Regioisomeric Polymer Semiconductors Based on Cyano-Functionalized Dialkoxybithiophenes: Structure–Property Relationship and Photovoltaic Performance

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Abstract
Cyano substitution is vital to the molecular design of polymer semiconductors toward highly efficient organic solar cells. However, how regioselectivity impacts relevant optoelectronic properties in cyano-substituted bithiophene systems remain poorly understood. Three regioisomeric cyano-functionalized dialkoxybithiophenes BT_HH, BT_HT, and BT_TT with head-to-head, head-to-tail, and tail-to-tail linkage, respectively, were synthesized and characterized in this work. The resulting polymer semiconductors (PBDTBTs) based on these building blocks were prepared accordingly. The regiochemistry and property relationships of PBDTBTs were investigated in detail. The BT_HH moiety has a higher torsional barrier than the analogs BT_HT and BT_TT, and the regiochemistry of dialkoxybithiophenes leads to fine modulation in the optoelectronic properties of these polymers, such as optical absorption, band gap, and energy levels of frontier molecular orbitals. Organic field-effect transistors based on PBDTBT_HH had higher hole mobility (4.4 × 10⁻³ cm²/(V·s)) than those (ca. 10⁻⁴ cm²/(V·s)) of the other two polymer analogs. Significantly different short-circuit current densities and fill factors were obtained in polymer solar cells using PBDTBTs as the electron donors. Such difference was probed in greater detail by performing space-charge-limited current mobility, thin-film morphology, and transient photocurrent/photovoltage characterizations. The findings highlight that the BT_HH unit is a promising building block for the construction of polymer donors for high-performance organic photovoltaic cells.

Keywords Cyano substitution · Regioselectivity · Organic photovoltaic cells · Polymer semiconductors · Mobility

Introduction
Organic electronics have attracted considerable interest over the last few decades because of their great potential for the production of flexible and large-area optoelectronic devices via solution processing technologies at low temperatures [1–9]. Through an in-depth understanding of chemical design and synthesis, material processing, and device performance of polymer semiconductors, unprecedented achievements have been made in organic thin-film devices, particularly in organic field-effect transistors (OFETs) and polymer solar cells (PSCs) [10–15]. In the design of organic
semiconducting materials, alkyl side-chains are typically attached to molecular backbones to endow materials with solubility, allowing quality films to be fabricated via spin-coating or other solution-based processing techniques [16, 17]. A detail that has become apparent is that the regiochemistry of alkyl-substituted aromatic building blocks in a conjugated polymer backbone has a high correlation with the molecular packing and film morphology, hence significantly affecting the device performance. Poly(3-alkylthiophene), for instance, is an excellent candidate for probing the effects of the regiochemistry of alkyl thiophene [18–20]. During the molecular chain growth in the polymerization process, three regioisomeric linkages, i.e., head-to-head (HH), tail-to-tail (TT), and head-to-tail (HT), can be generated in the formation of 3-alkythiophene dimers (Fig. 1a). The HH coupling typically results in a highly twisted molecular backbone due to the accompanying large steric hindrance, thereby reducing the effective π-conjugation and crystallinity of the resulting polymer. Poly(3-alkylthiophene) containing a small amount of HH linkage exhibited obviously inferior device performance in both OFETs and PSCs [21–23]. In contrast, the HT coupling yielded a higher polymer film crystallinity with a planar backbone conformation and achieved improved optoelectronic properties, as exemplified by the regioregular HT-linked poly(3-hexylthiophene) (rr-P3HT) [2, 24, 25]. However, when the TT-linked dialkylated bithiophene is incorporated into poly(alkylthiophenes) or other copolymers, it may result in a HH linkage somewhere in the polymer backbone, thereby inducing a large torsional angle at the junction and thus yielding a reduced backbone π-conjugation and loose interchain packing [26–28].

