y6 blended films possess the good charge mobilities but slightly enlarged for SW2:Y6, which should account for the greatly improved FF of SW2:Y6 based OSCs compared with that of SW1:Y6 based ones.

The microscopic morphologies of blended films in OSCs play a dominant role in device performance, therefore we first performed the atomic force microscopy (AFM) to investigate the phase separated morphologies of active layer at nanoscale level. Fig. 4a and b display the AFM images of two active layers with thermal annealing treatments. A

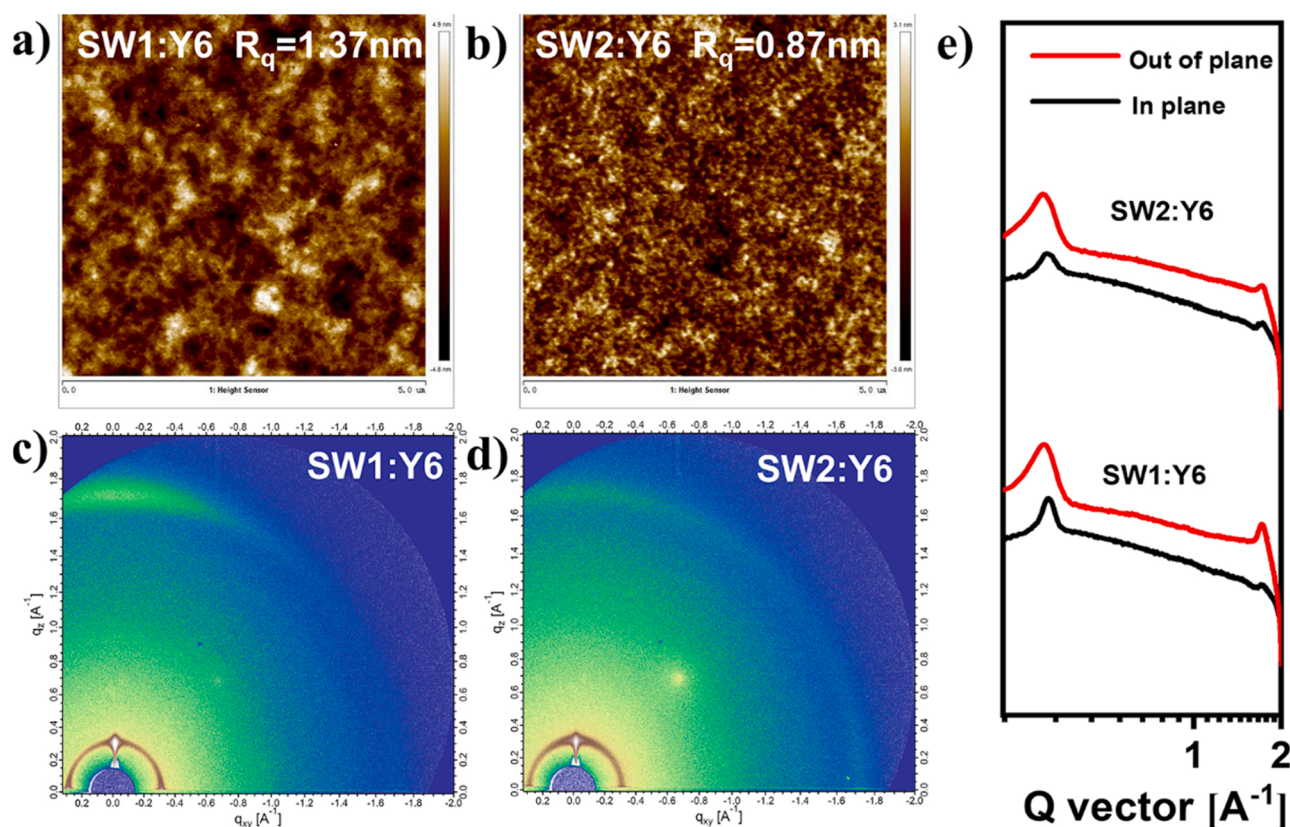


Fig. 4. AFM images a) SW1:Y6 blended film, b) SW2:Y6 blended film. GIWAXS pattern for c) SW1:Y6 blend, d) SW2:Y6 blend and e) In-plane and Out-of-plane line cuts of the corresponding GIWAXS patterns.

