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Graphical Abstract:



Overcoming the Trade-off between V_{oc} and J_{sc} : AsymmetricChloro-SubstitutedTwo-Dimensional

Benzo[1,2-b:4,5-b']dithiophene-based Polymer Solar Cells

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Abstract: To achieve the high PCE and simultaneously overcome the trade-off between open circuit voltage (V_{OC}) and short-circuit current density (J_{SC}), the reasonable design of the donor material is still a great challenge in non-fullerene polymer solar cells (PSCs). Herein, a pair of asymmetric 2D BDT-based wide band gap polymers, named PBPTBz-1Cl and PBPTBz-2Cl, respectively, were designed and synthesized through simultaneously introducing a chloro-substituted thiophene and another alkoxylphenyl groups as side chains onto the same BDT unit. As expected, the polymers PBPTBz-1Cl and PBPTBz-2Cl exhibit the deeper HOMO levels of -5.32 and -5.41 eV, respectively, compared with the HOMO value of -5.27 eV for chlorine-free substituted polymer PBPTBz-0Cl. Therefore, the PBPTBz-2Cl:IT-M based PSCs exhibited a higher V_{oc} of 0.99 V, with an enhanced J_{sc} of 14.92 mA cm⁻² and PCE of 7.18%. The $V_{\rm oc}$, $J_{\rm sc}$ and PCE were simultaneously enhanced from PBPTBz-0Cl:IT-M to PBPTBz-1Cl:IT-M, then to PBPTBz-2Cl:IT-M based PSCs successively. These results demonstrate that the challenge of the trade-off between $V_{\rm oc}$ and J_{sc} could be overcome through the asymmetric strategy of the chloro-substituted thiophene and alkylphenyl groups as different side chains onto the same BDT unit. Hence, considering the low cost of starting materials and convenient introduction of chlorine atoms, the asymmetric chlorination of the side chain of BDT unit would be the great potential for achieving the high-performance PSCs.

keywords: Asymmetric chloro-substitution, side-chain engineering, low photon energy loss, polymer solar cells,

1. Introduction

Polymer solar cells (PSCs) have drawn considerable attention because of the recent great breakthrough, and the power conversion efficiencies (PCEs) have reached up to 14% in single-junction devices as a few new wide band gap (WBG) donor polymers and narrow band gap acceptor-donor-acceptor (A-D-A) type small molecular acceptors were gradually developed.¹⁻⁵ PSCs as a promising and potential renewable energy technology possess many unique advantages, including light-weight, mechanical flexibility, large-area preparation through the solution processing.⁶⁻¹⁵ However, it is still a great challenge in the materials design and device engineering, and to further push the PCEs of PSCs toward industrial application with a simple device structure.^{16, 17} Lately, great progress in a series of narrow band gap non-fullerene acceptors has been achieved, such as IT-4F and IT-4Cl, making the photovoltaic performance exceed a PCE of 14% paired with a wide band gap donor material, and opening up a new window for PSCs.^{1, 2, 18, 19} Meanwhile, it is well known that the intrinsic properties, for instance, the complementary absorption spectra, the suitable energy levels and good miscibility of the active layer comprised of the donor and acceptor dominantly influence the device performance in PSCs.^{20, 21} Therefore, with regard to a specific narrow band gap acceptor material, the design of the corresponding donor materials would be of great importance.¹⁹ Recently, great efforts have focused on the development of the WBG donor polymers forming a good absorption and suitable energy levels which can boost the short-circuit current density (J_{SC}) and achieve a high open circuit voltage (V_{OC}) when matched with the narrow