In the early stage of the development of π-conjugated polymers, alkoxoxy-substituted polythiophenes were intensively studied because of their excellent electronic, thermal, and ionochromic properties, as exemplified by the well-known conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) [29–31]. The remarkable conductivity of PEDOT in the doped state is attributed to the planar polymer backbone enabled by consecutive intramolecular noncovalent (thienyl)S⋯(alkoxy)O coulombic interactions [32]. However, the strong electron-donating oxygen considerably elevates the energy level of the highest occupied molecular orbital (HOMO) of alkoxoxy-substituted polymer semiconductors [33, 34], thereby leading to a small open-circuit voltage ($V_{OC}$) in PSCs or poor stability in OFETs [35–37]. This drawback limits the usage of alkoxoxythiophene as a building block for constructing high-performance polymer semiconductors. Cyano functionalization of alkoxoxy-substituted thiophenes is a promising method of optimizing the physicochemical properties due to the strong electron-withdrawing capability of cyano functionality, which can effectively lower the frontier molecular orbital (FMO) energy levels [38–40]. A polymer donor that contains cyano-functionalized TT-linked dialkoxybithiophene (BT$_{TT}$, Fig. 1) and benzodithiophene had a higher $V_{OC}$ of 0.86 V and improved power conversion efficiency (PCE) up to 5.06% in PSCs [41]. Our group has a long-standing interest in the design and synthesis of semiconducting polymers based on HH-linked dialkoxybithiophenes [42–44]. We recently functionalized the HH-linked dialkoxybithiophene (BT$_{HH}$, Fig. 1) with a cyano group and synthesized a series of polymer semiconductors by copolymerizing it with benzodithiophenes. The strong electron-withdrawing cyano group endows the resulting polymers with decreased FMO energy levels. As a result, a remarkably high $V_{OC}$ of 1.0 V and a PCE up to 7% were achieved when the polymers were applied in PSCs. Therefore, the cyano group effectively optimizes the electrochemical property of semiconductors [45].

Unlike the well-studied dialkylbithiophenes, the structure–property correlations of dialkoxybithiophenes with different linkages in polymer semiconductors have not yet been studied. In this work, we synthesized three dialkoxybithiophene building blocks based on 3-dodecyloxy-4-cyanothiophene: HH-linked BT$_{HH}$, HT-linked BT$_{HT}$, and TT-linked BT$_{TT}$ (Fig. 1b). By copolymerizing them with a benzodithiophene comonomer, we prepared three polymer semiconductors to study their structure–property correlations and investigate their device performance in PSCs. According to cyclic voltammetry (CV) characterization, all polymers displayed a comparable HOMO energy level (−5.60 eV), whereas the lowest unoccupied molecular orbital (LUMO) energy levels showed a gradual decrease from PBDTBT$_{HH}$ (−2.5 eV) to PBDTBT$_{HT}$ (−2.62 eV) and to PBDTBT$_{TT}$ (−2.82 eV). UV–Vis absorption and film morphology of these polymers largely depended on the linkage fashions of the 3-dodecyloxy-4-cyanothiophene. When the polymers were applied in OFET, the hole mobility of polymer PBDTBT$_{HH}$ (4.4 × 10$^{-3}$

![Fig.1 Three different linkages of a alklythiophene dimers in poly(alklythiophene) and b cyano-functionalized alklythiophene dimers in this work](Image)
cm²/(V·s)) was one order of magnitude higher than that of the other two polymers (3.3 \times 10^{-4} - 4.0 \times 10^{-4} \text{ cm}²/(V·s)). The PSCs based on these polymer donors and PC71BM acceptor exhibited greatly different device performances, with the PCEs in the range of 2.94% to 7.06%. Various characterization techniques combined with theoretical calculation were applied to examine the relationship between the molecular structure regioisomerism of cyano-functionalized dialkoxybithiophene-based polymers and their optoelectronic properties. The results provide guidance for the development of alkoxythiophene-based organic semiconductors.

**Experimental Section**

**Material Synthesis**

Figure 2 presents the chemical structures of three regioisomeric polymers based on cyano-functionalized dialkoxybithiophenes, while the Supporting Information contains the synthetic details.

