Rational Design of Near-Infrared Polymer Acceptors Using Steric Hindrance Strategy for High-Performance Organic Solar Cells

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The unprecedented development of all-polymer solar cells (all-PSCs) is hindered by their low short-circuit current density (Isc), mainly due to the absence of near-infrared (NIR) polymer acceptor materials. To tackle this challenge, a molecular design principle is proposed, which involves the regulation of steric hindrance on the fused-ring backbone to obtain NIR polymer acceptors. Accordingly, three acceptors named PTz-Ph, PTz-Me, and PTz-H are synthesized by substituting the Phenyl, Methyl, and Hydrogen in the beta position of the thiophene unit based on fused-ring molecules. Different from the necessity of steric hindrance of small molecule acceptors in achieving an outstanding performance, polymer acceptor PTz-H without steric hindrance-substitution achieves a record-high efficiency for the benzotriazole-based all-PSCs. Then, introducing PTz-H into the binary PBDB-T:PTz-BO system, the ternary all-PSC exhibits a splendid efficiency of 18.16%, which has surpassed the efficiencies of most benzo[c][1,2,5] thiadiazole-based counterparts. In addition, an organic tandem solar cell is successfully fabricated, which exhibits a high efficiency of 17.49%. This work provides an effective and readily accessible design strategy for designing high-performance NIR polymer acceptors, showing the great potential for future organic photovoltaic applications.

which are expected to contribute toward the development of portable and wearable electronic devices.[1] With the rapid development of polymer acceptors based on Y6-series non-fullerene acceptors (NFAs), the power conversion efficiencies (PCEs) of the state-of-the-art all-PSCs have exceeded 18%.^[2] However, the advancement of all-PSCs has been significantly hindered by the scarcity of polymer acceptors with narrow optical band gaps ($E_g^{opt} < 1.33 \text{ eV}$), thereby severely impeding the endeavor to achieve high short-circuit current density (*I_{sc}*) in all-PSCs.^[3] Thus far, the PCE of all-PSCs based on polymer acceptors with a band gap below 1.33 eV has not exceeded 15%.^[4] Therefore, it is highly desirable to develop highperformance polymer acceptors with small bandgap, in order to surmount the existing photocurrent limitations on efficiency.

Previous advancements achieved in near-infrared (NIR) NFAs provide valuable references for the realization of high-performance polymer acceptors.^[5] For instance, one of the viable

1. Introduction

All-polymer solar cells (all-PSCs) have garnered extensive attention due to their excellent flexibility and mechanical stability,

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strategies involves integrating the benzotriazole unit to substitute the core units of benzo[c][1,2,5]thiadiazole (BT) in the NFAs system, which enhances the intramolecular charge transfer (ICT) effect, in turn, leading to a redshift in the optical absorption range

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Figure 1. a) High-performance non-fullerene small molecule acceptors and their design strategy in the literature. b) Design inspiration of polymer acceptors.

toward the NIR region.^[6] It is noteworthy that the majority of current research in NIR polymer acceptors primarily emphasizes the modulation of conjugated backbones or terminal groups, rather than the substitution of the central core.^[7] A molecular design of NFAs indicates that steric hindrance from outer side chains could reduce excess aggregation of small molecules by reducing the co-planarity between the electron-rich core and the electronaccepting end-groups, which is an effective strategy for regulating molecular interactions and donor-acceptor compatibility (Figure 1a).^[8] In contrast to NFAs, polymer acceptors should have good molecular planarity, thereby enhancing the ICT effect and $\pi - \pi$ stacking ability, ultimately resulting in a diminished energy band gap.^[9] Nevertheless, in polymer acceptors, the investigation of steric hindrance modulation and its consequential influence on molecular crystallinity, intermolecular interaction, and light harvesting performance is still in its infant stage. Therefore, there is a great room for the development of novel polymer acceptor systems with proper steric hindrance to clearly understand the relationship between structure and property, contributing to the achievement of high-performance all-PSCs.

