

Drastic Effect of Alkylation Position in Structurally Simple Benzobisthiazole–Terthiophene Copolymers on the Performance of Nonfullerene Organic Photovoltaics

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Itaru Osaka

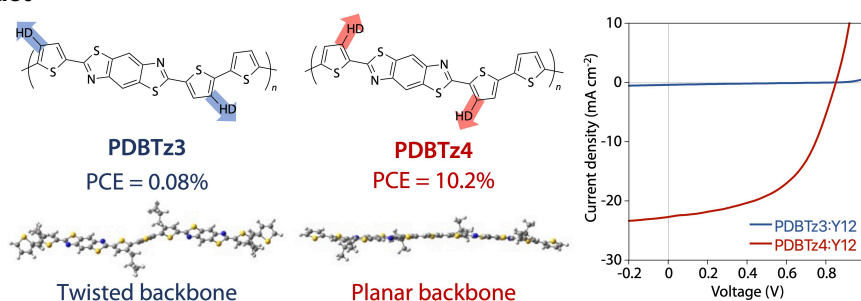
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Abstract

The development of cost-effective, high-performance polymer donors is essential for advancing the large-scale commercialization of organic photovoltaic cells (OPVs). Herein, we report photovoltaic performance of two structurally simple benzobisthiazole (BBTz)–terthiophene copolymers, **PDBTz3** and **PDBTz4**, in which the alkyl groups are introduced at the outer and inner β -positions of the thiophene rings flanking the BBTz core, respectively. Notably, when blended with the nonfullerene acceptor Y12, **PDBTz3** showed almost no photovoltaic effect, while **PDBTz4** showed a power conversion efficiency of 10.2%. A comprehensive investigation, in combination with optical, morphological, and computational analysis, revealed that this subtle variation in alkylation position drastically effects on backbone planarity, molecular packing, and donor–acceptor interfacial energetics. In polymer:Y12 blend film, **PDBTz3** adopts a highly twisted backbone conformation, leading to an unfavorable energy level alignment and inefficient hole transfer, while **PDBTz4** maintains a coplanar backbone, enabling a favorable energy level alignment and efficient hole transfer. Consequently, **PDBTz4** showed superior photovoltaic performance compared to **PDBTz3**. These findings highlight the critical role of alkylation position engineering in polymer design and provide a useful strategy for developing cost-effective, high-performance materials for next-generation OPVs.

Keywords: π -Conjugated materials, Semiconducting polymers, Organic photovoltaic cells

Graphical Abstract



1. Introduction

Organic photovoltaic cells (OPVs) have emerged as promising candidates for future renewable energy technologies due to their unique advantages, including mechanical flexibility, lightweight, semitransparency, solution processability, and the potential for low-cost fabrication.^{1,2,3} Continuous improvements in the power conversion efficiency (PCE) of OPV have been primarily driven by advances in donor-acceptor (D-A) type semiconducting polymers and nonfullerene acceptors (NFAs), which serve as p-type and n-type materials, respectively.^{4,5,6,7,8} A common molecular design strategy for achieving high-performance semiconducting polymers is the incorporation of π -extended, multi-fused heteroaromatic rings into the polymer backbone.^{9,10} These π -extended structures provide rigid backbones and strong interchain interactions, resulting in superior electronic and optical properties essential for efficient photovoltaic performance.^{11,12} In addition, halogen atoms are often introduced into heteroaromatic rings to finely tune the electronic properties of polymers, allowing for better energy level alignment with NFAs.¹³ Indeed, most state-of-the-art polymers, such as PM6 and D18, incorporate one or more multi-fused heteroaromatic rings with halogen atoms—most notably the widely used benzodithiophene (BDT) unit (Fig. 1a).^{14,15} Whereas these structural motifs are crucial for achieving high efficiency, they also introduce significant synthetic complexity. In fact, PM6 and D18 require lengthy synthetic routes (≥ 15), posing a major barrier to industrial scalability and cost-effective large-scale production.

On the other hand, several structurally simple benzoheterodiazoles–thiophene copolymers, such as PTQ10, PTQ11, and FO6-T, have been developed to overcome these synthetic limitations (Fig. 1b).^{16,17,18,19} By employing the readily accessible monomer distannylated thiophene in place of distannylated BDT, these polymers can be synthesized in significantly fewer steps (≤ 10) compared to PM6 and D18, while still achieving competitive PCEs in the range of 15–19%.^{20,21} In parallel, thiazole-based fused rings, such as thiazolo[5,4-*d*]thiazole (TzTz) and benzo[1,2-*a*:4,5-*d'*]bisthiazole (BBTz), have attracted attention as promising building units for cost-effective, high-performance polymers, owing to the straightforward synthesis of their thiophene-flanked derivatives.^{22,23,24} Moreover, these cores enhance backbone rigidity and interchain interactions due to both their π -extended multi-fused heteroaromatic rings and the intramolecular S...N noncovalent interactions.²⁵ Notably, a simple TzTz–terthiophene copolymer bearing alkyl groups, PTTz-3HD, synthesized in only seven steps starting from commercially available materials, has demonstrated PCEs exceeding 16% in NFA-based OPV cells (Fig. 1c).²⁶ More recently, our group reported TzTz–terthiophene copolymers bearing ester groups PTz3TE achieved even higher PCEs of over 17%.²⁷ Encouraged by these reports, we turned our attention to BBTz–terthiophene copolymers as a new class of donor materials for NFA-based OPVs. Given that BBTz-based polymers inherently exhibited significantly deeper HOMO energy level than their TzTz-based counterparts, we assumed that

