Chlorination of Side Chains: A Strategy for Achieving a High Open Circuit Voltage Over 1.0 V in Benzo[1,2-b:4,5-b′]dithiophene-Based Non-Fullerene Solar Cells

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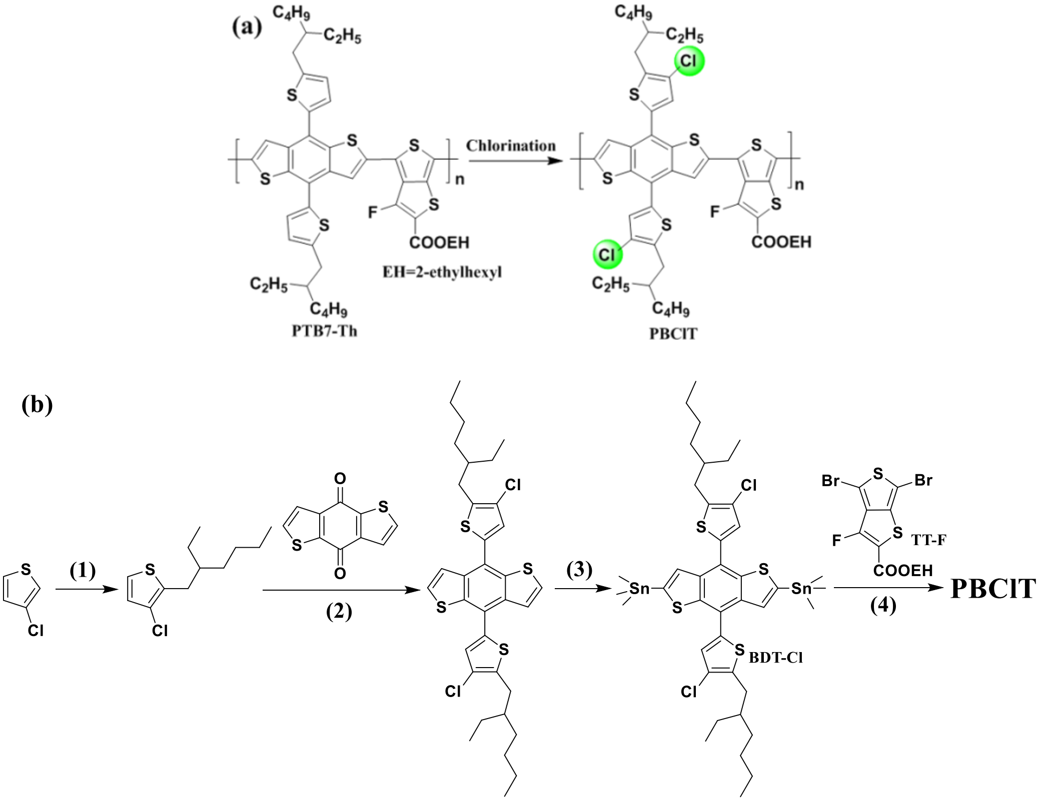
Abstract: A benzo[1,2-b:4,5-b′]dithiophene-based donor material with chlorine atoms substituted on its side chains, named PBClT, was designed and developed for application in non-fullerene solar cells to enhance the open-circuit voltage (V_{oc}) without decreasing charge carrier transfer in the corresponding blend films. The results demonstrated that the chlorinated PBClT polymer was an efficient donor in non-fullerene polymer solar cells (PSCs) and exhibited a blue-shifted absorbance, resulting in more complementary light absorption with non-fullerene acceptors, such as ITIC. In addition, the chlorine substitution decreased the HOMO level of PBClT, and as a result, the V_{oc} of the corresponding solar cell increased dramatically to 1.01 V, which is much higher than that of the non-chlorine analog, PTB7-Th, with a V_{oc} of approximately 0.82 V. The 2D-GIWAXS results illustrated that the PBClT/ITIC blend film exhibited a "face-on" orientation, which suggested that the chlorine substituents on the side chains favored π-π stacking in the direction perpendicular to the electron flow in photovoltaic devices. Furthermore, the PBClT/ITIC blend film showed a π-π stacking distance of 3.85 Å, which was very close to that of its non-chlorine analog blend film with a distance of approximately 3.74 Å. Based on this result, the introduction of multiple chlorine atoms on the conjugated side chains not only adjusted the energy level of the low-band-gap polymer through the electron withdrawing ability of the chlorine atoms but also subtly avoided obvious morphological changes that could result from strong steric hindrance in the main chain of the polymers. The PBClT/ITIC-based PSCs exhibited a maximum PCE of 8.46% with a V_{oc} of 1.01 V, which is an increase in the PCE of approximately 22% compared to the PTB7-Th-based device based on our parallel experiments.