**Fabrication of Field-Effect Transistors and Photovoltaic Devices**

OFETs that have a top-gate/bottom-contact structure were fabricated to determine the charge transport characteristics of the polymer semiconductors [46, 47]. Source and drain electrodes (3 nm-thick Cr and 30-nm-thick Au) were patterned on borosilicate glass by performing typical photolithography. The active layers were then spin-coated from 5 mg/mL \(\text{o-DCB}\) solutions and then subjected to thermal annealing at 190 °C for 15 min. Afterward, the dielectric layer was cast from a dilute CYTOP solution (CTL-809 M/CT-SOLV180 = 2:1 (v/v), Asahi Glass Co., Ltd.) and annealed at 100 °C for 10 min. Al (50 nm thick) was thermally evaporated under vacuum as the gate electrode to complete the devices. The OFETs were characterized in a nitrogen-filled glove box using a semiconductor characterization system (Keithley 4200-SCS). The PSCs were fabricated with a conventional device architecture of glass/indium tin oxide (ITO)/MoO3/polymer:PC71BM/Ca/Al [48, 49]. The ITO was cleaned via sonication in deionized water, acetone, and isopropanol, followed by UV-ozone treatment for 15 min. MoO3 (10 nm) was deposited as the hole transport layer onto the ITO via thermal evaporation. The active layer was systematically optimized; findings show that 90-nm-thick film that was spin-coated from the \(\text{o-DCB}\) solution containing polymer and PC71BM (w/w = 1/2, 10 mg/mL for polymer) facilitated the optimal device performance. After being dried, the devices were loaded into an evaporator, where Ca (15 nm thick) and Al (100 nm thick) were deposited sequentially as cathode via thermal evaporation. The effective area of the solar cells was ~ 0.045 cm². Device characterization was conducted in a nitrogen-filled glove box using a xenon lamp-based solar simulator (Newport, Oriel AM 1.5 G, 100 mW/cm²), which was calibrated with a National Renewable Energy Laboratory-certified standard silicon cell and recorded using a Keithley 2400 digital source meter.

**Results and Discussion**

**Synthesis of Materials**

The synthetic routes to the three building blocks (BT_{HH}, BT_{HT}, and BT_{TT}) and polymers are illustrated in Scheme S1. PBDTTBT_{HH} and PBDTTBT_{TT} were synthesized by following previously reported procedures [50–52]. The synthesis of PBDTTBT_{HT} is a straightforward process that uses 4-(dodecyloxy)thiophene-3-carbonitrile as the starting material. As a result of the different acidity of two \(\alpha\)-protons in 4-(dodecyloxy)thiophene-3-carbonitrile, the proton next to cyano in the presence of \(n\)-BuLi could be selectively deprotonated, and subsequent quenching with chlorotrimethyltin afforded

![Fig. 2 Chemical structures of three regioisomeric polymers](https://example.com/fig2.png)
4-(dodecyloxy)-2-(trimethylstannyl)thiophene-3-carbonitrile. The key intermediate BTHT was readily obtained via Stille coupling between 4-(dodecyloxy)-2-(trimethylstannyl)thiophene-3-carbonitrile and 5-bromo-4-(dodecyloxy)thiophene-3-carbonitrile in a 45% yield, and the sequential treatment with n-BuLi and Br₂ gave the monomer 5,5’-dibromo-3’,4'-bis(dodecyloxy)-[2,2’-bithiophene]-3,4'-dicarbonitrile for synthesizing polymer PBDTBTHT [53]. The 1H NMR spectra of BTHH, BTHT, and BTTT were compared to investigate the electron distribution of the aromatic protons (Fig. S1). The chemical shifts of the aromatic protons of the symmetrical BTHH and BTTT are 7.79 ppm and 6.36 ppm, respectively. For the asymmetrical BTHT, two aromatic protons were observed to have a chemical shift of 7.85 ppm and 6.22 ppm, respectively. With regard to the symmetric BTHH, two aromatic protons showed a single down-shifted peak at 7.79 ppm because both α-protons are next to the highly electron-withdrawing cyano group. We thus predict that the monomer based on BTHH may yield a polymer with higher molecular weight by facilitating its oxidative addition to the active catalytic sites during the Stille coupling process [54]. All the monomers were purified by recrystallization from a solvent mixture of methanol and dichloromethane. The molecular structures and purity of compounds were confirmed by 1H NMR, 13C NMR, and elemental analyses. After polymerization, PBDTBTs were subjected to the standard Soxhlet extraction to remove low molecular weight fractions and impurities. All polymers displayed good solubility in chlorobenzene and o-DCB and comparable number-average molecular weights ($M_n$). The $M_n$ values were 24 kDa, 24 kDa, and 26 kDa with a dispersity index of 3.4, 2.0, and 2.3 for PBDTBTBTHH, PBDTBTHT, and PBDTBTTT, respectively.