Based on the aforementioned thoughts, we herein present a steric hindrance strategy to effectively modulate both the ICT effect and intermolecular interactions through the straightforward introduction of different alkyl chains onto the polymer acceptor backbone. A series of small-molecule acceptors (SMAs), Tz-H, Tz-Me, and Tz-Ph, were synthesized by incorporating various side chains with distinct steric hindrance into the outer of the DA'D central unit. Subsequently, these SMAs were polymerized with

a thiophene unit to generate the corresponding polymer acceptors, PTz-H, PTz-Me, and PTz-Ph (Figure 1b). It is noticed that these two types of acceptors have opposite trends in the steric hindrance effects. The twisted acceptor Tz-Ph performs well in solar cells due to suppressed aggregation by large steric hindrance and increased LUMO energy level. On the contrary, the highest efficiency is achieved for the device based on the polymer acceptor PTz-H without steric hindrance substitution, which possesses considerable red-shifted absorption and strong π - π stacking interaction. Considering that PTz-H possesses ordered molecular packing and wide-range absorption spectra, which was introduced as a guest into the PBDB-T:PTz-BO binary system. The ternary device obtains a record high efficiency of 18.16%, which even surpasses the PCEs of most benzo[c][1,2,5]thiadiazole (BT)based counterparts. Furthermore, the PTz-H was applied to the tandem solar cell, which yielded a higher PCE of 17.49%. These findings present a promising avenue to explore more efficient NIR polymer acceptors, consequently expediting the advancement of both high-efficiency all-PSCs and tandem solar cells.

2. Results and Discussion

The synthetic routes of target monomers and polymer acceptors are depicted in **Scheme 1**, and the detailed synthetic routes are provided in Supporting Information. Thieno[3,2-b]thiophene (TT) was purchased from Leyan.com. Phenyl, methyl substituted in the beta position of the TT unit were synthesized according to the previously reported literature.^[Sc,10] Compound 1,





Scheme 1. Synthetic route of three polymer acceptors (PTz-X).

compound 5, and compound 9 were synthesized via a Stille coupling reaction between 4,7-dibromo-2-(2-ethylhexyl)-5,6-dinitro-2H-benzo[d][1,2,3]triazole and tributyl(thieno[3,2-b]thiophene-2yl)stannane, compound 4 or compound 8, respectively. These products adopted the double intramolecular Cadogan reductive cyclization to obtain the complete ladder-type fused ring backbone. Next, 11-(bromomethyl)tricosane was introduced to the heptacyclic units under alkaline conditions. Then, the small molecules Tz-H, Tz-Me, and Tz-Ph were obtained via hierarchic sequences of a Vilsmeier-Haack reaction and Knoevenagel condensation reaction. The molecular structure was confirmed by ¹H nuclear magnetic resonance and time-of-flight analyses. Finally, three polymer acceptors, PTz-H, PTz-Me, and PTz-Ph were synthesized by using Stille cross-coupling polymerization of three small molecules and the 2,5-bis (trimethylstannyl) thiophene bridge-unit. The weight-average molecular weights (M_{us}) of three polymer acceptors are in the range of 14-24 kDa as measured by gel permeation chromatography (Figure S1, Supporting Information).

UV-vis absorption spectra of these acceptors were characterized to reveal the steric hindrance effect of side-group modification in SMAs and polymer acceptors. As shown in **Figure 2a**,b, the three SMAs exhibit similar absorption characteristics in solution, while the corresponding polymer acceptors have a significant difference. Especially, as steric hindrance decreases, the maximum absorption peaks (λ_{max}) for the polymer acceptors start to redshift. It can be seen that the impact of steric hindrance regulation on aggregation is more pronounced for polymer acceptors compared to small molecules in the solution state. In comparison to Tz-H in solution, the absorption main peak is red-shifted 80 nm in PTz-H, which can attribute to enhanced ICT effect and better π – π stacking (Figure 2c). For polymer acceptors, the maximum absorption peaks (λ_{max}) start to redshift with reduced steric hindrance, which is located on 827, 832, and 849 nm for PTz-Ph, PTz-Me, and PTz-H, respectively (Figure 2d). Obviously, PTz-H shows a larger red shift than those of PTz-Ph and PTz-Me, which attributes to its planar backbone enhancing ICT effect. The corresponding $E_{\rm g}$ of PTz-Ph, PTz-Me, and PTz-H are 1.36, 1.33, and 1.31 eV, respectively. Compared to PTz-Ph and PTz-Me with larger steric hindrance, the extinction coefficient of PTz-H film exhibits a significant enhancement, increasing from 0.91× 10⁵ cm⁻¹ and 1.10×10⁵ cm⁻¹ to 1.21×10⁵ cm⁻¹ (Figure S2a, Supporting Information). However, as steric hindrance decreases, the absorption of small molecules shows an irregular change, and Tz-H shows a slightly larger $E_{\rm g}$ compared to that of Tz-Me. It should be noted that PTz-H has a narrower $E_{\rm g}$ compared to that of PTz-Me, which is in favor of achieving higher $J_{\rm sc}$ in all-PSCs.^[11] The diverse features indicate that the effect of steric hindrance modulation is different between SMAs and polymer acceptors.