much smaller root-mean-square (RMS) roughness of 0.87 nm can be afforded by SW2:Y6 blended film comparing to that of 1.37 nm for SW1:Y6 blend, suggesting a smaller domain size for the SW-2:Y6 blend film. Such a trend can be also observed from the corresponding TEM results (Fig. S7) and please note that the slightly smaller domain size for SW-2:Y6 blend film, implying a well-mixed and better bi-continuous interpenetrating morphology, which may result in the more favorable charge separation with respect to that of SW-1:Y6 [43,57]. To further understand the effect on molecular stacking after thiazole substitution, the GIWAXS measurements have been carried out. For the GIWAXS patterns of neat films in Fig. S8, a typical edge-on oriented π - π stacking can be indicated for both SW1 and SW2 by the very strong scattering peaks locating at $\sim 0.31 \text{ \AA}$ in the out-of-plane (OOP) direction. A peak at $1.73 \text{ \AA}^{-1}$ in the in-plane (IP) direction of SW2 can be observed, corresponding to a π - π stacking distance of $3.64 \text{ \AA}$, demonstrating the more compact molecular packing than that of SW1 with a π - π stacking distance of $3.71 \text{ \AA}$. Bearing the similar chemical structures and almost the same configurations of SW1 and SW2 in mind, the stronger π - π stacking for SW2 should be attributed to the enhanced intermolecular secondary actions caused by thiazole side group [58]. Moreover, the crystal coherence length (CCL) in the (010) region for SW1 and SW2 neat films can be calculated based on the Scherrer equation of $\text{CCL} = 2\pi/\text{fwhm}$. The larger CCL of $\sim 84 \text{ \AA}$ has been estimated for SW2 comparing that of $\sim 73 \text{ \AA}$ for SW1, suggesting the more ordered molecular stacking for SW2. Both the stronger and more ordered intermolecular π - π stacking of SW2 should account for the less trap-assisted recombination, higher charge mobility and thus greatly improved FF for SW2 based ASM-OSCs with respect to that of SW1 based ones. After blending with Y6, both the blended films of SW1:Y6 and SW2:Y6 display the strong stacking behaviors both in the IP and OOP directions. Fig. 4c and d show the 2D GIWAXS patterns of SW1:Y6 and SW2:Y6 after TA treatments, respectively, and Fig. 4e illustrates the corresponding IP and OOP line cut

curves. As shown in Table S6, the CCLs in the (010) region for SW1:Y6 and SW2:Y6 blends can be determined as ~ 65 and $\sim 78 \text{ \AA}$, respectively, agreeing well with the tendency in neat films.

As we have discussed above, the downshifted HOMO energy levels of SW2 caused by thiazole substitution can reduce the energy offset with Y6 and thus decrease the thermodynamic loss during exciton dissociation. In addition, the smaller energy offset between donor and acceptor may also enhance the hybridization of charge transfer states and local exciton states at the donor/acceptor interface, thus further suppress the non-radiative recombination of OSCs [52]. Therefore, we estimated the total energy loss (E_{loss}) of OSCs through the equation of $E_{\text{loss}} = E_g - qV_{\text{OC}}$, and also estimated the most concerned non-radiative recombination losses (ΔE_3) by measuring the EQE_{EL} of blended films (Table S3). As it can be expected, the E_{loss} of SW2:Y6 based device is 0.528 eV , much smaller than that of 0.563 eV for SW1:Y6 based one. Furthermore, as recorded in Fig. S3, the SW2:Y6 based device exhibits a higher EQE_{EL} of 5.6×10^{-5} than that of 2.4×10^{-5} for SW1:Y6, indicating a lower non-radiative recombination loss of 0.252 eV for SW2:Y6 comparing to that of 0.274 eV for SW1:Y6.

3. Conclusion

Two new small molecule donors of SW1 and SW2 have been designed and synthesized with thiophene and thiazole conjugated side group substituting on BDT core. The typical electron-withdrawing characteristic of thiazole renders a downshifted HOMO energy level for SW2, matching much better with the state-of-the-art NFA Y6 and reducing the energy loss of SW2 based device greatly. Moreover, despite the highly similar molecular geometries of SW1 and SW2, the more compact and ordered molecular packing of SW2 can be observed because of the enhanced secondary intermolecular actions caused by thiazole group, resulting in the lower recombination and higher charge mobility for

SW2:Y6 blend. As a consequence, SW2:Y6 based device affords a significantly improved PCE of 15.51% comparing to that of 12.90% for SW1:Y6 based one, ranking it as one of the best ASM-OSCs thus far. Our work has developed thiazole substitution as a simple and effective strategy to optimize the energy levels, molecular stackings and microscopic morphologies in donor molecules, and will stimulate its further explorations in OSCs with the aim of improving PCEs.

CRediT authorship contribution statement

S. W. and W. F. contributed equally to this work. Y. C. and Z.Y. conceived and directed the study. S. W. synthesized the **SW-1** and **SW-2**. W. F. fabricated and characterized the photovoltaic devices. The manuscript was mainly prepared by Y. C., S. W., W. F. Z. Y. and all authors participated in the manuscript preparation and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

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Supporting Information

Supporting Information is available online at xxx. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.107801.

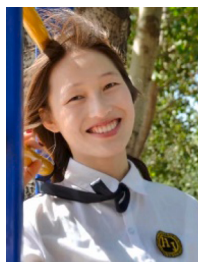
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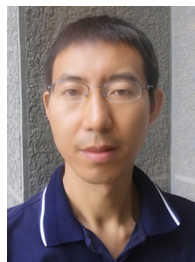
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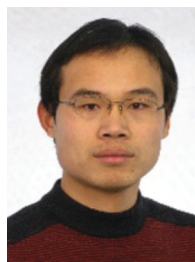
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