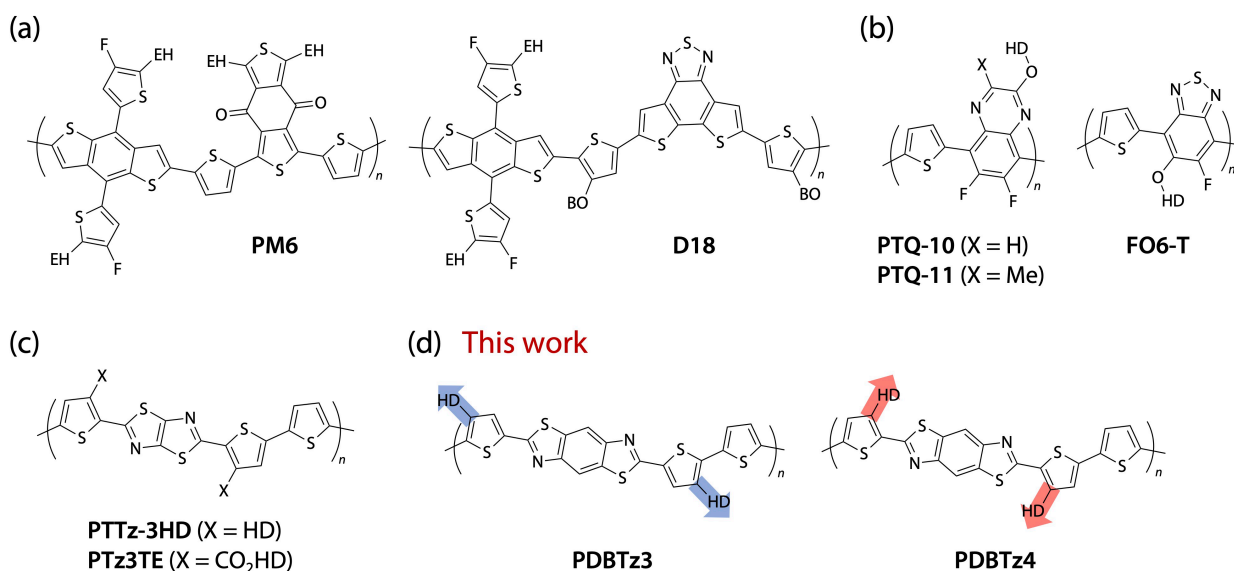
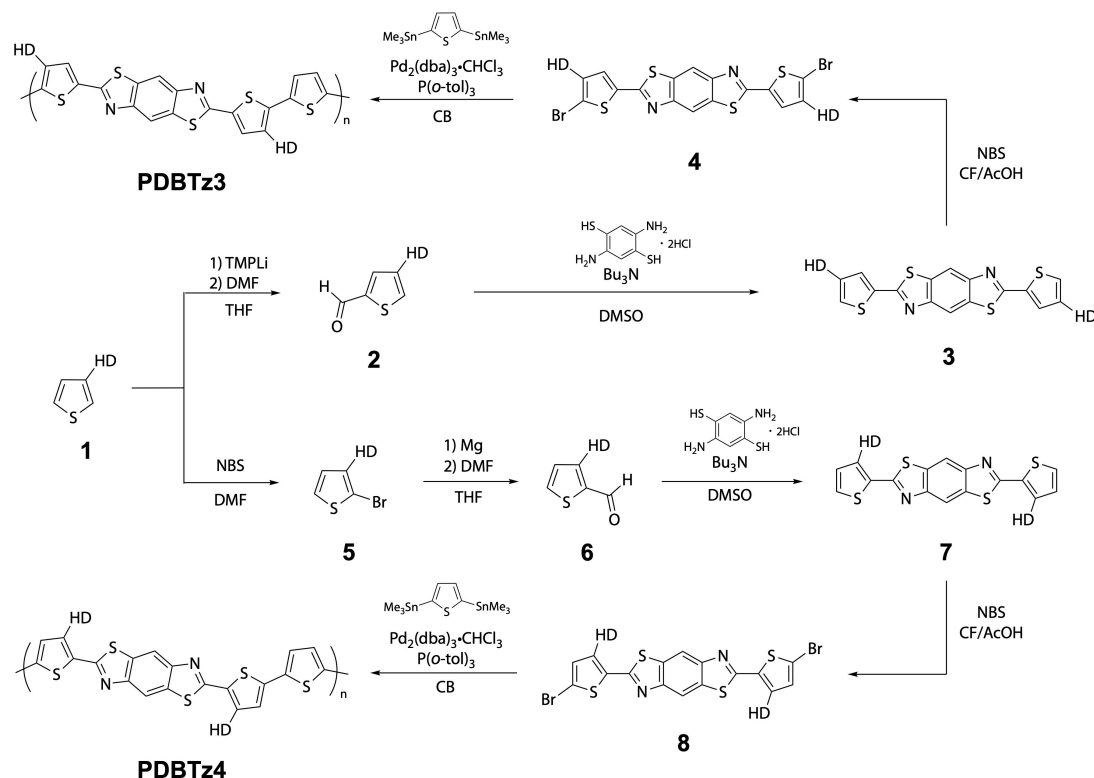


Fig. 1 Chemical structures of (a) representative polymers PM6 and D18, (b) benzoheterodiazoles–thiophene copolymers PTQ-10, PTQ-11, and FO6-T, (c) TzTz–terthiophene copolymers bearing alkyl and ester groups PTTz-3HD and PTz3TE, and (d) BBTz–terthiophene copolymers PDBTz3 and PDBTz4. EH = 2-ethylhexyl, BO = 2-butylloctyl, and HD = 2-hexyldecyl group.



Scheme 1. Synthetic route to **PDBTz3** and **PDBTz4**. HD = 2-hexyldecyl group.