**Optoelectronic Properties of Building Blocks**

Figure 3a shows the UV–Vis absorption spectra of the regioisomeric building blocks (BTHH, BTHT, and BTTT) in tetrahydrofuran (ca. $10^{-4}$ mol/L). Interestingly, the fine structures were clearly different, although their absorption was measured in the same wavelength range. The UV–Vis absorption spectra are in good agreement with the time-dependent density functional theory (TDDFT) calculation, as shown in Fig. 3b. According to the calculation, the lowest energy transition for these building blocks is associated with the transition of HOMO→LUMO. With regard to BTHT and BTTT, a higher energy transition was measured and could be assigned by TDDFT as follows: HOMO − 2 → LUMO at 264 nm for BTHT and HOMO − 1 → LUMO at 269 nm for BTTT. The energy minimum geometries and electronic structures of BTHH, BTHT, and BTTT were calculated by DFT at the B3LYP/6-31G level using Gaussian 03 W. The results are shown in Fig. 4a–c. The alkyl groups in the calculated structures were truncated with methyl groups to reduce the computational burden.

The calculated HOMO levels are located at the same level (ca. −6.1 eV), and the LUMO levels of BTHH, BTHT, and BTTT were calculated as −1.96, −2.20, and −2.48 eV, respectively. CV measurements determined that the LUMO energy levels are −2.5 eV for BTHH, −2.62 eV for BTHT, and −2.82 eV for BTTT (Fig. 3c, Fig. S2). Both calculated and experimental LUMO values show the same trend, and the lowest LUMO energy level of BTTT suggests that it has the strongest electron-accepting ability among the three building blocks. All these building blocks adopt a highly anti-planar conformation, which was confirmed previously by single X-ray crystal data [53, 55]. Figure 4d plots torsional profiles as a function of the dihedral angle between two thiophene rings. Interestingly, BTHT and BTTT show almost the same torsional profiles, while a higher torsional energy barrier is needed to break the anti-planar conformation in BTHH. The higher torsional barrier with a conformation lock in BTHH can be attributed to the double noncovalent S⋯O intramolecular interactions, which may influence the interchain packing and the resulting film morphology. According to the energy minimum geometry based on their
trimers (Fig. S3), the torsional angle between BDT and bithiophene was calculated as PBDTBTN: 3.8°, PBDTBTH: 6°, and PBDTBTT: 9°, respectively. A more planar conformation was observed in PBDTBTN [56].

**Polymer Thermal Properties**

The thermal properties of polymers were evaluated by performing thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA thermograms in Fig. S4a show that the thermal breakdown of all polymers ($T_d$ with a loss of 5 wt%) occurs when they are heated at more than 330 °C in the presence of nitrogen. The second heating and cooling DSC traces are displayed in Fig. S4b. PBDTBTN shows one endothermal transition (at 156 °C) and one exothermal transition (at 111 °C), which could be attributed to the side-chain melting and recrystallization. Interestingly, PBDTBTN and PBDTBTT show featureless DSC thermograms, although they have a similar backbone as PBDTBTN [57]. DSC data suggest that PBDTBTN differs from the other two polymers in terms of polymer packing, and PBDTBTN with the HH geometry shows a higher crystallinity.