Electrochemical cyclic voltammetry (CV) measurement was performed to determine the lowest unoccupied molecular orbitals (LUMO) levels of these SMAs and polymer acceptors. As demonstrated in Figure 2f and Figures S3 and S4 (Supporting Information), the LUMO levels of PTz-Ph, PTz-Me, and PTz-H are -3.79, -3.81, and -3.84 eV, respectively. All the SMAs show down-shifted molecular energy levels compared with their nonbrominated polymer acceptors. Density functional theory (DFT) calculations (B3LYP functional with 6-31G (d, p) basis set) were performed to evaluate the conformational freedom to understand the effect of different steric hindrances between the central core and terminal group on molecular properties.^[12] As shown in Figure 2e, there are apparent differences in the energy curves against torsion degree among different side groups. By polymerizing NFAs with a thiophene unit, the energy difference (0° and 180°) of TT-H is five times larger than the potential rotamers of TT unit and end-groups in H-substituted small molecules, suggesting that the polymerization could restrict the rotation of the single bonds well.^[13] Thus, even without conformational locking





Figure 2. UV-vis absorption spectra of a) Tz-Ph, Tz-Me, and Tz-H. b) PTz-Ph, PTz-Me, and PTz-H in solution states. c) UV-vis absorption spectra of Tz-H and PTz-H in solution and film states. d) UV-vis absorption spectra of PTz-Ph, PTz-Me, and PTz-H in film states. e) Torsional energy profiles between the central core and terminal group. f) Energy levels for PBDB-T and three polymer acceptors.

by steric hindrance, the structure of polymer acceptors could be well defined. After eliminating the outer side chains, PTz-H has higher co-planarity and ICT absorptivity, thereby facilitating intermolecular charge transport.

To investigate the different steric hindrance effects on photovoltaic performances, the devices were fabricated with a conventional bulk heterojunction (BHJ) structure (ITO/PEDOT:PSS/active layer/PNDIT-F3N/Ag) to evaluate the device performances of the SMAs and polymer acceptors. A wide-bandgap donor PBDB-T was used to match with these polymer acceptors. The detailed device optimizations were provided in Tables S1–S6 (Supporting Information). The optimized current density-voltage (*J*-*V*) curves of three SMA- devices are depicted in Figure S5a (Supporting Information), under simulated AM 1.5 G illumination at 100 mW cm⁻², and the specific photovoltaic parameters are listed in Table S7 (Supporting Information). Compared to Tz-H (without steric hindrance)-based devices, the Tz-Me (with small steric hindrance)-based devices exhibit analogous V_{oc} , but higher J_{sc} and FF, and thus better PCE (14.78% vs 13.16%). The steric hindrance of the Tz-Me is further increased to obtain the small molecule Tz-Ph, whose devices have a higher PCE of 15.41%. On the contrary, there is an opposite trend in terms of the polymer acceptors with the same steric hindrance (**Figure 3** and **Table 1**). When the large steric hindrance is incorporated in polymer acceptors, the PTz-Ph-based device exhibits a high V_{oc} 0.893 V, but the relatively low J_{sc} leads to inferior device performance (12.82%), mainly attributed to the poor crystallinity and enlarged optical bandgap.