INTRODUCTION

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) comprised of conjugated polymers as the donors and fullerene derivatives as the acceptors have attracted considerable attention because of their advantages of light weight, light cost, and potential application in flexible devices as well as large-area devices through roll-to-roll printing.[1-7] In recent years, substantial progress has been made, and a high power conversion efficiency (PCE) of more than 11% has been achieved for traditional single PSCs by utilizing a fullerene derivative as an electron acceptor.[8-10] Despite the great achievements, fullerene derivatives still exhibit intrinsic drawbacks, such as weak absorption and poor chemical and electronic adjustability, and thus, their application remains challenging.[11-14] To date, the PCE of BHJ PSCs based on fullerene-free solar cells has exceeded 13.8%.[15] Accordingly, tremendous efforts have been devoted to the development of non-fullerene acceptors to replace fullerene derivatives in BHJ polymer solar cells owing to their unique properties, such as strong absorption, low cost of purification and readily tunable energy levels.[14, 16-21] Apart from the extensive exploration of novel non-fullerene acceptors, it is also important to develop matching donor polymers for efficient non-fullerene organic solar cells.[14] Therefore, the amount of attention focused on exploring donor polymers specifically for fullerene-free acceptors is rapidly increasing. However, the process of investigating matching donor polymers for non-fullerene acceptors has mostly been performed in a trial-and-error manner, and in addition, a definitive structure-property relationship has not been established to guide the theoretical design and development of donor polymers. Meanwhile, some high-performance donor polymers (such as PTB7-Th shown in Scheme 1a) in fullerene-based devices cannot match well with non-fullerene small molecule acceptors.

As is well known, in the construction of highly efficient donor-acceptor (D-A) conjugated polymers, benzodithiophene (BDT) has attracted great interest as an electron donor unit in the PSC field.[1, 22-25] According to previous studies, for D-A polymers of BDT and thieno[3,4-b]thiophene (TT), introducing fluorine atoms onto the TT units could significantly improve the photovoltaic performance of the D-A polymers; however, the target polymers exhibited poor photovoltaic performance when F atoms were attached to the BDT unit.[26] Therefore, it is still of great interest and significance to extend the application of this approach and design highly efficient BDT-TT-based photovoltaic polymers. Chlorine is the second-most electronegative halogen after fluorine in the halogen group. From the literature, it was revealed that chlorination is equally, even better efficient at finetuning the frontier energy levels and molecular packing in some cases as fluorination because the chlorine contains empty 3d orbitals that can accept π-electrons from the conjugated backbone, while fluorine does not have such kind of π-electrons delocalization capability.[27, 28, 29] Furthermore, according to our previous study, taking the large change in the molecular energy levels and easier incorporation of chlorinated precursors compared to fluorinated ones into consideration, chlorine-substituted D-A conjugated polymers should be more attractive for improving both the performance of PSCs and their potential for industrial applications.[30-34]

In this work, we attached chlorine atoms to the side chains of BDT units and synthesized a new D-A conjugated polymer, PBClT, based on 2,6-bis(trimethyltin)-4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene (BDT-Cl) and 2-ethylhexyl 4,6-dibromo-3-fluorothieno-[3,4-b]thiophene-2-carboxylate (TT-F), as shown in Scheme 1a. Herein, we observed striking and surprising effects upon attaching chlorine atoms to the repeating BDT units in the PBClT polymer, with dramatic improvements in the open circuit voltage (V_{oc}) to over 1.0 V and the device performance when combined with a small molecule acceptor named ITIC that was previously reported by Zhan.[20] The chlorination of the conjugated side chain would not only adjust the energy level of the low-band-gap polymer through the resonance effect of the chlorine atoms with empty 3d orbitals, giving a deep lying HOMO level, but also subtly prevent strong steric hindrance with the main chain of the polymers without damaging the planarity of the conjugated polymers. The combination of PBClT and ITIC produced non-fullerene PSCs with 8.46% PCE and a high V_{oc} of 1.01 V, which were both better than those of the non-chlorine analog, PTB7-Th, whose ITIC device obtained a PCE of only 6.91% and a V_{oc} of 0.82 V, indicating that PBClT, as well as the chlorination of the side chains of the low-band-gap polymers, is a promising material for photovoltaic applications.