1 incorporating electron-donating alkyl group would be
 2 more effective than incorporating the electron-
 3 withdrawing ester group in optimizing energy level
 4 alignment with NFAs.²⁸ Herein, we report two BBTz-
 5 terthiophene copolymers **PDBTz3** and **PDBTz4**, which
 6 differ only in the alkylation position on the thiophene
 7 units adjacent to the BBTz core (Fig. 1d). Interestingly,
 8 when paired with NFA Y12, **PDBTz3** showed a twisted
 9 backbone conformation, while **PDBTz4** showed a more
 10 planar rigid backbone conformation. This difference
 11 resulted in more efficient hole transfer in **PDBTz4** than
 12 in **PDBTz3**. Consequently, **PDBTz4** showed superior
 13 photovoltaic performance compared to **PDBTz3**. Our
 14 findings reveal that subtle changes in the alkylation
 15 position in BBTz-terthiophene copolymers can
 16 significantly affect polymer ordering and, in turn,
 17 modulate the electronic structure in the polymer:Y12
 18 blend films.

20 **2. Results and discussion**

21 **2-1. Polymer synthesis**

22 Scheme 1 illustrates the synthetic route to BBTz-
 23 terthiophene copolymers. Formylation at the 5-position
 24 of 3-(2-hexyldecyl)thiophene **1** was achieved via
 25 lithiation using tetramethylpiperidyl lithium (TMPLi),
 26 followed by treatment with *N,N*-dimethylformamide
 27 (DMF), affording aldehyde **2**.²⁸ On the other hand,

28 formylation at the 2-position of **1** was achieved via
 29 bromination using *N*-bromosuccinimide (NBS) in DMF
 30 to afford intermediate **5**, followed by Grignard reagent
 31 formation using magnesium and subsequent treatment
 32 with DMF, affording aldehyde **6**.²³ We note that
 33 attempts to formylate **1** using the Vilsmeier-Haack
 34 reagent, generated in situ from phosphoryl chloride
 35 (POCl₃) and DMF, resulted in the mixture of **2** and **6**.
 36 Condensation of aldehydes **2** and **6** with 2,5-
 37 diaminobenzene-1,4-dithiol dihydrochloride in dimethyl
 38 sulfoxide (DMSO) provided the alkylthiophene-flanked
 39 BBTz derivatives **3** and **7**, respectively. Subsequent
 40 dibromination of **3** and **7** using NBS in a chloroform
 41 (CF)/acetic acid (AcOH) co-solvent system furnished
 42 the corresponding monomers **4** and **8**, respectively.
 43 Finally, **4** and **8** were copolymerized with 2,5-
 44 bis(trimethylstannyl)thiophene in chlorobenzene (CB) via
 45 the Stille coupling reaction using Pd₂(dba)₃·CHCl₃ and
 46 P(*o*-tol)₃ as the catalyst system, to afford **PDBTz3** and
 47 **PDBTz4**. Molecular weights were evaluated by high-
 48 temperature gel permeation chromatography (GPC)
 49 using trichlorobenzene (TCB) as the eluent at 180 °C.
 50 The number-average molecular weight (*M_n*) and a
 51 dispersity (*D*) were 38,600 and 1.6 for **PDBTz3**, and
 52 40,300 and 2.3 for **PDBTz4**, respectively (Fig. S1, Table
 53 S1). Remarkably, both polymers exhibited high
 54 solubility, dissolving immediately upon the addition of

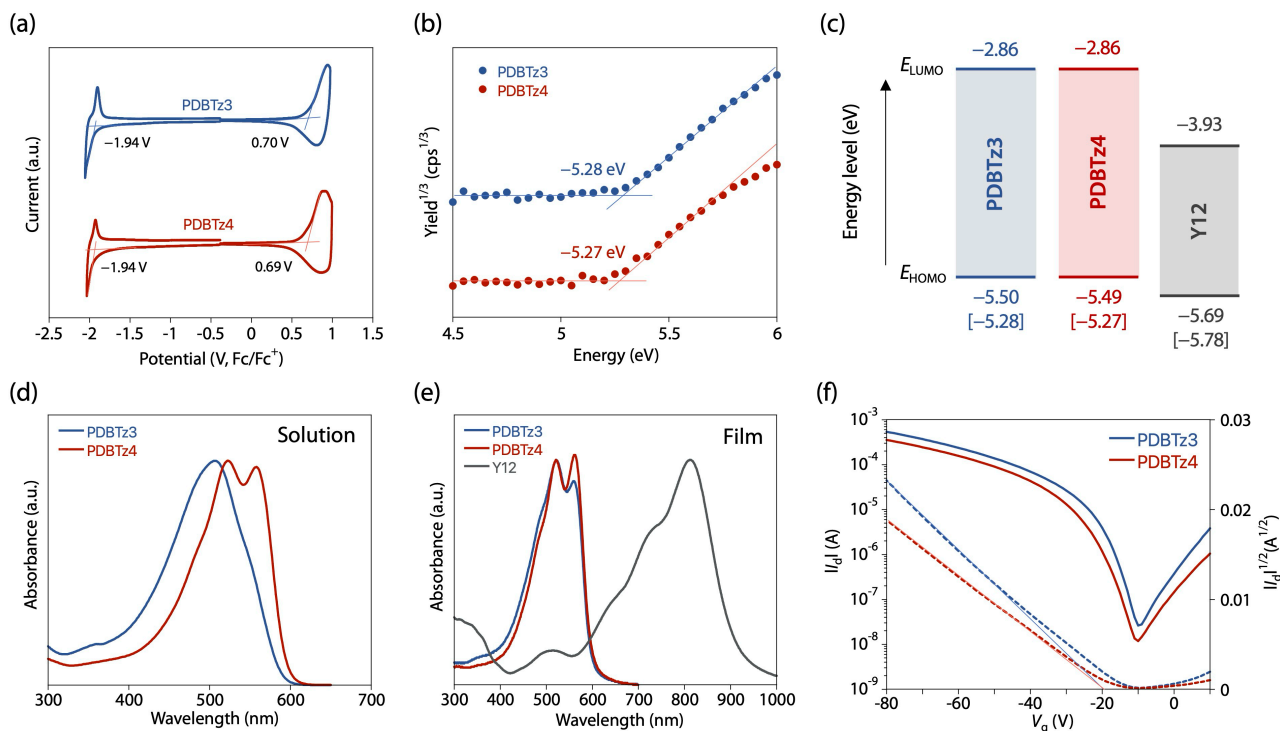


Fig. 2 (a) Cyclic voltammograms and (b) PYS of the polymer neat films. (c) Energy diagrams of the polymers along with Y12. The value in brackets is the E_{HOMO} determined by the PYS measurement. UV-Vis absorption spectra of the polymers in (d) CB solution and (e) in thin films. (f) Transfer curves of OFET devices based on the polymers.