Figure 3. a) J-V characteristics of the optimized devices. b) EQE spectra and integrated current densities of the optimized devices. c) Plots of J_{sc} versus E_{σ}^{opt} for the all-PSCs reported in the literature and this work.

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Table 1. Device parameters of the optimized devices.

V _{oc} [V]	$J_{\rm sc}$ [mA cm ⁻²]	FF [%]	PCE [%] ^{max a)}
0.833 (0.832±0.006)	26.43 (26.23±0.30)	75.1 (73.6±1.8)	16.53 (16.28±0.19)
0.843 (0.837±0.007)	24.30 (24.10±0.27)	70.7 (70.3±0.5)	14.48 (14.22±0.22)
0.893 (0.896±0.008)	21.95 (21.80±0.32)	65.4 (65.2 <u>±</u> 0.6)	12.82 (12.56±0.25)
	V _{oc} [V] 0.833 (0.832±0.006) 0.843 (0.837±0.007) 0.893 (0.896±0.008)	V_{oc} [V] J_{sc} [mA cm ⁻²] 0.833 (0.832±0.006) 26.43 (26.23±0.30) 0.843 (0.837±0.007) 24.30 (24.10±0.27) 0.893 (0.896±0.008) 21.95 (21.80±0.32)	V_{oc} [V] J_{sc} [mA cm ⁻²]FF [%]0.833 (0.832±0.006)26.43 (26.23±0.30)75.1 (73.6±1.8)0.843 (0.837±0.007)24.30 (24.10±0.27)70.7 (70.3±0.5)0.893 (0.896±0.008)21.95 (21.80±0.32)65.4 (65.2±0.6)

^{a)} Average values with standard deviation were obtained from 30 devices.

Weakening steric hindrance sequentially in polymer acceptors, photovoltaic performance has been further improved due to the higher J_{sc} and FF. Ultimately, polymer acceptor PTz-H without steric hindrance substitution based on the device obtains a splendid PCE of 16.53% with a high J_{sc} of 26.43 mA cm⁻². Up to now, as shown in Figure 3c and Table S9 (Supporting Information), the J_{sc} is 26.43 mA cm⁻² accompanied by an E_{σ} approaches 1.3 eV, which is rarely reported for all-PSCs. Furthermore, the voltage losses of the three polymer acceptors-based devices were calculated to explore the steric hindrance effect. As shown in Figure S6 (Supporting Information), the BHJ optical bandgaps were estimated from the intersections between the optical absorption spectra and photoluminescence spectra of blend films. Specification of voltage loss follows the Equation below: $\Delta V_{\rm loss}$ $= E_{o}/q V_{oc}$ ^[2a] The PTz-Me-based device suffers a large V_{loss} of 0.585 V, however, a slightly reduced $V_{\rm loss}$ 0.572 V is achieved for the device based on the polymer acceptor PTz-H without steric hindrance substitution. Compared with PTz-H-based devices, PTz-Ph-based device exhibits a lower V_{loss} 0.552 V than those of PTz-H and PTz-Me, which explains the high $V_{\rm oc}$ achieved in PTz-Ph-based devices.

To explain the distinct difference of J_{sc} , the EQE curves were performed for SMAs and polymer acceptors-based devices. In accordance with their bandgaps, the Tz-Me-based device has a wider EQE response than its Tz-Ph and Tz-H counterparts (Figure S5b, Supporting Information), and the integrated current densities have a small error, which is consistent with their I-V curves. Compared to the other devices, the PBDB-T:PTz-H-based device has a broader EQE spectral range and strong photo-response, and a large J_{sc} is thereby obtained (Figure 3b). Compared with PTz-H, PTz-Ph possessing larger steric hindrance shows a shorter absorption spectrum and weaker photo-response. The integrated photocurrents from the EQE spectra agree well with the measured $J_{\rm sc}$ values, with an error ⁵%, which confirmed the reliability of the experimental results. Considering that PTz-H possesses ordered molecular packing and wide-range absorption spectra, three different types of polymer acceptors (Figure S7, Supporting Information), were selected as the host acceptor or the third component to fabricate ternary all-PSCs. The J-V curves of the optimal binary and ternary devices are exhibited in Figures 4a and S8 (Supporting Information), and the related photovoltaic parameters are listed in Table 2 and Table S8 (Supporting Information). When PFFO-Th was chosen as the guest acceptor in PBDB-T:PTz-H-based system, where a slightly increased V_{oc} is achieved, but a decent J_{sc} and FF are afforded, resulting in an ordinary PCE of 14.09%. Then PTz-H as the third component was introduced to the PBDB-T:PA-5 host system, the corresponding devices show a higher PCE of 16.67% compared to those of binary devices, which can be ascribed to simultaneously improved