Scheme 1. (a) Molecular structures of PTB7-Th and PBClT and (b) synthetic routes to the monomer, BDT-Cl, and the polymer, PBClT: (1) THF, LDA, 0 °C, 2 h; then 2-ethylhexyl bromide, 60 °C, overnight. (2) 3-chloro-2-(2-ethylhexyl)-thiophene, THF, *n*-BuLi, 0 °C, 2 h; benzo[1,2-b:4,5-b′]dithiophene-4,8-dione, 50 °C, 2 h; $SnCl_2 \cdot 2H_2O$, HCl, room temperature, and then 50 °C, overnight. (3) LDA, THF, -78 °C, 4 h; $Sn(CH_3)_3Cl$, -78 °C to room temperature, overnight. (4) Ar, $Pd(PPh_3)_4$, dry toluene/DMF, 120 °C.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic route to the chloro-thienyl-substituted BDT monomer (BDT-Cl) is shown in Scheme 1b. TT-F was prepared according to previous reports.[35, 36] Polymer PBClT was prepared through a Stille cross-coupling reaction using $Pd(PPh_3)_4$ as the catalyst. The molecular weight and polydispersity index (PDI) were determined by high-temperature gel-permeation chromatography (GPC) on an Agilent Technologies PL-GPC 220 instrument using 1,2,4-tricholorobenzene as the eluent at 150 °C. Polymer PBClT was readily soluble in common organic solvents such as chloroform ($CHCl_3$), chlorobenzene (CB) and dichlorobenzene, and exhibited good thermal stability with a decomposition temperature (5% weight loss) of 365 °C in a nitrogen atmosphere, as measured by thermogravimetric analysis (Figure S1).