Table 1. Properties of the polymers in thin films.

Polymer	E_{HOMO} (eV) ^a	E_{LUMO} (eV) ^c	λ_{max} (nm)	λ_{edge} (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^d	μ_{h} (cm ⁻² V ⁻¹ s ⁻¹) ^e
PDBTz3	-5.50 [-5.28] ^b	-2.86	521, 561	595	2.08	0.19
PDBTz4	-5.49 [-5.27] ^b	-2.86	521, 560	596	2.08	0.13

^aEstimated with $E_{\text{HOMO}} = -4.80 - E_{\text{ox}}^{\text{onset}}$. ^bThe E_{HOMO} determined by PYS measurement. ^cEstimated with $E_{\text{LUMO}} = -4.80 - E_{\text{red}}^{\text{onset}}$. ^dOptical bandgap determined from the absorption onset. ^eMaximum charge carrier mobility.

1 chloroform even at room temperature, despite BBTz
2 being a π -extended building unit lacking any solubilizing
3 substituents.

2-2. Polymer properties

6 The energy levels of the polymer in thin film were
7 evaluated by cyclic voltammetry (CV) and
8 photoemission yield spectroscopy (PYS)
9 measurements, as shown in Figs. 2a and 2b,
10 respectively. The extracted energy levels, along with
11 those of a benchmark NFA Y12, are summarized in Fig.
12 2c and Table 1. The HOMO and LUMO energy levels
13 (E_{HOMO} and E_{LUMO} , respectively) were determined from
14 the onset redox potentials observed in the cyclic
15 voltammograms, calibrated with the
16 ferrocene/ferrocenium (Fc/Fc⁺) redox couple. For
17 **PDBTz3**, the onset oxidation and reduction potentials
18 were 0.70 and -1.94 V, while those for **PDBTz4** were
19 0.69 and -1.94 V, respectively. These values

20 corresponded to E_{HOMO} and E_{LUMO} of -5.50 and -2.86
21 eV for **PDBTz3** and -5.49 and -2.86 eV for **PDBTz4**.
22 These results indicate that the positional variation of the
23 alkyl side chains exerts negligible influence on the
24 frontier energy levels in the polymer neat films. The
25 similarity in E_{HOMO} values was further confirmed by PYS
26 measurements, which yielded -5.28 eV for **PDBTz3**
27 and -5.27 eV for **PDBTz4**, in good agreement with the
28 CV results. Moreover, these experimental results were
29 also consistent with density functional theory (DFT)
30 calculations at the B3LYP 6-31G(d) level (Fig. S2).
31 Collectively, both polymers possess sufficient E_{HOMO}
32 offset with Y12 to enable efficient hole transfer from
33 Y12 to the polymer.

34 The UV-Vis absorption spectra of the polymers in
35 CB solution and as thin films are shown in Figs. 2d and
36 2e, and the optical parameters in thin film are listed in
37 Table 1. In solution, **PDBTz3** exhibited a broad,
38 featureless absorption band with an absorption maxima

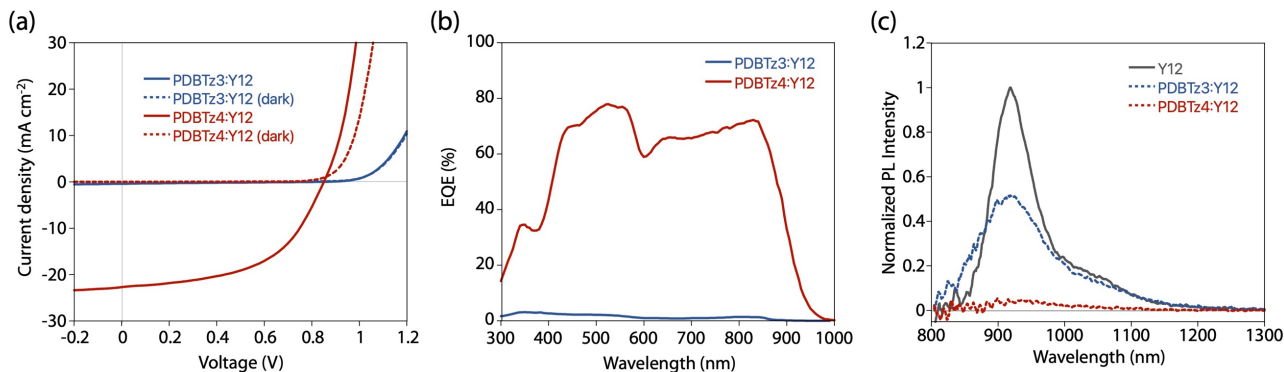


Fig. 3 (a) J - V curves and (b) EQE spectra of the polymer:Y12 cells. (c) PL spectra of Y12 neat film and polymer:Y12 blend films upon excitation at 680 nm (Y12 excitation).

Table 2. Photovoltaic parameters of the polymer:Y12 cells.

Polymer	J_{sc} [J_{sc}^{EQE}] (mA cm ⁻²) ^a	V_{oc} (V)	FF	PCE _{max} (%)	PL quenching efficiency (%) ^c
PDBTz3	0.41 [0.46]	0.84	0.22	0.08 [0.06] ^b	20
PDBTz4	22.7 [23.0]	0.85	0.53	10.2 [9.9] ^b	95

^aThe value in bracket is the calculated J_{sc} from EQE spectra. ^bThe value in bracket is the average PCE of 10 devices. ^cExcited at 680 nm (Y12 excitation).