 $J_{\rm sc}$ and FF. Subsequently, when PTz-BO was selected as the host acceptor for blending with PBDB-T, and PTz-H as the guest acceptor, the optimal ternary device yielded an outstanding PCE of 18.16%, with a $V_{\rm oc}$ of 0.887 V, a $J_{\rm sc}$ of 26.80 mA cm $^{-2}$ and an FF of 76.4%. To the best of our knowledge, the PCE of 18.16% represents the highest efficiencies for benzotriazole-based all-PSCs reported thus far, which even surpasses the PCEs of most BT-based counterparts. For a highly efficient ternary system, the related EQE spectra of ternary and binary all-PSCs are displayed in Figure 4b, with the incorporation of PTz-H, the ternary device shows a higher photo-response in the wavelength ranges of 400–920 nm in comparison with the binary devices. And the edge of the EQE curve is also slightly red-shifted, which contributes to the improved $J_{\rm sc}$. Note that the $J_{\rm sc}$ of 26.80 mA cm $^{-2}$ and PCE of 18.16% are the highest values for all-PSCs to date (Figure 4c).

Inspired by a small band gap of 1.31 eV, a tandem device was fabricated by using it as a rear cell. The detailed characterization information is provided in Supporting Information. The tandem device structure is shown in Figure 4d, in which D18:FBr-ThCl system as a front cell.^[14] As shown in Figure 4e, the optimal tandem solar cell exhibits an outstanding PCE of 17.49%, with a $V_{\rm oc}$ of 1.831 V, a J_{sc} of 12.95 mA cm⁻² and an FF of 73.78%. This successful attempt benefits from the complementary absorption between the front cell and the rear cell. To verify the matching behavior of the subcells in tandem devices, EQE measurement was carried out as presented in Figure 4f. The integrated J_{sc} value is 12.91 mA cm⁻² for the front cell, and its EQE curve has a strong response in 500-700 nm. The rear cell shows a broad EQE spectrum to 950 nm with higher response values in 750-900 nm, and the integrated I_{sc} value is 12.92 mA cm⁻². The well-balanced integrated I_{sc} agreed with the value obtained from the I-V measurement, which is ascribed to the complementary absorption range.

To explore the charge transport properties of three polymer acceptors with different steric hindrances, space-charge-limited current (SCLC) measurements were carried out.[15] The hole-only and electron-only device structures are ITO/PEDOT:PSS/active layers/MoO₃/Ag and ITO/ZnO/active layers/PNDIT-F3N/Ag, respectively. As shown in Figure S9 (Supporting Information), the average electron mobility ($\mu_{\rm e}$) value of PTz-Ph film is 2.70 × 10⁻⁴ $cm^2 V^{-1} s^{-1}$, which is lower than the neat films of PTz-Me (4.37 $\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and PTz-H (4.95 $\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Thus we speculated that a high μ_e is obtained due to the small steric hindrance in polymer acceptors, which causes a more ordered molecular stacking in thin films. This agrees well with the GI-WAXS results in the described above. Then, the hole mobility $(\mu_{\rm b})$ and $\mu_{\rm e}$ of the all-polymer blends were measured, which were estimated to be $2.43 \times 10^{-4}/1.96 \times 10^{-4}, \, 3.91 \times 10^{-4}/3.21 \times 10^{-4},$ and 4.0 \times $10^{-4}/3.58 \times 10^{-4}~cm^2~V^{-1}~s^{-1}$ for the PBDB-T:PTz-Ph, PBDB-T:PTz-Me, and PBDB-T:PTz-H-based devices with the