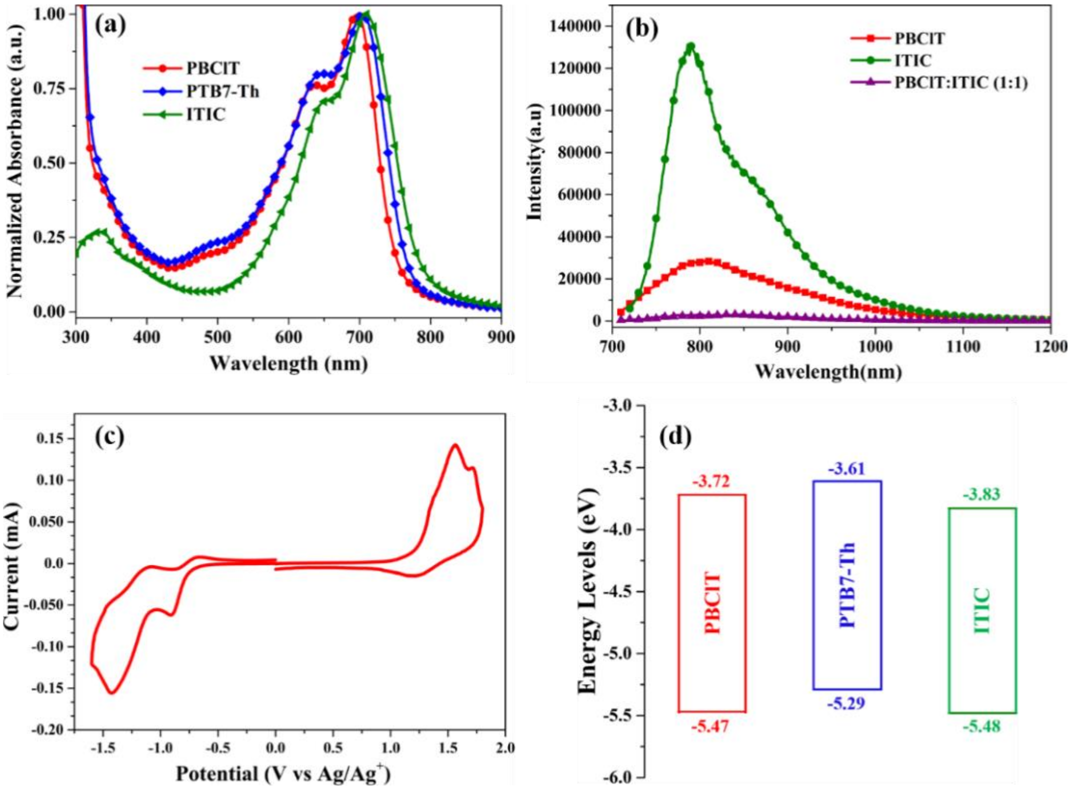


Figure 1. a) Normalized UV-Vis absorption spectra of thin films spin-coated from a chlorobenzene solution; b) photoluminescence spectra of the pure and blend films upon excitation at 700 nm; c) cyclic voltammogram of the PBClT polymer film; and d) energy levels of PBClT, PTB7-Th and ITIC.

The UV-vis absorption spectra of polymers PBClT, PTB7-Th and ITIC in solution (10^{-5} M) and as thin films are depicted in Figure 1a and S1, respectively, and the specific characteristics of the polymer absorption are summarized in Table 1. Polymer PBClT displayed an absorption peak at approximately 691 nm in solution, which was a blueshift of approximately 10 nm relative to the absorption peak of PTB7-Th (Figure S1). Similar to the absorption spectra in solution, as shown in Figure 1a, the absorption of the PBClT film exhibited an absorption peak at approximately 697 nm, which was a slight blueshift of 6 nm relative to that of PTB7-Th. The slight blueshift in the absorbance of PBClT both in solution and as a film implied that the chlorination of the side chains did not create strong steric hindrance that distorted the planarity of the conjugated core and minimally affected the effective conjugated length of the backbone. The optical bandgap of the PBClT polymer film calculated from the film absorption edge according to the equation $E_g^{opt} = 1240/\lambda$ was 1.64 eV, which was slightly larger than that of its non-chlorine analog, PTB7-Th (1.61 eV). To investigate the exciton dissociation and charge transfer behaviors between PBClT and ITIC, the photoluminescence (PL) spectra of the pure and blend films were collected, as shown in Figure 1b. The broad emission peaks of the pure PBClT and ITIC films were located at 800 and 790 nm, respectively. For the blends of PBClT and ITIC with a weight ratio of 1:1, the PL emissions of both PBClT and ITIC were completely quenched, indicating efficient electron transfer from PBClT to ITIC in the blend films. Moreover, the PL results provided obvious evidence that highly efficient hole transfer and separation could easily occur for the nearly identical HOMO energy levels of PBClT and ITIC, as shown in Figure 1d. As displayed in Figure 1c, the onset potentials of reduction and oxidation *vs* $FeCp_2^{+/0}$ (0.44 V) were 0.70 and 1.11 V, respectively, Thus, the LUMO and HOMO energy levels of PBClT were calculated to be -3.72 and -5.47 eV, respectively. As shown in Figure

1d, notably, the HOMO energy level of PBClT (- 5.47 V) was much lower than that of PTB7-Th (- 5.29 V), which could be attributed to the strong resonance effect of the chlorine atoms on the side chains, implying that the solar cells based on this kind of material could have an obviously enhanced open circuit voltage. More interestingly, the UV-vis absorption of PBClT already indicated that the molecular planarity did not change much, with a blueshift of less than 10 nm after chlorine substitution of the side chains. This result indicates that the large change in the HOMO level of the chlorinated PBClT did not result from structural torsion of the polymer backbone, and instead, the change was likely caused by the strong resonance effect of the chlorine atoms on the side chains. In this view, the side chain substitution using larger atoms with strong electron delocalization abilities, such as the chlorine atoms reported here, would be a very important structure rebuilding strategy for enhancing the open circuit voltage without affecting the planarity of the conjugated core.

Table 1. Optical properties and energy levels of the polymers.