(λ_{max}) at 506 nm, whereas **PDBTz4** exhibited two absorption peaks with λ_{max} values at 558 and 527 nm, corresponding to the 0-0 and 0-1 transitions, respectively (Fig. 2d). These features suggest that **PDBTz3** possesses a highly twisted backbone in solution, which disrupts π -conjugation and leads to a blue-shifted absorption, while **PDBTz4** possesses a more coplanar backbone and exhibits a stronger intermolecular aggregation. In thin films, both polymers showed similar absorption profiles, with 0-0 and 0-1 transition peaks at 561 and 521 nm for **PDBTz3** and at 560 and 521 nm for **PDBTz4**, respectively (Fig. 2e). The optical bandgap (E_g^{opt}), estimated from the absorption onset (λ_{onset}), was 2.08 eV (λ_{onset} = 595 nm) for **PDBTz3**, which was comparable to that for **PDBTz4** (E_g^{opt} = 2.08 eV, λ_{onset} = 596 nm). The absorption range of both polymers were complementary to that of Y12, which are beneficial for efficient light harvesting in blend films. We note that the 0-0/0-1 intensity ratio (I_{0-0}/I_{0-1}) was higher in **PDBTz4** (1.02) than in **PDBTz3** (0.9). In addition, **PDBTz4** exhibited a slightly shaper absorption band than **PDBTz3**. These results suggest that, although the backbone coplanarity of **PDBTz3** increased significantly upon film formation, **PDBTz4** consistently maintains a more coplanar backbone.²⁹

The charge transport properties of the polymers were investigated by fabricating organic field-effect transistor (OFET) device using top-gate/bottom-contact (TG/BC) architecture. The transfer curves showed that both polymers exhibited unipolar p-type behavior, with relatively low threshold voltage of approximately -20 V and relatively high current on/off ratios in order of 10⁴ (Fig. 2f and Fig. S3). **PDBTz3** demonstrated a hole

mobility (μ_h) of 0.19 cm² V⁻¹ s⁻¹, which was slightly higher than that of **PDBTz4** (0.13 cm² V⁻¹ s⁻¹) (Table 1).

2-3. Photovoltaic characteristics

OPV cells were fabricated using a conventional architecture of ITO/PEDOT:PSS/active layer/PNDIT-F3N-Br/Ag. The active layers were spin-coated from a 5.0 g L⁻¹ CF solutions of polymer:Y12 blends at 1:1.2 weight ratio, containing 0.5% (v/v) diphenyl ether as an additive. Figs. 3a and 3b show the current density-voltage (J - V) curves and external quantum efficiency (EQE) spectra of the cells, and the photovoltaic parameters are listed in Table 2. Remarkably, the **PDBTz3** cells showed almost no photovoltaic effect, while the **PDBTz4** cell showed power conversion efficiency (PCE) of 10.2% with a short-circuit current density (J_{sc}) of 22.7 mA cm⁻², open-circuit voltage (V_{oc}) of 0.85 V, and fill factors (FF) of 0.53 (Figure 3a). In agreement with these results, the maximum EQE for the **PDBTz3** cell was 3% at 350 nm, while that for the **PDBTz4** cells reached 79% at 520 nm (Fig. 3b). The integrated J_{sc} values calculated from EQE spectra were consistent with those obtained from the J - V measurements.

The stark contrast in photovoltaic performance was further investigated through photoluminescence (PL) quenching studies of the polymer:Y12 blend films (Fig. 3c, Table 2). When excited at 560 nm (polymer excitation), nearly complete PL quenching was observed for both **PDBTz3**:Y12 and **PDBTz4**:Y12 blend films, suggesting electron transfer and energy transfer from the polymer to Y12 occurred efficiently (Fig. S4). In contrast, when excited at 680 nm (Y12 excitation),