band gap acceptor materials.²²⁻²⁶ Donor-acceptor (D-A) type conjugated polymers based on a two-dimensional (2D) benzodithiophene (BDT) moiety have been widely developed for design and synthesis of the donor materials in PSCs, because the energy levels can be readily modified through tuning the polymer backbone and side chain substitution units.²⁷⁻²⁹ The 2D-BDT based polymer could strengthen the intermolecular π - π interactions through extending the effective region of π - π conjugation, contributing to enhance light-harvesting ability, exciton diffusion and charge transport.³⁰⁻³² In addition, the highest occupied molecular orbitals (HOMO) level of those polymers could be decreased when introducing the phenyl type of substitutions due to its high ionization potential and low electron densities, which was helpful to achieve high V_{oc} in PSCs.³³ At the same time, introducing the halogen, especially fluorine (F), was regarded as a quite effective method to downshift the HOMO level and obtain high V_{oc} without sacrificing the light-harvesting ability and causing the evident steric hindrance used in the donor and acceptor materials of PSCs.^{17, 34-36} However, except fluorine, the other halogen, such as chlorine which possesses strong electronegativity after the fluorine in the halogen family, has not been widely explored in the field of PSCs.²⁸ It has been demonstrated that although the electronegativity of F is stronger than Cl, the dipole moment of the carbon-chlorine (C-Cl) bond is a little larger than carbon-fluorine (C-F), which could contribute to modulate the ICT effect in comparison with F.¹ In addition, the empty 3d orbitals in chlorine endow their capability to accept lone pair electrons and π -electrons from the conjugated system, which would form the intermolecular non-covalent

interactions of Cl···S and Cl··· π . Such delocalization is even more beneficial to adjust the energy level and ordered molecular stacking in films.^{37, 38} Our recent results demonstrated that the chloro-substitution of 4-position of conjugated thiophene as a side chain of BDT core could efficiently decrease the HOMO level without causing the steric hindrance, and push the V_{oc} to beyond 1.0 V with reasonable energy loss (E_{loss}) of 0.63 eV.³⁷ E_{loss} is an important factor hindering the device performance, and the empirical threshold is believed to be around 0.6 eV.³⁹ In order to overcome the large E_{loss} as far as possible, the acceptor with narrow band gap and the donor with the deeper HOMO level would be simultaneously and reasonably selected to fabricate the bulk heterojunction (BHJ) PSCs.⁴⁰

Herein, inspired by our previous investigations, three novel asymmetric 2D-2D BDT-based donor units with alkoxylphenyl and alkylthiophene/chloro-substituted thiophene as the different side chain on the same BDT unit were designed and prepared, named PBPTBz-OCl, PBPTBz-1Cl and PBPTBz-2Cl, respectively (Scheme 1), in which the advantages of those two kinds of side chains were anticipated to be combined. The phenyl group has a high ionization potential and low electron density which can downshift the HOMO level keeping a high V_{oc} , and the chlorinated thienyl group could enhance the intermolecular non-covalent interaction because of the empty 3d orbitals of chlorine, resulting in a good molecular stacking and charge transfer in vertical direction.^{33, 41-43} In order to obtain the better complementary absorption of these three WBG polymers, the small molecular acceptor IT-M with a narrow optical band gap was selected to optimize the photovoltaic performance.²⁶ As a result, among

the three polymers, the V_{oc} , J_{sc} and PCEs were boosted as the increasing of the amount of chlorine atoms, in particular, the PSCs based on PBPTBz-2Cl:IT-M show a maximum V_{oc} of 0.99 V with a simultaneously enhanced J_{sc} of 14.92 mA cm⁻². This non-fullerene device exhibits an excellent PCE of 7.18% with a very low E_{loss} of 0.58 eV, which was below the typical threshold of 0.6 eV.⁴⁴ In other words, the strategy of simultaneous substitution of phenyl and chloro-substituted thiophene into the same BDT unit could simultaneously improve the V_{oc} and J_{sc} with improved E_{loss} . Thus, the strategy of asymmetric BDT building block seems to be a promising method and accelerate the development of the photovoltaic materials in PSCs.





Scheme 1. The structures and synthetic route of monomers M1, M2, M3 and polymers PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl.