Polymer	**Solution**		**Film**			**HOMO (eV)**	**LUMO (eV)**
	λ_{max} (nm)	**λ_{onset} (nm)**	**λ_{max} (nm)**	**λ_{onset} (nm)**	**E_g^{opt} (eV)**		
PBClT	691	731	695	755	1.64	-5.47	-3.72
PTB7-Th	701	764	705	772	1.61	-5.29	-3.61

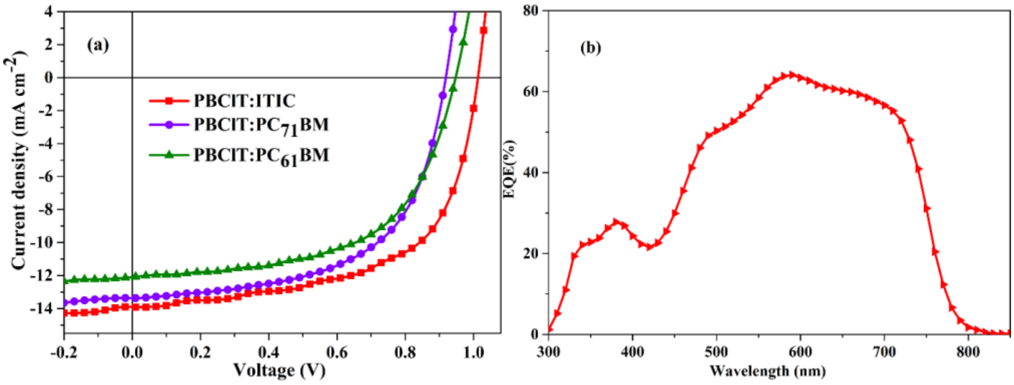


Figure 2. a) J-V curves of PSCs with the structures ITO/ZnO/PBClT:ITIC, PC71BM and PC61BM/MoO3/Ag, and b) EQE spectrum of the PBClT:ITIC (1:1, w/w)-based PSC.

Table 2. Device data of the PSCs based on PBClT:ITIC under AM 1.5G, 100 mW cm^{-2} illumination.

Donor:acceptor (w/w)	**Thickness (nm)**	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF (%)**	**(PCE)$_{max}$(PCE^{a}) (%)**
PBClT:ITIC (1:1.5)	90	1.02	12.89 (12.76±0.22)	57.58 (57.49±1.20)	7.53 (7.38±0.21)
PBClT:ITIC (1:1)	100	1.01	13.95 (13.81±0.15)	60.05 (59.89±1.25)	8.46 (8.33±0.17)
PBClT:ITIC (1.5:1)	95	1.00	12.63 (12.55±0.14)	49.14 (49.03±0.90)	6.23 (6.05±0.12)
PBClT:PC$_{61}$BM (1:1.5)	110	0.95	12.11 (12.02±0.12)	58.20 (58.47±0.90)	6.68 (6.54±0.11)
PBClT:PC$_{71}$BM (1:1.5)	100	0.92	13.25 (13.21±0.15)	59.32 (59.22±1.40)	7.23 (7.14±0.13)
PTB7-Th:ITIC (1:1)	90	0.82	14.76 (14.65±0.22)	57.09 (56.77±1.03)	6.91 (6.80±0.11)

[a] The average PCE was obtained from at least 25 devices.