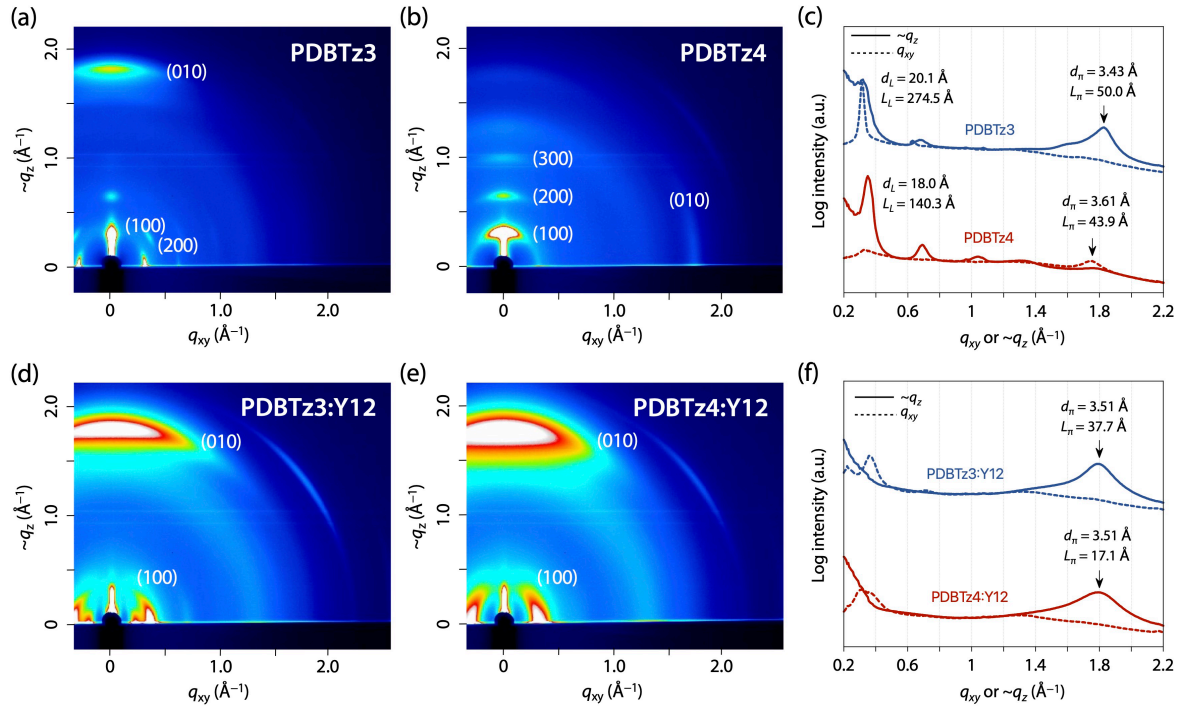


Fig. 4 (a,b,d,e) 2D GIXD patterns of the polymer neat films and polymer:Y12 blend films. (a) **PDBTz3**, (b) **PDBTz4**, (c) **PDBTz3:Y12**, and (d) **PDBTz4:Y12**. (c, f) Cross-sectional diffraction profiles cut from the 2D GIXD patterns along the q_{xy} (solid line) and $\sim q_z$ (dashed line) axes. (c) Polymer Neat films. (f) Polymer:Y12 blend films. The coherence length for the π - π stacking (L_n) and lamellar structure (L_L), which were estimated from the simplified Scherrer's equation, $L_c = 2\pi/\text{fwhm}$, where fwhm is the full-width at half-maximum.

1 the PL quenching efficiency was 20% for the
 2 **PDBTz3:Y12** blend film, while it reached 95% for the
 3 **PDBTz4:Y12** blend film. These results indicated that
 4 hole transfer from Y12 to **PDBTz3** was significantly
 5 suppressed, while that to **PDBTz4** occurred efficiently.
 6 In addition, upon polymer excitation, energy transfer is
 7 most likely dominant in this case, considering the low
 8 EQE values in the polymer absorption region for the
 9 **PDBTz3** cell; if the electron transfer occurs with a
 10 certain ratio, the extremely low EQEs cannot be
 11 explained. More specifically, hole transfer from Y12 to
 12 **PDBTz3**, which should occur after the energy transfer
 13 to Y12, is inefficient as evidenced by the low PL
 14 quenching efficiency, resulting in the low EQE values.
 15 Thus, the difference in hole transfer is the primary
 16 factor underlying the stark contrast in photovoltaic
 17 performance between the two polymers.

19 2-4. Packing order and morphology of the blend film

20 Grazing-incidence X-ray diffraction (GIXD)
 21 measurements were conducted to investigate the
 22 molecular packing and crystallinity of the polymers.
 23 Figures 4a–f present the two-dimensional (2D) GIXD
 24 patterns and the corresponding out-of-plane (solid lines)
 25 and in-plane (dotted lines) diffraction profiles for both
 26 neat and blend films. In neat films (Figs. 4a–c), **PDBTz3**
 27 exhibited a predominantly face-on orientation, as
 28 characterized by (0 1 0) π - π stacking diffraction at $\sim q_z$

29 $\approx 1.83 \text{ \AA}^{-1}$ and (h 0 0) lamellar diffractions at $q_{xy} \approx 0.31$
 30 $\text{\AA}^{-1}$. In contrast, **PDBTz4** exhibited a predominantly
 31 edge-on orientation, as characterized by (0 1 0) π - π
 32 stacking diffraction at $q_{xy} \approx 1.74 \text{ \AA}^{-1}$ and (h 0 0) lamellar
 33 diffractions at $\sim q_z \approx 0.35 \text{ \AA}^{-1}$. **PDBTz3** showed a
 34 significantly shorter π - π stacking distance ($d_n = 3.43 \text{ \AA}$)
 35 and slightly longer the lamellar distance ($d_L = 20.1 \text{ \AA}$)
 36 compared to **PDBTz4** ($d_n = 3.61 \text{ \AA}$ and $d_L = 18.0 \text{ \AA}$,
 37 respectively), suggesting stronger interchain
 38 interactions in **PDBTz3**. To further quantify crystallinity,
 39 we evaluated the coherence lengths corresponding to
 40 the π - π stacking (L_n) and lamellar (L_L) structures. The
 41 coherence length of the π - π stacking (L_n) was greater
 42 in **PDBTz3** (50.0 $\text{\AA}$) than in **PDBTz4** (43.9 $\text{\AA}$), indicative
 43 of more extended π - π stacking structure. Furthermore,
 44 L_L was significantly greater in **PDBTz3** (275 $\text{\AA}$) than in
 45 **PDBTz4** (140 $\text{\AA}$), clearly indicating higher long-range
 46 order. Overall, these results indicated that **PDBTz3**
 47 possessed a more crystalline structure than **PDBTz4**.
 48 Whereas interchain charge transport occurs in the out-
 49 of-plane direction in face-on orientations and in the in-
 50 plane direction in edge-on orientations, intrachain
 51 charge transport is generally considered to occur in the
 52 in-plane direction in both orientations. Therefore,
 53 although **PDBTz3** adopted the face-on orientation,
 54 which is typically unfavorable for in-plane charge
 55 transport, the superior charge carrier mobility observed
 56 for **PDBTz3** compared to **PDBTz4** may be attributed to

enhanced intrachain transport resulting from higher crystallinity.