2. Results and discussion

2.1 Synthesis and characterization

The structure and synthetic routes of the M1, M2, M3 molecules and polymers PBPTBz-OC1, PBPTBz-1C1 and PBPTBz-2C1 are shown in Scheme 1. All products were characterized through ¹H NMR, ¹³C NMR and high-resolution mass spectroscopy (HRMS). The key intermediates monomer M1, M2 and M3 were synthesized through Grignard reagent, and then n-butyllithium (*n*-BuLi) with a high yield. The detailed synthetic procedure is provided in the Supporting Information. Polymer PBPTBz-OC1, PBPTBz-1C1 and PBPTBz-2C1 were synthesized through Stille coupling reaction catalyzed by Tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) in toluene with a yield of 64.55, 64.29 and 34.48%, respectively, as displayed in Table 1. In order to remove the remaining monomers, oligomers and catalytic impurities, soxhlet extraction was conducted successively with methanol, acetone, and hexane solvents. The structures of the polymers were characterized by ¹H NMR spectroscopy. Polymers PBPTBz-OC1, PBPTBz-1C1 and PBPTBz-1C1 and PBPTBz-2C1 all exhibit good solubility in chloroform, chlorobenzene and o-dichlorobenzene, which is favorable for solution processing. The

average molecular weight was measured via gel permeation chromatography (GPC) using 1,2,4-trichlorobenzene as the eluent at high temperature (160 °C), as displayed in Table 1, the corresponding M_n values were 44.93, 21.49 and 23.66 K Da with the PDI of 1.33, 1.57 and 1.99 for PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl, respectively. The thermal properties of the polymers PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl were estimated through thermogravimetric analysis (TGA) in nitrogen atmosphere shown in Figure S1 and the relevant results were summarized in Table 1. The TGA results demonstrate that the decomposition temperature (T_d) with 5% weight loss are determined to be 428, 412 and 426 °C for polymers PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl, respectively. These T_d values demonstrate that these three polymers all possess good thermal stability for future PSCs applications.

Polymer	Yield (%)	M _n (K Da)	M _w (K Da)	PDI	$T_{\rm d}$ (°C)
PBPTBz-0Cl	64.55	44.93	60.04	1.33	428
PBPTBz-1Cl	64.29	21.49	33.78	1.57	412
PBPTBz-2Cl	34.48	23.66	47.11	1.99	426

Table 1. The yield, molecular weights and thermal properties of the donor polymers

2.2. Theoretical calculations



Figure 1. Optimized molecular backbone conformations of polymers using DFT calculations at the B3LYP/6-31g*(d, p) level: top views and side views, and the HOMO and LUMO electron distributions based on two repeat units.

In order to gain deeper insight into the effects of the side chain of phenyl and chloro-substituted conjugated thiophene on the molecular geometry and orbital electron cloud density distribution, density functional theory (DFT) calculations with a the B3LYP/6-31G* (d, p) level were carried out. For the simulation shown in Figure 1, two repeating units were chosen, and a methyl group was used to replace the alkyl substituent to simplify the calculations. The changes of the HOMO levels with the phenyl and chloro-substituted thiophene side chain into one BDT unit with the number of substituted chlorine atoms were studied. As shown in Figure 1, for the polymer PBPTBz-1C1 and PBPTBz-2C1, The HOMO and the lowest unoccupied molecular orbital (LUMO) levels were gradually decreased with increasing the chlorine atoms from one to two, compared to the polymer PBPTBz-0C1. The orbital distribution of those three polymers is similar because of the same backbone. The calculated HOMO levels of the model of PBPTBz-0C1, PBPTBz-1C1 and

PBPTBz-2Cl were -4.74, -4.83 and -4.86 eV, respectively. It is noted that the HOMO energy levels of PBPTBz-1Cl and PBPTBz-2Cl were 0.09 and 0.12 eV lower, respectively, as compared with the HOMO level of PBPTBz-0Cl, demonstrating that the HOMO level is decreased by 0.09 eV through introducing one chlorine atom. Besides, the band gap of the three polymers were almost the same, revealing that the planarity of the backbones did not change upon the chlorination of conjugated thiophene side chain of asymmetric BDT unit. Moreover, the molecular polarity was enhanced and the corresponding dipole moment (δ) was 1.56, 5.47 and 6.69 for PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl, respectively, revealing that the dipole moment of polymer is boosted through chlorination of side chain, which in consequence contributes to the ICT and intermolecular dipole-dipole effect. The results from the present theoretical calculations indicate that the chlorination of conjugated thiophene side chains of asymmetric BDT is a promising strategy to decrease the HOMO level of donor materials.