To evaluate the photovoltaic performance, inverted non-fullerene solar cells were fabricated with a device architecture of ITO/ZnO/PBClT:ITIC/MoO$_3$/Ag, where ITO is indium tin oxide and Ag was used as the cathode. For the devices based on the polymer blended with the ITIC acceptor material, different D/A weight ratios were used to investigate the photovoltaic performance (Figure S3a and Table S1). It was noted that the blend with a D/A weight ratio of 1:1 gave the best performance. CB was chosen as the processing solvent through screening experiments (Figure S3b and Table S2). Moreover, to ensure that the optimized film morphology was achieved for the blends in the active layer, the effect of adding 1,8-diiodiooctane (DIO) as an additive was systematically studied. The detailed data of the optimized device performance are summarized in Table S3, and the current density-voltage (*J-V*) curves are displayed in Figure S3c. The results indicated that the device processed without DIO showed higher Jsc and FF values, and as a result, the PCE was enhanced compared with those of the devices processed with the additive. The photovoltaic performance was independent of the additive, thus indicating that PBClT was potentially a good candidate for commercial applications because it avoided the need for an additive to achieve the optimized device performance. The *J-V* curve and the corresponding data for the PSCs device based on PBClT:ITIC (1:1, wt/wt) under AM 1.5 G, 100 mW cm^{-2} illumination are provided in Figure 2a and Table 2, respectively. The PCE result for a PTB7-Th:ITIC device showed a similar PCE of 6.91%, with a V_{oc} of 0.82 V, a J_{sc} of 14.76 mA cm^{-2} and an FF of 57.09% as reported.[20] However, when Cl atoms were incorporated on the thienyl-substituted BDT units, the photovoltaic performance based on PBClT:ITIC was significantly improved. The PBClT-based device showed a maximum PCE of 8.46% with a better FF of 60.05%, and furthermore, an outstanding V_{oc} of 1.01 V resulting from the deep HOMO energy level. It was clearly observed that attaching chlorine atoms to the side chains of the BDT backbone simultaneously enhanced the crucial parameters of photovoltaic devices, with an especially large enhancement of the V_{oc}, which could be ascribed to the fact that chlorine atoms contain empty 3d orbitals that can accept π-electrons from the conjugated core to adjust the molecular energy levels. Furthermore, it is worth mentioning that the PBClT:ITIC-based devices did not require the addition of any additives or the completion of a post-treatment process, such as thermal annealing or solvent vapor annealing, which greatly simplified the device fabrication procedure. Control devices based on PBClT:PC$_{71}$BM and PBClT:PC$_{61}$BM showed a slightly lower V_{oc} of 0.92-0.95 V and an FF of 0.58-0.59; the PC$_{61}$BM-based device gave a lower J_{sc} of 12.11 mA cm^{-2} and lower average PCE of 6.68%, and the PC$_{71}$BM-based device produced a slightly higher J_{sc} of 13.25 mA cm^{-2} and a higher average PCE of 7.23%, as shown in Table 2. As shown in Figure 2b, to verify the accuracy of the PCE measurements, the corresponding external quantum efficiency (EQE) plots of the device with a PBClT/ITIC weight ratio of 1:1 was measured. This non-fullerene polymer solar cell based on the combination of PBClT and ITIC yielded a broad EQE spectrum from 300 nm to 800 nm, in agreement with the corresponding absorption spectra of the polymers. Moreover, the EQE values in the wavelength range of 560 to 660 nm were observed to be higher than 60%, suggesting efficient photon harvesting and charge collection. The integrated J_{sc} value calculated from the EQE curve was consistent with the J_{sc} value observed in the J-V measurement, and the deviation was within 5%. Charge-carrier mobility is another significant factor for achieving high-efficiency PSC devices. The hole mobilities of the polymers were measured using the space-charge-limited current (SCLC) method with the device structure of ITO/PEDOT:PSS/PBClT:ITIC/MoO_3/Ag. As shown in Figure S4, the hole mobility was calculated to be 2.45×10^{-4} cm^2 V^{-1} s^{-1} for PBClT. Compared with the hole mobility (7.41×10^{-5} cm^2 V^{-1} s^{-1}) of the PTB7-Th-based device, the chlorinated polymer PBClT possessed a relatively higher hole mobility, which could be attributed to the introduction of chlorine atoms and the improved molecular packing, leading to enhanced electron transport. These SCLC results were roughly consistent with the PCE data of the polymers, where a higher μ_{hole} value was beneficial for improving the fill factor in photovoltaic devices.