**Optical and Electrochemical Properties**

The UV–Vis absorption spectra of three polymers in dilute $o$-DCB (10⁻⁵ mol/L) and in films cast from $o$-DCB solutions (5 mg/mL) are shown in Fig. 5a, and detailed optical data are compiled in Table 1. The absorption profiles in solution and film indicate that all the polymers are expected to be significantly aggregated, even in solution. In
the film, the absorption onset shifted to longer wavelengths from PBDTBT_HH (697 nm) to PBDTBT_H (747 nm) to PBDTBT_TT (780 nm). Thus, the optical band gap derived from the optical onset of the film decreased in the order of PBDTBT_HH (1.78 eV), PBDTBT_H (1.66 eV), and PBDTBT_TT (1.59 eV). The electrochemical properties of polymers were investigated by conducting CV measurements relative to ferrocene as a reference, as shown in Fig. 5b. The HOMO energy levels of PBDTBT_HH, PBDTBT_H, and PBDTBT_TT were −5.56, −5.52, and −5.58 eV, respectively (Table 1). The low-lying HOMOs, which are generated by the strong electron-withdrawing cyano group, should lead to a high V_OC in PSCs and good air stability in OFETs \([58, 59]\).

Unfortunately, the LUMO energy levels of polymers were not obtained successfully from CV measurements. Instead, the LUMO values of PBDTBT_HH, PBDTBT_H, and PBDTBT_TT were calculated as −3.78, −3.86, and −3.99 eV, respectively, according to the equation LUMO = HOMO + \(E_g\) (eV).

### Photovoltaic Properties

PSCs were fabricated with a conventional device architecture of glass/ITO/MoO_3/polymer: PC_71BM/Ca/Al to investigate the regiochemistry effect on polymers’ photovoltaic properties. The devices were optimized by varying the blend ratio of donor: acceptor, film thickness, and processing solvent. A weight ratio of donor/acceptor of 1:2, a film thickness of 130 nm, and a processing solvent of chlorobenzene could lead to the optimum photovoltaic parameters.

The current density–voltage (J-V) curves under the illumination of air mass (AM) 1.5 G (100 mW/cm²) are shown in Fig. 6a, and the resulting photovoltaic parameters are summarized in Table 2. All the devices displayed a similarly high V_OC of 0.9 V, which was attributed to the similar low-lying HOMOs determined by CV. For devices based on PBDTBT_HH, PBDTBT_H, and PBDTBT_TT, the average PCEs were 6.22%, 2.94%, and 3.83%, respectively. Both higher short-circuit current density (J_sc) and fill factor (FF) values are responsible for a higher PCE for PBDTBT_HH.

Several solvent additives were also tested for further device optimization \([60, 61]\). The addition of 2 vol% 1-chloronaphthalene (CN) resulted in clearly improved photovoltaic performance. The resulting PCEs of the PBDTBT_HH-, PBDTBT_H-, and PBDTBT_TT-based PSCs reached 7.06%.

### Table 1

Molecular weights and optical and electrochemical properties of PBDTBTs

| Polymer | \(M_n\) (kDa) | \(T^\circ\) | \(\lambda_{\text{max}}\) (soln) (nm) | \(\lambda_{\text{max}}\) (film) (nm) | \(E_{\text{HOMO}}\) (eV) | \(E_{\text{LUMO}}\) (eV) | \(E_{\text{g, opt}}\) (eV) |
|---------|--------------|----------|-------------------------------|-----------------|----------------|----------------|------------------|
| PBDTBT_HH | 24           | 3.4     | 625                           | 595, 626        | −5.56          | −3.78          | 1.78             |
| PBDTBT_H | 24           | 2.0     | 630                           | 636             | −5.52          | −3.86          | 1.66             |
| PBDTBT_TT | 26           | 2.3     | 650                           | 662             | −5.58          | −3.99          | 1.59             |

*\(^{a}\) Determined by high-temperature GPC relative to a polystyrene standard.  \(^{b}\) \(E_{\text{HOMO}} = -(E_{\text{onset}} + 4.80)\) eV, and \(E_{\text{onset}}\) was determined electrochemically using the ferrocene/ferrocenium (Fc/Fc⁺) couple as the internal standard.  \(^{c}\) \(E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g, opt}}\).  \(^{d}\) Optical band gap derived from absorption onset of the as-cast film: \(E_{\text{g, opt}} = 1240/\lambda_{\text{onset}}\) (eV).  