2.3. Optical and electrochemical properties



Figure 2. (a) Normalized absorption spectra of four polymers in diluted chlorobenzene (CB) solution at 20 °C; (b) normalized UV–vis absorption spectra of thin films; (c) cyclic voltammogram of the donor polymers; and (d) energy levels diagram of the corresponding donor polymers and acceptor IT-M in this work.

The UV-vis absorption spectra of the polymers in diluted chlorobenzene (CB) solution (10^{-5} M) and in thin films at room temperature are displayed in Figure 2a and 2b, respectively, and the corresponding absorption data are collected in Table 2. As shown in Figure 2a, the polymers PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl show the relatively similar hump-shaped absorption curves from 400 to 650 nm with a shoulder peak for each polymer. The maximum absorption peaks of PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl are located at 541, 539 and 533 nm with the corresponding molar extinction coefficients of 1.35×10^5 , 1.26×10^5 and 1.19×10^5 cm⁻¹ L mol⁻¹, indicating that they all possess a strong light-harvesting ability at the same order of magnitude, respectively. Figure 2b displays the absorption in solid thin films,

polymer PBPTBz-2Cl exhibits a redshift (5 nm) in the maximum absorption from solution to thin film, but PBPTBz-0Cl and PBPTBz-1Cl almost does not change. The E_{g}^{opt} of PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl are calculated to be 1.96, 1.97 and 1.98 eV according to $E_{g}^{opt} = 1240/\lambda_{onset}$. The HOMO energy levels are evaluated through electrochemical cyclic voltammetry (CV) shown in Figure 2c and the corresponding energy diagrams is depicted in Figure 2d. The HOMO and LUMO level values are summarized in Table 2. The HOMO level values of PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl are -5.27, -5.32 and -5.41eV, respectively. PBPTBz-0Cl exhibits deeper HOMO than J52 (-5.21 eV), which is attributed to the relatively low electron densities and high ionization potential of phenyl group compared with thienyl group.^{24, 33} The lower HOMO levels of PBPTBz-1Cl and PBPTBz-2Cl are attributed to the synergistic effect of the phenyl groups and chloro-substituted thiophene into the BDT units, which is beneficial to achieve a high V_{OC} in PSCs.⁴⁵ The variation trend of HOMO level from CV results agrees well with the DFT calculation.

Polymer -	Solution		Film		E_g^{opt}	номо	LUMO	$E_{ m g}^{ m cv}$
	$\lambda_{\max}(nm)$	$\epsilon (M^{-1} cm^{-1})$	$\lambda_{max}(nm)$	$\lambda_{onset} (nm)^a$	$(eV)^b$	(eV)	(eV)	(eV) ^c
PBPTBz-0Cl	541, 584	1.35×10^{5}	542, 588	631	1.96	-5.27	-3.56	1.71
PBPTBz-1Cl	539, 582	1.26×10^5	540, 584	629	1.97	-5.32	-3.55	1.77
PBPTBz-2Cl	532, 571	1.19 × 10 ⁵	537, 578	626	1.98	-5.41	-3.54	1.87

Table 2. Physical, Electronic, and Optical Properties of the Donors Materials

^{*a*} Absorption edge of the polymer films spin-coated from CB solution. ^{*b*} Calculated from the absorption edge of the polymer films: $E_g^{opt} = 1240/\lambda_{edge}$. ^{*c*} Electrochemical bandgap obtained from $E_{LUMO} - E_{HOMO}$.



2.4. Temperature-dependent aggregation

Figure 3. Temperature-dependent absorption spectra of the solutions of (a) PBPTBz-0Cl, (b) PBPTBz-1Cl, (c) PBPTBz-2Cl in CB solution (10^{-5} M) and (d) the blueshift variation trend of absorption edge λ_{edge} of polymers with increasing temperature from 20 to 110 °C.