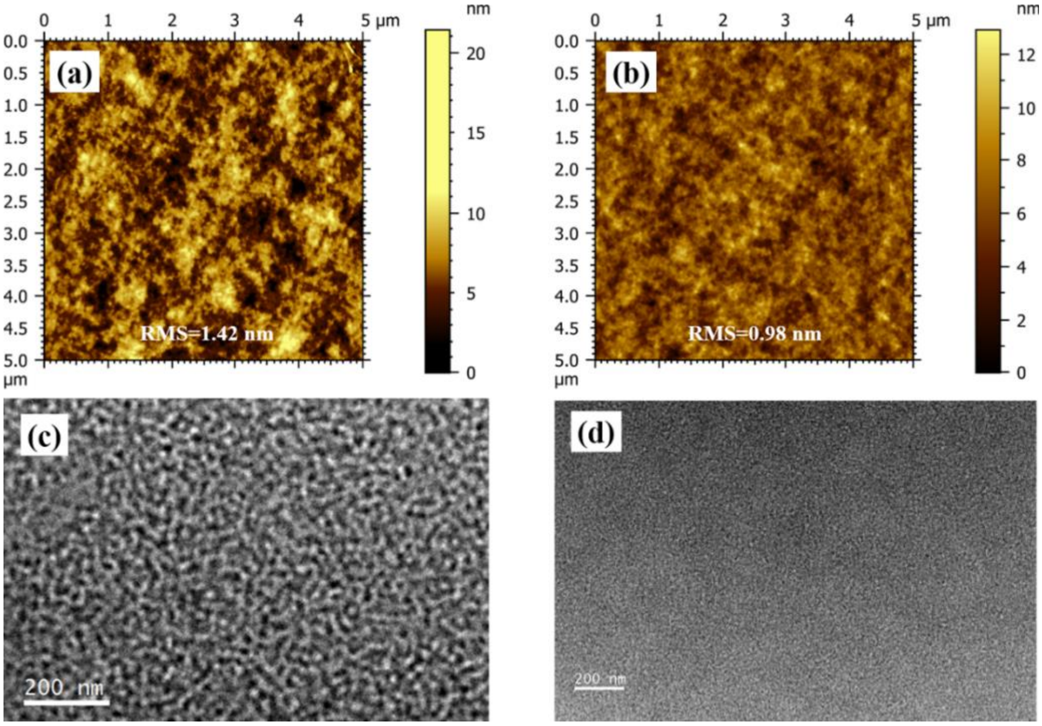


Figure 3. Tapping mode AFM height images (5×5 um) of the blend films of: a) PBClT:ITIC, 1:1, w/w and b) PTB7-Th:ITIC. TEM images of the polymer:ITIC blend films of: c) PBClT:ITIC and d) PTB7-Th:ITIC.

Morphological characterization techniques were carried out to better understand the improved performance of the PBClT:ITIC-based device. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were applied to investigate the microstructure of the PBClT:ITIC blend active layer. As shown in Figure 3a, the blend film of PBClT with ITIC showed a surface roughness with a root-mean-square (RMS) value of 1.42 nm (for PTB7-Th:ITIC, RMS = 0.98 nm, Figure 3b), and a relatively large phase separation, which indicated that the PBClT:ITIC blend film exhibited not only good miscibility but also sufficient interphase connections between the donor and acceptor components. As observed in Figure 3c, the blend film of PBClT:ITIC exhibited fibrous features, and a nanoscale interpenetrating network could be clearly observed from the TEM images, which was greatly beneficial for exciton diffusion to the PBClT:ITIC interface and for charge transfer. The microstructure of PTB7-Th:ITIC (Figure 3d) blend film showed relatively too small phase separation feature size to further improve the performance of PTB7-Th:ITIC based device. As a result, the PBClT-based device showed much better photovoltaic performance than its non-chlorine analog in parallel experiments.

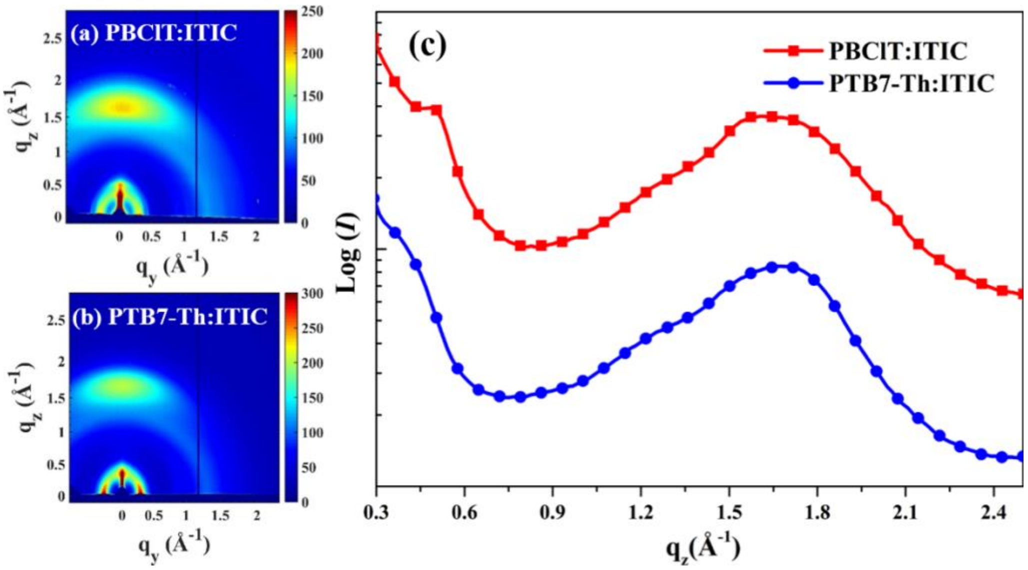


Figure 4. (a) and (b) Two-dimensional GIWAXS patterns of PBClT and PTB7-Th blend films with ITIC. (c) Out-