### Table 2

Summary of photovoltaic parameters in PSCs

| Polymer | CN \(^{a}\) | V_OC (V) | J_sc (mA/cm²) | FF (%) | PCE (%) \(^{b}\) |
|---------|------------|----------|---------------|--------|----------------|
| PBDTBT_HH | N | 0.92 | 10.94 | 62 | 6.22 |
| | Y | 0.92 | 12.21 | 64 | 7.06 |
| PBDTBT_H | N | 0.91 | 6.10 | 53 | 2.94 |
| | Y | 0.92 | 8.36 | 52 | 3.96 |
| PBDTBT_TT | N | 0.88 | 8.23 | 53 | 3.83 |
| | Y | 0.91 | 11.55 | 48 | 5.08 |

*\(^{a}\) PSCs were prepared from blend solutions without (N) or with (Y) 2% (v/v) CN additive.  \(^{b}\) Data are the average values based on 12 devices.
3.96%, and 5.08%, respectively, which mainly originated from the increased \( J_{sc} \) values (Fig. 6a). The enhancement is reflected by the higher external quantum efficiency in their photo-response regions (Fig. 6b). The underlying mechanism for such enhancement in PCEs will be discussed in terms of charge mobility and blend morphology in the following sections. The impressive device performances of our polymers in fullerene solar cells also prompted us to explore their application in non-fullerene solar cells. We fabricated polymers in fullerene solar cells also prompted us to explore lowing sections. The impressive device performances of our polymers in fullerene solar cells also prompted us to explore.

The film, as confirmed by the POM images (Fig. S11a, f). These findings suggest poor compatibility between PBDTBTHH with Y6. The AFM phase images of two blend films are shown in Fig. S11. The PBDTBTHH:Y6 blend film exhibits a more obvious state of aggregation and rough domain-like morphology (Fig. S11b–e). The root-mean-square roughness of the PBDTBTHH:Y6 blend film (Fig. S11b) is \(~8.5\) nm within the \(3 \mu\text{m} \times 3 \mu\text{m} \) scanned area, which is much rougher than those (< \(2 \mu\text{m} \)) of PM6:Y6 and PBDTBTHH:PC\(_{71}\)BM blend films (Fig. S6b and Fig. S11). Such blend morphology results in a negative effect on the charge separation and transportation. Therefore, the PBDTBTHH:Y6-based device produces a poor \( J_{sc} \) and FF.

### Charge Carrier Mobility

To investigate the charge carrier transport properties of polymers, an OFET device was first fabricated. The hole mobilities of polymer films after annealing at 190 °C for 15 min are summarized in Table 3, and the corresponding transfer curves are displayed in Fig. S5. The hole mobility (\( \mu_h \)) of OFETs based on PBDTBTHH (4.4 x 10\(^{-3}\) cm\(^2\)/(V·s)) was ~10 times higher than those of PBDTBTTT (3.3 x 10\(^{-4}\) cm\(^2\)/(V·s)) and PBDTBTTT (4.0 x 10\(^{-4}\) cm\(^2\)/(V·s)). Aside from the OFET mobility in a parallel direction, the vertical charge mobility was also studied by applying a space-charge-limited current (SCLC) method [62]. The hole-only and electron-only devices, which have a device architecture of glass/ITO/PEDOT:PSS/polymer:PC\(_{71}\)BM/MoO\(_3\)/Ag and a glass/ITO/ZnO/polymer:PC\(_{71}\)BM/Ca/Al, respectively, were then prepared. The resulting \( J-V \) characteristics are plotted in Fig. 7, and the calculated data are collected in Table 3.