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0.2

Aq

PBDB-T:PTz-H

PMA

PEDOT:PSS

ZnO

D18:FBr-ThCl

PNDIT-F3N

PBDB-T:PTz-BO

PBDB-T:PTz-BO:PTz-H PBDB-T:PTz-H

0.4

Voltage (V)

0.6

0.8

Current Density (mA cm⁻²)

-3

-6

-9

-12

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(a)

Current Density (mA cm⁻²)

0

-5

10

-15

-20

-25

(d)

0.0



60

40

20

EQE (%)



PBDB-T:PTz-H, and PBDB-T:PTz-BO:PTz-H. c) Comparison of this work with reported J_{sc} of the all-PSCs with PCEs over 15% in the literatures. d) architecture of tandem OSC. e) J-V curve and f) EQE spectra of the tandem solar cell.

/..= 1.831 V

FF = 73.78%

PCE =17.49%

 $J_{co} = 12.95 \text{ mA cm}^{-2}$

corresponding $\mu_{\rm h}/\mu_{\rm e}$ ratios are 1.24, 1.22, and 1.12, respectively. The most balanced carrier mobility in the PTz-H blend is beneficial to charge transport, which partially contributes to the high $J_{\rm sc}$ and FF achieved in the all-PSCs.^[16]

The photocurrent density ($J_{\rm ph}$) versus effective voltage ($V_{\rm eff}$) of all-PSCs with three polymer acceptors were tested to study the effect of different polymer acceptors on the charge generation and dissociation process. $J_{\rm ph}$ is defined as $J_{\rm ph} = J_{\rm L} - J_{\rm D}$, where $J_{\rm L}$ and $J_{\rm D}$ are current densities that measure under illumination and darkness. $V_{\rm eff}$ is calculated through the difference between V_0 and $V_{\rm a}$, where V_0 is the voltage under $J_{\rm ph} = 0$ and $V_{\rm a}$ is the applied bias voltage.^[17] The $J_{\rm ph}/J_{\rm sat}$ values under the short-circuit conditions were used to calculate the exciton dissociation and charge collection probability ($P(\rm E,T)$) of these devices. As shown in Figure S10a (Supporting Information), among the all-PSCs, $J_{\rm ph}$ of the PBDB-T:PTz-H-based device reaches saturation is fastest, manifesting that all of the photogenerated excitons are dissociated and collected, more efficiently than those of PBDB-T:PTz-Ph and PBDBT:PTz-Me-based devices. A high $J_{\rm ph}/J_{\rm sat}$ value

of 97.8% was estimated for PTz-H-based device, higher than the PTz-Ph-based device (92.4%), indicating that the PTz-H-based device could improve charge extraction and suppress carrier recombination significantly. Then, J_{sc} and V_{oc} versus light intensity (P_{light}) were plotted to investigate the charge recombination process.^[18] As presented in Figure S10b,c (Supporting Information), the recombination parameter *S* in the PTz-H-based device is 0.989 in the power-law dependence of $J_{sc} \propto P_{light}$, with the *S* close to 1, indicating negligible bimolecular recombination. Furthermore, the slopes of the V_{oc} versus P_{light} curves are 1.25 kT/q, 1.39 kT/q, and 1.40 kT/q for PTz-H, PTz-Me, and PTz-Ph-processed devices, respectively. The smallest slope value suggests that trapassisted recombination was suppressed in the PBDB-T:PTz-H-based device.

The molecular orientation and crystallinity of the pure films were performed to explore the influence of alkyl chain substitution with different steric hindrances. Figure S11a (Supporting Information) displays the 2D grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of pristine films, and the

Table 2. Device parameters of	of the optimized	binary and	ternary devices.
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Devices	V _{oc} [V]	$J_{\rm sc}$ [mA cm ⁻²]	FF [%]	PCE [%] ^{max a)}
PBDB-T:PTz-H	0.833 (0.832±0.006)	26.43 (26.23±0.30)	75.1 (73.6±1.8)	16.53 (16.28±0.19)
PBDB-T:PTz-BO	0.920 (0.918±0.008)	23.86 (23.70±0.32)	71.6 (71.2±0.6)	15.72 (15.46±0.23)
PBDB-T:PTz-BO:PTz-H	0.887 (0.882±0.006)	26.80 (26.62±0.30)	76.4 (75.6±1.0)	18.16 (17.86±0.25)

^{a)} Average values with standard deviation were obtained from 30 devices.