of-plane line-cut profiles of the GIWAXS patterns. Note that the line-cuts in Figure 4c have been vertically shifted for easy observation.

To comprehensively understand the improved performance of the PBClT-based polymer solar cells, we used the grazing-incidence wide-angle X-ray scattering (GIWAXS) method to further investigate the microstructures of the blend films. The PBClT:ITIC blend film was prepared by spin-coating from chlorobenzene solutions under the same conditions (10 mg mL^{-1}). The GIWAXS images and their corresponding out-of-plane (OOP) line-cuts for the PBClT:ITIC and PTB7-Th:ITIC blend films are shown in Figure 4a, 4b and 4c, respectively. As displayed in Figure 4a and 4b, the PBClT:ITIC blend film showed a broad (010) scattering arc in the out-of-plane direction at $q_z = 1.63$ $Å^{-1}$, while the PTB7-Th:ITIC blend film exhibited a slightly narrower (010) scattering arc in the out-of-plane direction at $q_z = 1.68$ $Å^{-1}$. Both of them corresponded to a preferred face-on packing orientation for the polymer molecules in the films, which is commonly associated with better device performance. Moreover, the π-π stacking distances of PBClT:ITIC and PTB7-Th:ITIC decreased from 3.85 to 3.74 Å, respectively, indicating that the introduction of chlorine did not disturb the π-π stacking of aromatic system significantly, but enhanced the intermolecular interactions of π system. Consequently, charge carrier transport was improved, in consistent with the previous hole mobility tests and device performance data. Both the compact π-π stacking and the face-on molecular orientation facilitated interchain π-electron transport in these chlorinated conjugated polymer films and improved the solar energy conversion in their corresponding solar devices.

CONCLUSIONS

In summary, a new electron donor material, PBClT, with chlorine atoms attached to the side chains of the BDT units was designed and synthesized, and the experimental results demonstrated that the introduction of chlorine atoms was an effective method for developing promising donor materials based on non-fullerene acceptors. The attachment of chlorine atoms to the side chains did not increase the steric hindrance of the conjugated backbone or damage the π-π stacking interactions, and at the same time, the structural design substantially modified the energy levels of the corresponding low-band-gap polymer, especially the HOMO level, through the resonance effect of the chlorine atoms. From this method, the corresponding PBClT:ITIC non-fullerene solar cell showed a high PCE of 8.46% with an outstanding V_{oc} of 1.01 V. In this contribution, the strategy of chlorinating the side chains rather than the main chain of the conjugated polymers provided an alternative method for designing π-conjugated polymer semiconductors that could achieve better control of the polymer energy levels without damaging the intermolecular π-π stacking interactions.

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Notes

The authors declare no competing financial interest.

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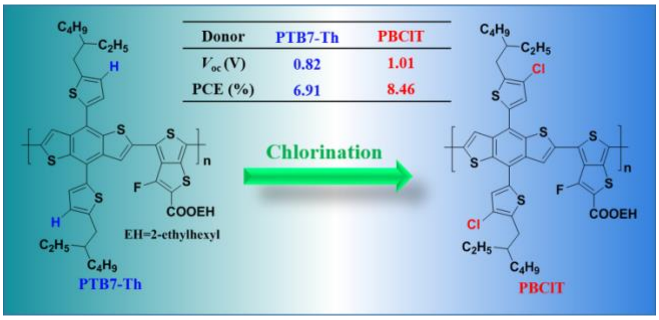

A low-band-gap polymer, PBClT, with chlorine atoms substituted on its side chains was designed and developed for application in non-fullerene solar cells, producing an enhanced open circuit voltage over 1.0 V and an improved power conversion efficiency up to 8.46% when ITIC was used as the acceptor.