| Polymer     | \( \mu_{\text{sat}} \) (cm\(^2\)/(V·s)) | \( \mu_{\text{h}} \) (SCLC) | \( \mu_{\text{e}} \) (SCLC) | \( \mu_{\text{h}}/\mu_{\text{e}} \) |
|-------------|---------------------------------|-----------------|-----------------|------------------|
| PBDTBTHH    | 4.4 x 10\(^{-3}\)              | 2.3 x 10\(^{-4}\) | 1.7 x 10\(^{-4}\) | 1.4              |
| PBDTBTHH    | 3.3 x 10\(^{-4}\)              | 2.2 x 10\(^{-6}\) | 2.6 x 10\(^{-5}\) | 1.2              |
| PBDTBTHH    | 4.0 x 10\(^{-4}\)              | 2.4 x 10\(^{-6}\) | 4.6 x 10\(^{-5}\) | 0.08             |

AFM measurements were performed to understand the surface morphology of active layers in PSCs (Fig. S6). All the blend films, with or without the CN additive, displayed smooth surface topographies. For the PBDTBTHH-based blend films, CN addition affected the surface roughness noticeably, with the root-mean-square roughness decreasing sharply from 2.58 nm to 1.58 nm. Despite the positive effect of the additive on PCEs for PBDTBTHH- and PBDTBTTT-based devices, no discernible morphological...
changes could be observed. We also measured the blend film morphology using TEM. As shown in Fig. 8, the three blend films exhibit obvious nanofibrillar structures after the addition of CN, leading to significantly improved $J_{sc}$ and thus better PCE compared with those of additive-free ones [65, 66]. PBDTTBH-based blend film has the most uniform morphology with finer phase separation, which yields the highest $J_{sc}$ (12.21 mA/cm$^2$) and is the best PCE in this series. Interestingly, no recognizable changes in TEM morphologies were observed for the other two systems. On the basis of the AFM and TEM characterizations, we conclude that morphology transformation that results from the addition of CN is clearly observed in the PBDTTBH-based film.

The detailed interchain packing and molecular orientation in pristine films and donor:acceptor blends were investigated by 2D-GIXD. Figure 9 shows the 2D diffraction
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patterns, and Fig. S7 presents the corresponding line-cut profiles. The pristine PBDTBT$_{HH}$ film has a face-on dominant bimodal orientation, as confirmed by a strong out-of-plane (OOP) $\pi-\pi$ stacking peak (010) and an in-plane (IP) lamellar (100) scattering, together with lamellar peaks (up to (300)) in the OOP direction (Fig. 9a). The PBDTBT$_{HH}$ film showed a $\pi-\pi$ stacking distance of 0.39 nm ($q_z = 1.61$ Å$^{-1}$) and lamellar interdigitation distances of 3.1 nm and 2.7 nm in the IP and OOP directions, respectively. PBDTBT$_{HT}$ and PBDTBT$_{TT}$ showed a similar 2D-GIXD diffraction pattern, reflecting the bimodal orientation of polymer chains with a hump-shaped peak (100) (Fig. 9b, c). However, their OOP (010) scattering intensities are lower than those of the polymer PBDTBT$_{HH}$. In the blend films, an isotropic broad and strong PC$_{71}$BM aggregation diffraction was observed at $q = 1.24–1.34$ Å$^{-1}$. Blending with PC$_{71}$BM resulted in all three blend films showing an edge-on dominant bimodal orientation with lamellar scatterings up to (300) in the OOP direction (Fig. 8d, e, f). In the case of PBDTBT$_{HH}$:PC$_{71}$BM, a clear OOP peak (010) still remains relative to the other blends. In the polymer:PC$_{71}$BM blends, the lamellar interdigitation distances were 2.7–3.1 nm for all three polymers, showing a similar lamellar $d$-spacing to the pristine polymer films. Upon the addition of CN, the diffraction peaks became stronger for all blends. Particularly for the PBDTBT$_{HH}$:PC$_{71}$BM blend film, the OOP peak (010) became clearer without any noticeable change in the lamellar interdigitation distance (Fig. 9g–i). The enhanced face-on stacking is beneficial for charge extraction in the vertical direction in photovoltaic cells, thereby improving the values of both $J_{sc}$ and FF [67, 68].