The polymer:Y12 blend film exhibited a predominantly face-on orientation, as characterized by the (0 1 0) π - π stacking diffraction appearing along the $\sim q_z$ axis (Figs. 4d-f). Although both blends displayed similar d_s of 3.51 Å, for the **PDBTz3**:Y12 blend film exhibited a markedly greater L_π of 37.7 Å compared to the **PDBTz4**:Y12 blend film (17.1 Å). It is noted that the observed d_π values along $\sim q_z$ axis in the blend films differed from those seen in the polymer neat films, suggesting that the π - π stacking diffraction originated from the ordered domains of Y12 rather than from the polymers. Indeed, the d_π values of the blend films closely match those observed in the Y12 neat film (Fig. S5). These results suggest that **PDBTz3**:Y12 blend film contained larger and more ordered Y12 aggregates than the **PDBTz4**:Y12 blend film.

Subsequently, atomic force microscopy (AFM) was performed to examine the surface morphology of the blend films (Figs. 5a and 5b). Both blend films exhibited smooth surface with the root-mean-square (RMS) roughness values below 1 nm. However, **PDBTz3**:Y12 blend film appeared to exhibit larger domain features compared to the **PDBTz4**:Y12 blend film, suggesting differences in phase separation at the nanoscale. To further prove the internal morphology, transmission electron microscopy (TEM) measurement was carried out (Figs. 5c and 5d). The TEM images revealed more pronounced phase separation in the **PDBTz3**:Y12 blend film than in the **PDBTz4**:Y12 blend film, likely indicating the formation of larger Y12 domains. Such larger-scale phase separation is generally detrimental to exciton diffusion, resulting in diminished PL quenching efficiency due to the reduced donor/acceptor interfacial area.³⁰

2-5. Understanding the origin of distinct photovoltaic performances

We observed that, whereas the polymer neat films exhibited a similar vivid pink color, the polymer:Y12 blend films displayed different appearances—reddish brown for the **PDBTz3**:Y12 blend film and deep wine red for the **PDBTz4**:Y12 blend film (Fig. 6a). Consistent with these visual observations, the polymer:Y12 blend films exhibited markedly different UV-vis-NIR absorption spectra in both the polymer and Y12 absorption regions (Fig. 6b). In the **PDBTz3**:Y12 blend films, the polymer showed the broad and featureless absorption band, resembling that observed in solution, while Y12 showed a sharp and blue-shifted absorption. In addition, the absorption coefficient (α) of **PDBTz3** in the blend film ($1.03 \times 10^5 \text{ cm}^{-1}$) was significantly lower than that of **PDBTz4** ($1.38 \times 10^5 \text{ cm}^{-1}$), even though the polymer neat films exhibited similar α values (Fig. S6). This suggests that **PDBTz3** is more disordered than **PDBTz4** in the blend films and possesses a shorter effective conjugation length in the blend film.³² Taking together with the packing order and morphology of the

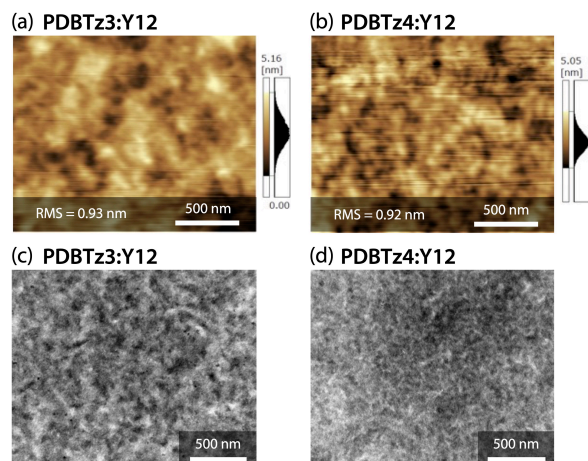


Fig. 5 (a,b) AFM and (c,d) TEM images of (a,c) **PDBTz3**:Y12 and (b,d) **PDBTz4**:Y12.

PDBTz3:Y12 blend film, the results suggest that **PDBTz3** formed an amorphous with a highly twisted polymer backbone, while Y12 formed the excessive aggregations. In contrast, the **PDBTz4**:Y12 blend film showed clear 0-0 and 0-1 transition peaks for the polymer, indicative of preserving a coplanar backbone conformation, and a typical Y12 absorption band corresponding to moderate aggregations, consistent with those observed in benchmark polymer:Y12 blend systems.

In fact, PYS measurements of the polymer:Y12 blend films revealed that the E_{HOMO} of **PDBTz3** (-5.51 eV) was significantly deeper than that of **PDBTz4** (-5.36 eV) (Fig. 6c). Notably, the polymers exhibited comparable E_{HOMO} values in their neat films, while blending with Y12 markedly modulated their E_{HOMO} values likely due to the difference in the backbone coplanarity. Furthermore, although the detailed aggregation state of Y12 in the **PDBTz3**:Y12 blend film remains unclear, previous studies have reported that a blue shift in the absorption spectrum of Y-series is associated with an upward shift of its E_{HOMO} .³¹ CV measurements of the polymer:Y12 blend films exhibited two oxidation peaks corresponding to the polymer and Y12. The peak corresponding to Y12 appeared at 1.62 V for **PDBTz3**:Y12 and 1.69 V for **PDBTz4**:Y12 blend films (Figure S7), suggesting that the E_{HOMO} of Y12 was elevated in **PDBTz3**:Y12 blend film. Additionally, the peak corresponding to the polymer was observed at 1.35 V for **PDBTz3**:Y12 and 1.30 V for **PDBTz4**:Y12 blend film, suggesting that **PDBTz3** had deeper E_{HOMO} than **PDBTz4**. This trend is consistent with the PYS results. These energetic modulations in both the polymer and Y12 resulted in a significantly reduced E_{HOMO} offset in the **PDBTz3**:Y12 blend, which hindered efficient hole transfer, as evidenced by the suppressed PL quenching efficiency and the absence of the photovoltaic effect. In contrast,