=12 92 mA

=12.91 mA cm

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Figure 5. a) 2D GIWAXS patterns of blend films, and b) the corresponding in-plane and out-of-plane line cuts.

corresponding line-cut profiles are shown in Figure S11b (Supporting Information). As shown in Figure S11b (Supporting Information), these neat films show similar (100) peaks at 0.37 $Å^{-1}$ in the in-plane (IP) direction, nevertheless, the (010) peaks have significant differences in the out-of-plane (OOP) direction with reduced steric hindrance. The PTz-Ph film exhibits a broad diffraction peak with the smallest crystal coherence length (CCL) of 42.0 Å in this series, thus it bears the lowest $\pi - \pi$ stacking for large steric hindrance decoration. The polymer acceptors are well conformed into a face-on orientation as indicated by distinct (010) peaks in the OOP direction. A weak (010) diffraction is seen in out-of-plane diffraction profile for PTz-Ph, suggesting that PTz-Ph has low molecular crystallinity. However, PTz-H shows the highest (010) diffraction intensity among the three polymer acceptors, demonstrating that weakening steric hindrance can enhance the interchain interaction and π - π stacking. To correlate the different crystalline behavior caused by various steric hindrances with the photovoltaic performance, all three polymer acceptors-based blend films were also characterized (Figure 5). After mixing with PBDB-T, all the blend films are preferentially face-on oriented in terms of π - π stacking peak locations, which are conducive to carrier transport.^[19] In comparison to PBDB-T:PTz-Ph and PBDB-T:PTz-Me blends, PBDB-T:PTz-H blend has

the highest degree of molecular crystallinity. The corresponding CCL associated with π – π stacking in the OOP direction are calculated to be 12.50, 19.90, and 20.63 Å for PBDBT:PTz-Ph, PBDB-T:PTz-Me, and PBDB-T:PTz-H, respectively. The morphology of the blend films was investigated by atomic force microscopy (AFM). As shown in Figure S12a–f (Supporting Information), PBDB-T:PTz-Me and PBDB-T:PTz-H devices show uniform fibrillar texture with similar root-mean-square (RMS) roughness of 1.32 and 1.48 nm compared to that of PBDBT:PTz-Ph blend (1.88 nm). These results demonstrate that weakening the steric hindrance of side-groups and terminal-group can regulate the molecular aggregation and further optimize morphology, and thus promoting charge generation and exciton dissociation.^[20]

3. Conclusion

In conclusion, we proposed a new strategy for achieving different optical bandgaps by regulating steric hindrance on the backbone of polymer acceptors, rather than lengthening the conjugate backbone or attaching halogens to the terminal groups. Different from the importance of the steric hindrance of small molecule acceptors in achieving an outstanding performance, polymer acceptors with small hindrances exhibit strong ICT effects and ADVANCED SCIENCE NEWS www.advancedsciencenews.com

intermolecular interaction, as well as significant bathochromic absorption. Benefitting from the remarkable light harvesting, polymer acceptor PTz-H performs well in all-PSCs, delivering the highest PCE of 16.53% for benzotriazole-based devices. In the PBDB-T:PTz-BO binary system, adding PTz-H as a third component improved photon utilization in the NIR region, the optimal ternary device exhibited an outstanding PCE of 18.16%, which represented one of the highest PCE values reported for all-PSCs to date. To probe the potential application of the NIR polymer acceptors, we further fabricated tandem solar cells, which produced an outstanding PCE of 17.49%. Our results demonstrated an effective strategy toward promising near-infrared polymer acceptors by investigating steric hindrance in polymer acceptors, revealing the significant potential to satisfy requirements for many applications with NIR polymer acceptors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

all-polymer solar cells, efficiency, near-infrared, polymer acceptor, steric hindrance

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