In order to investigate the influence of the two different side chains of asymmetric BDT units on the aggregation behaviors of polymers PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl, the temperature-dependent absorption measurements were conducted in the temperature range from 20 to 110 °C as shown in Figure 3. All three polymers exhibit distinct redshift as the temperature decreases, indicating a strong molecular aggregation at room temperature. In addition, the polymers PBPTBz-0Cl and PBPTBz-1Cl exhibit the obvious shoulder at about 570 nm in the high temperature regime (100-110 °C), however, the shoulder peak of polymer PBPTBz-2Cl has disappeared at 90 °C, revealing that the chains of polymer PBPTBz-2Cl are completely disaggregated at high temperature of 100-110 °C beneficial to the

morphology controlling of the active layer. The two polymers PBPTBz-OCl and PBPTBz-1Cl maintain their strongly aggregated behaviors at 20-110 °C which could result in the severe phase separation. In addition, as shown in Figure 1d, the absorption edge of PBPTBz-2Cl is very sensitive to the increase of temperature from 40 to 90 °C with the gradually disappeared shoulder peak, but PBPTBz-0Cl and PBPTBz-1Cl exhibit the weaker response to the change of temperature. These results demonstrate that the side chain of 3,4-dichloro-substituted thiophene for PBPTBz-2Cl provides a sufficient steric twist to allow PBPTBz-2Cl to fully disaggregate at high temperatures but tend to more coplanar orientation upon the cooling process, which is consistent with the absorption spectra in solid thin film at room temperature.⁴⁵ However, the steric hindrance of the bare and 4-chloro-substituted thiophene for PBPTBz-0Cl and PBPTBz-0Cl and PBPTBz-0Cl and PBPTBz-0Cl and PBPTBz-1Cl is not sufficient to overcome the strong aggregation at high temperature.

2.5. Photovoltaic properties



Figure 4. (a) The *J*–*V* curves of PSCs based on polymer:IT-4M (1:1, wt/wt) under the illumination of AM 1.5G, 100 mW cm⁻², (b) EQE curves based on corresponding PSCs, (c) Photocurrent (J_{ph}) against effective voltage (V_{eff}) curves of the polymer:IT-4M blends and (d) Short-circuit current density (J_{SC}) versus light intensity plots of the three polymer devices.

The photovoltaic performance of the three polymers was evaluated with a conventional architecture of ITO/PEDOT:PSS/polymer:IT-M/PDINO/Al under the illumination of AM 1.5 G (100 mW cm⁻²).⁴⁶ Considering the complementary absorption spectra, IT-M was selected as the acceptor material. The optimum D/A weight ratios were found to be 1:1. CB was used as processing solvent without any solvent additives and post treatment according to our previous research.²⁸ The optimum current density–voltage (*J*–*V*) curves, external quantum efficiency (EQE) curves, and the relevant photovoltaic results are displayed in Figure 4a-4b, and Table 3, respectively. PBPTBz-0CI:IT-M based device exhibited a PCE of 6.15%, with a V_{oc} of 0.81 V, a J_{sc} of 14.26 mA cm⁻² and a fill factor (FF) of 52.95%. As for device based

on PBPTBz-1Cl:IT-M under the same condition, a higher PCE of 6.46% with an enhanced J_{sc} of 14.78 mA cm⁻², an increased V_{oc} of 0.87 V and a slightly decreased FF of 50.20% were obtained. As anticipated from the lowest HOMO level of PBPTBz-2Cl among the three polymers, the PBPTBz-2Cl:IT-M based device exhibits a much higher $V_{\rm oc}$ of 0.99 V. The PSCs based on PBPTBz-2Cl:IT-M exhibit a higher PCE of 7.18% with a quite low E_{loss} of 0.58 eV, and a further enhanced J_{sc} of 14.86 mA cm⁻² compared with PBPTBz-0Cl and PBPTBz-1Cl. It is noted that the PCEs, J_{sc} and V_{oc} are simultaneously enhanced for PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl based PSCs, respectively, which we attribute to the synergistic effect from the side chains of phenyl group and 3,4-dichloro-substituted thiophene into asymmetric BDT units. We believe that there is still a possibilities to further boost the PCEs for PBPTBz-2Cl based PSCs. As shown in Figure 4b, the PBPTBz-2Cl based device exhibits a broad, and stronger photoresponse than that of PBPTBz-0Cl and PBPTBz-1Cl in the range of 300-800 nm, which is ascribed to the better complementary absorption. In addition, the EQE value stays above the line of 60-70% in the range of 500–720 nm, contributing to achieve the high J_{SC} of the PSCs. Furthermore, as displayed in Table 3, the integrated current densities from the EQE spectra are 13.69, 14.71 and 14.86 cm² v⁻¹ s⁻¹ for PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl based PSCs, respectively, which agrees well with the J_{SC} from the J-Vmeasurements within a mismatch of 4%. The hole mobility as an important factor of PSCs were also measured by the space-charge limited current (SCLC) method. As shown in Figure S2, the hole mobility was calculated to be 1.4×10^{-4} , 1.6×10^{-4} and