**Charge Transfer, Extraction, and Recombination**

Photoluminescence (PL) is a simple method of examining the photo-induced charge transfer at the interface between the donor and the acceptor in PSCs (Fig. S8). Unlike that of pristine polymer films, the PL emission of blend films was strongly quenched via photo-induced electron transfer to fullerene by exciting polymers at 345 nm. The PL intensity in blends was further reduced upon the addition of CN, indicating that the exciton separation was more effective due to morphological optimization. We conducted transient photocurrent (TPC) measurement to analyze the charge carrier extraction process in the series of blends [69]. The TPC measurements were performed at zero bias, and the results are shown in Fig. 10a. The photocurrent decay time of the PBDTBT$_{HH}$:PC$_{71}$BM-based device was 0.32 μs, which is shorter than those of the PBDTBT$_{HT}$:PC$_{71}$BM and PBDTBT$_{TT}$:PC$_{71}$BM-based PSCs (0.41 μs and 0.50 μs). The shorter charge extraction time is attributed to the well-balanced and higher SCLC charge
mobilities in PBDTBT$_{HH}$:PC$_{71}$BM compared with those of the other two blends, as discussed above. The decay time of the PBDTBT$_{HH}$-based device dropped from 0.32 to 0.24 μs with the addition of CN, showing good agreement with the enhancement of $J_{sc}$ and PCE. Transient photovoltage (TPV) measurements, which facilitate the investigation of the charge recombination dynamics [70], were also performed. As shown in Fig. 10b, the addition of CN produced a longer charge recombination time, revealing improved photovoltaic performance in PSCs. Notably, the recombination time for the PBDTBT$_{HH}$-based PSCs with CN was 78.8 μs, indicating a remarkably slower charge recombination compared with that of the other two devices (26.1 and 36.6 μs for PBDTBT$_{HT}$:PC$_{71}$BM and PBDTBT$_{TT}$:PC$_{71}$BM, respectively). The results from charge carrier dynamics are well consistent with the device performances, suggesting that BT$_{HH}$ is a promising building block for realizing semicrystalline high-performance semiconducting polymers.

Conclusions

Three regioisomeric building blocks (BT$_{HH}$, BT$_{HT}$, and BT$_{TT}$) based on the 3-alkoxy-4-cyanothiophene were synthesized. The HOMO energy levels of dialkoxybithiophenes decreased substantially when a strong electron-withdrawing cyano substituent was incorporated. The LUMO energy level was down-shifted gradually from BT$_{HH}$ to BT$_{HT}$ and to BT$_{TT}$. A higher torsional energy barrier was found in the BT$_{HH}$ moiety, which is likely due to the double noncovalent coulombic S···O interactions. When integrated into OFETs, PBDTBT$_{HH}$ exhibited 10 times higher hole mobility ($4.4 \times 10^{-3}$ cm$^2$/V·s) compared with the other two polymers (ca. $10^{-4}$ cm$^2$/V·s). When blended with PC$_{71}$BM, PBDTBT$_{HH}$, PBDTBT$_{HT}$, and PBDTBT$_{TT}$-based PSCs showed the best PCEs of 7.06%, 3.96%, and 5.08%, respectively. Such difference in PCEs is due to the variation of $J_{sc}$ values and FF values. The data from SCLC measurements, morphological characterization, and transient photocurrent/photovoltage analyses enabled us to understand the varied electrical and photovoltaic characteristics that depend on polymer regiochemistry. The HH-linked cyano-functionalized dialkoxybithiophene has great potential for the construction of crystalline semiconducting polymers for optoelectronic applications. More importantly, our study emphasizes that the regiochemistry of alkoxy-substituted building blocks needs to be carefully considered to fine-modulate the molecular conformation and the electrochemical, morphological, and resulting electrical properties.

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Author Contributions HS LN and XG proposed and supervised the project. QB performed device fabrication and characterization. JH and HS synthesized these monomers and polymers. HYW conducted 2D-GIWAXS measurements. MS and BL performed TRPL measurements. HG and QB carried out OTFT tests and analyses. JY and YK performed CV and GPC measurements. QB, JH, HS, LN, and XG co-wrote the manuscript. All authors discussed the results and participated in revising the manuscript.

Declarations

Conflict of Interest The authors declare that there is no conflict of interest.
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design and synthesis of organic polymer semiconductors and their application in solar cells and thin film transistors.

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