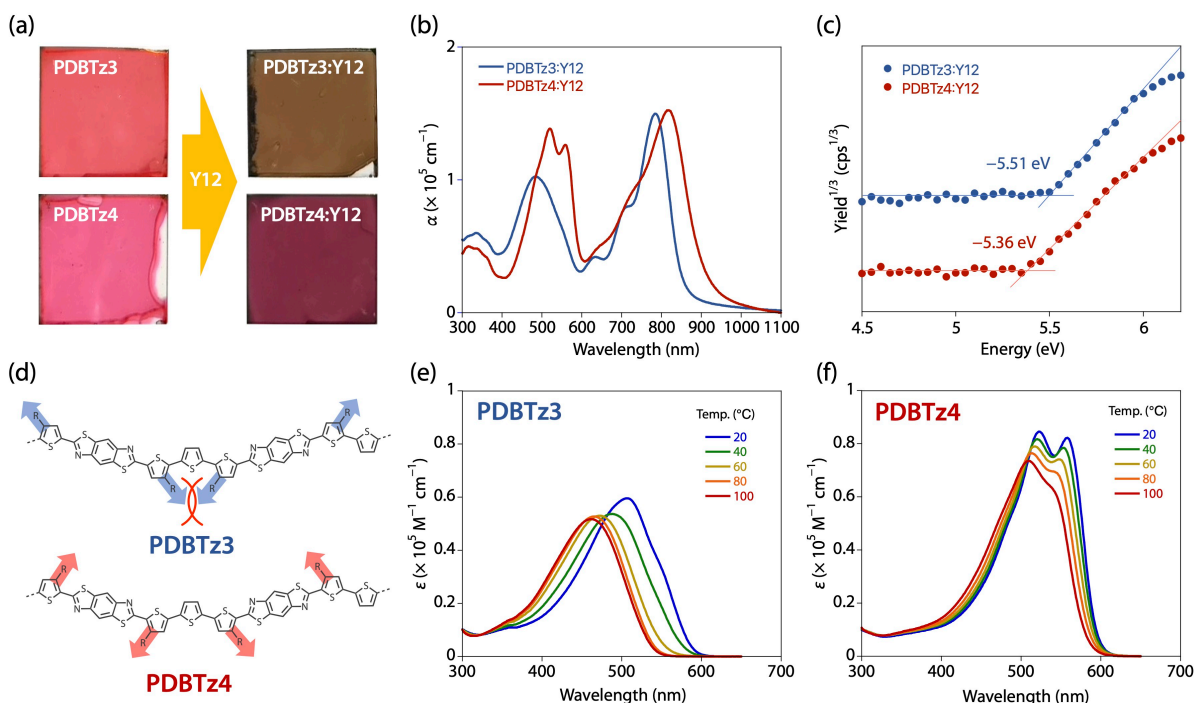


Fig. 6 (a) Photographs of the polymer neat films (left) and polymer:Y12 blend films (light) on quartz glass substrates. (b) UV-vis-NIR absorption spectrum of polymer:Y12 blend films. (c) PYS of the polymer:Y12 blend films. (d) Schematic illustrations of plausible polymer structures: **PDBTz3** (upper panel) and **PDBTz4** (lower panel). (e, f) Temperature-dependent UV-Vis absorption spectra of (d) **PDBTz3** and (e) **PDBTz4** in CB solution.

the coplanar backbone of **PDBTz4** preserved a favorable E_{HOMO} offset upon blending, thereby enabling efficient hole transfer and resulting in a superior photovoltaic performance.

The difference in the backbone coplanarity between the polymers can be explained by the degree of steric interference from the alkyl groups (Fig. 6d). DFT calculations using polymer models bearing isobutyl groups indicated that the backbone of **PDBTz3** is highly twisted due to significant steric interference between the alkyl groups in both of the two optimized conformations (Fig. S8), while that of **PDBTz4** adopts a more coplanar backbone by minimizing such steric hindrance (Fig. S9). As a result, **PDBTz3** exhibited a substantially lower E_{HOMO} (-5.26 eV) than **PDBTz4** (-5.01 eV), which is due to the disruption of π -conjugation caused by its twisted backbone. To further investigate backbone rigidity, we measured the temperature-dependent UV-Vis absorption spectra of the polymers in the CB solution (Figs. 6e and 6f). For **PDBTz3**, the absorption spectrum became completely featureless upon heating at 40 °C, indicating rapid disruption of π -conjugation. In contrast, the spectrum of **PDBTz4** showed minimal blue-shift and retained 0-0 and 0-1 transition peaks even at 100 °C. These results suggest that **PDBTz4** possesses a more coplanar and rigid

backbone compared to **PDBTz3**, enabling it to retain its conformation in the Y12 blend film.

3. Conclusion

In conclusion, we found that drastic effect of the alkylation position in structurally simple, synthetically accessible BBTz-terthiophene copolymers—namely, whether substitution introduced at the outer (**PDBTz3**) or inner (**PDBTz4**) β -positions of the thiophene units flanking the BBTz core. Combined optical, electrochemical, morphological, and computational analysis revealed that, after blending Y12, **PDBTz3** showed a twisted backbone conformation due to steric hindrance between alkyl groups, while **PDBTz4** showed a more planar and rigid backbone conformation. The twisted backbone of **PDBTz3** in the blend film resulted in a deeper E_{HOMO} and consequently a reduced E_{HOMO} offset, which suppressed hole transfer and rendered photovoltaic performance negligible. In contrast, the coplanar backbone of **PDBTz4** retained favorable E_{HOMO} offset, facilitating efficient hole transfer and yielding a superior PCE of 10.2%. These results highlight how even minor structural modifications—such as subtle change in alkylation position—can profoundly affect the electronic structure, packing order, and morphology of the polymer in blend films. Our

findings provide a rational molecular design strategy for synthetically accessible, high-performance polymer donors for OPVs, and offer insights for the broader development of semiconducting materials in optoelectronic applications.

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Supplementary data

Supplementary material is available at *Bulletin of the Chemical Society of Japan*.

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Conflict of interest statement

None declared.

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