 1.3×10^{-4} cm² v⁻¹ s⁻¹ at the same order of magnitudes for the optimal PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl based PSCs, respectively.

Polymer	Thickness	$V_{ m oc}$	$J_{ m sc}$	$J_{ m sc}{}^a$	FF	PCE _{max}	$\mu_{\rm h}^{\ b}$
	(nm)	(V)	(mA cm ⁻²)	(mA cm ⁻²)	(%)	(%)	$(\mathbf{cm}^2 \mathbf{v}^{-1} \mathbf{s}^{-1})$
PBPTBz-0Cl	95	0.81	14.26	13.69	52.95	6.15	1.4×10 ⁻⁴
PBPTBz-1Cl	105	0.87	14.78	14.71	50.20	6.46	1.6×10 ⁻⁴
PBPTBz-2Cl	100	0.99	14.92	14.86	48.61	7.18	1.3×10 ⁻⁴

Table 3. Photovoltaic parameters of the PSCs based on polymer:IT-M (1:1, wt/wt), under the illumination of AM 1.5G, 100 mW cm⁻²

^{*a*}The J_{sc} calculated from the EQE spectrum, ^{*b*} μ_h measured by the SCLC model.

To further explore the photocurrent behaviors of three devices based on PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl under the optimal conditions, the exciton dissociation probability P (E,T) was carried out shown in Figure 4c. J_{ph} is defined as the difference between the light and dark current densities, and V_{eff} as the difference of the applied voltage and the voltage V_a (when J_{ph} is zero). J_{ph} saturates at sufficiently high reverse voltage and the J_{ph}/J_{sat} ratio (P (E,T)= J_{ph}/J_{sat}) can be measured to account for the exciton dissociation and charge collection ability. As displayed in Figure 4c, the calculated P (E,T) for optimal PBPTBz-0Cl:IT-M, PBPTBz-1Cl:IT-M and PBPTBz-2Cl:IT-M based PSCs are 0.97, 0.98 and 0.98, respectively, revealing that the P (E,T) of the three devices are equally efficient, and PBPTBz-1Cl:IT-M and PBPTBz-2Cl:IT-M device exhibits slightly better exciton dissociation and charge collection and charge collection. Besides, the process of bimolecular recombination

was investigated. Figure 4d exhibits the linear relation between log (J_{sc}) and incident light power log(P_{light}) described by $J_{sc} \propto (P_{light})^{S}$, the slope (S) suggests the extent of the bimolecular recombination and the recombination is weak and negligible in the device when the value of the slope is close to 1. As displayed in Figure 4d, the relatively high S values were calculated to be 0.90, 0.91 and 0.92 for optimal PBPTBz-0Cl:IT-M, PBPTBz-1Cl:IT-M and PBPTBz-2Cl:IT-M based PSCs, respectively, demonstrating the bimolecular recombination is distinctly suppressed in the corresponding devices which contributes to achieve a higher J_{sc} .

2.6. Blended film morphology



Figure 5. Tapping mode AFM height images $(5 \times 5 \text{ um})$ of blend films (polymer:IT-M, 1 : 1, wt/wt), (a) PBPTBz-0Cl:IT-M, (b) PBPTBz-1Cl:IT-M and (c) PBPTBz-2Cl:IT-M; TEM images of polymer:IT-M blend films (polymer:IT-M, 1 : 1, wt/wt): (d) PBPTBz-0Cl:IT-M, (e) PBPTBz-1Cl:IT-M and (f) PBPTBz-2Cl:IT-M.

It is well known that the surface and the bulk morphology of the active layers plays a significant role for the photovoltaic performance. Thus, atomic force microscopy

(AFM) and transmission electron microscopy (TEM) were adopted to further investigate the surface and the bulk morphology in the corresponding devices. As shown in Figure 5a-c, the three blends exhibit smooth surfaces with the small root-mean-square (RMS) roughness of 0.70, 0.74 and 0.89 nm, respectively. The smooth surface of the active layer is beneficial to achieve a better contact behavior between the hole or electron transport layers and the two electrodes, which contributes to boost the photovoltaic performance. In the TEM images (Figure 5d-5e), the overlarge dark regions were observed for PBPTBz-OCI:IT-M blend and the scales of phase separation were too small for PBPTBz-1C1:IT-M blend. However, the blend film of PBPTBz-2CI:IT-M exhibits a uniform fibrillar and interpenetrating network structure with a suitable scale (Figure 5f), which contributes to achieve better exciton dissociation and charge transport, resulting in a higher J_{sc} .

2.7. GIWAXS



Figure 6. (a), (b) and (c) Two-dimensional GIWAXS patterns of PBPTBz-0Cl, PBPTBz-1Cl and PBPTBz-2Cl blend films with IT-M. (d) The out-of-plain and (e) In-plain line-cut profiles of GIWAX patterns for the three optimized blends.

In order to further explore the molecular packing and microstructure of the corresponding blends, grazing incidence wide-angle X-ray scattering (GIWAXS) was carried out. As displayed in Figure 6, similar GIWAXS patterns and the obvious (010) diffraction peaks in the out-of-plane (OOP) direction are observed for the three blends, suggesting that the existence of face-on oriented π - π stacking in blends, which could contribute to the charge transport. As shown in Figure 6d, the (010) diffraction peaks in the OOP direction located at q_z = 1.71, 1.71 and 1.70 Å⁻¹, corresponding to the π - π stacking distances are 3.67, 3.67 and 3.69 Å for PBPTBz-OCl, PBPTBz-1Cl and PBPTBz-2Cl based blend films, respectively. In addition, the lamellar distances were calculated to be 19.69, 19.36 and 19.36 Å for PBPTBz-OCl, PBPTBz-1Cl and PBPTBz-2Cl based blends according to the (100) diffraction peaks in the Figure 6e,

respectively. The results above demonstrate that the multiple-substitution of the larger chlorine atoms has no distinct impact on the π - π stacking distance, which could be attributed to the strong intermolecular non-covalent interactions of Cl···S and Cl··· π .

3. Conclusions

In summary, two asymmetric chloro-substituted 2D BDT-based wide band gap polymers, named PBPTBz-1Cl and PBPTBz-2Cl, respectively, were designed and prepared through simultaneously introducing the alkoxylphenyl groups and the chloro-substituted thiophene as the two different side chains onto the same BDT unit. On the one hand, the introduction of the chlorine atoms could enhance the ICT effect due to the large dipole moment of C-Cl bond while efficiently downshift the HOMO energy level of the donor polymers. On the other hand, the introduction of the phenyl group could lower the HOMO level because of the high ionization potential and low electron density. As a result, the polymers PBPTBz-1Cl and PBPTBz-2Cl exhibit the deeper HOMO levels of -5.32 and -5.41 eV, respectively, compared with the HOMO value of -5.27 eV for chlorine-free substituted polymer PBPTBz-0Cl. Therefore, a high $V_{\rm oc}$ of 0.99 V was achieved for the PBPTBz-2Cl based PSCs when matched with a small molecular acceptor IT-M. This device exhibited a much higher PCE of 7.18% with a further enhanced J_{sc} of 14.92 mA cm⁻² compared to other two polymer based devices. It's noted that the asymmetric design of chloro-substituted thiophene and the alkySlphenyl group onto the same BDT unit could simultaneously enhance the $V_{\rm oc}$, PCE and J_{sc} , indicating the great challenge of the trade-off between V_{oc} and J_{sc} has

been overcome using the above method, which would be an efficient way for next high-performance polymer solar cell investigation.

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Notes

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Supplementary data

Supplementary data related to this article can be found at ********

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the side-chains of non-fullerene small molecule acceptors to match with appropriate