

Donor–Acceptor Systems

Side-Chain Engineering of Benzodithiophene-Fluorinated Quinoxaline Low-Band-Gap Co-polymers for High-Performance Polymer Solar Cells

Xiaopeng Xu,^[a] Yulei Wu,^[b] Junfeng Fang,^{*[b]} Zuojia Li,^[a] Zhenguo Wang,^[a] Ying Li,^[a] and Qiang Peng^{*[a]}

Abstract: A new series of donor-acceptor co-polymers based on benzodithiophene and quinoxaline with various side chains have been developed for polymer solar cells. The effect of the degree of branching and dimensionality of the side chains were systematically investigated on the thermal stability, optical absorption, energy levels, molecular packing, and photovoltaic performance of the resulting co-polymers. The results indicated that the linear and 2D conjugated side chains improved the thermal stabilities and optical absorptions. The introduction of alkylthienyl side chains could efficiently lower the energy levels compared with the alkoxylsubstituted analogues, and the branched alkoxyl side chains could deepen the HOMO levels relative to the linear alkoxyl chains. The branched alkoxyl groups induced better lamellar-like ordering, but poorer face-to-face packing behavior. The 2D conjugated side chains had a negative influence on the crystalline properties of the co-polymers. The performance of the devices indicated that the branched alkoxyl side chains improved the V_{ocr} but decreased the J_{sc} and fill factor (FF). However, the 2D conjugated side chains would increase the V_{ocr} J_{scr} and FF simultaneously. For the first time, our work provides insight into molecular design strategies through side-chain engineering to achieve efficient polymer solar cells by considering both the degree of branching and dimensionality.

Introduction

Polymer solar cells (PSCs) based on bulk heterojunction (BHJ) structures, incorporating conjugated polymers as donor materials and fullerene derivatives as acceptors, have attracted much attention due to their promising applications in fabricating flexible and large-area solar panels by using low-cost solution-processing methods.^[1] Tremendous efforts have been made toward developing highly efficient BHJ PSCs, including the design and preparation of new p-type polymeric donors and n-type accepting materials, by changing various additives to finely tune the morphology of the active layer, by optimizing device fabrication techniques, and by adopting novel device architectures.^[2] Electron-donating conjugated polymers have received extensive attention because they make a greater contribution to harvesting photons in BHJ PSCs than fullerene

[a]	X. Xu, ⁺ Dr. Z. Li, Z. Wang, Prof. Y. Li, Prof. Q. Peng Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry Sichuan University, Chengdu 610064 (P.R. China) Fax: (+ 86) 28-86510868 E-mail: giangpengjohnny@yahoo.com
[b]	Y. Wu, ⁺ Prof. J. Fang Ningbo Institute of Materials and Technology and Engineering, Chinese Academy of Sciences Ningbo 315201 (P.R. China) E-mail: fangjf@nimte.ac.cn

[⁺] These authors contributed equally to this work.

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derivatives.^[3] A low-band-gap (LBG) co-polymer featuring electron donor/acceptor (D/A) units in the main chain may be the most successful candidate, which can form a push–pull configuration and facilitate intramolecular charge transfer (ICT) between the donor and the acceptor parts.^[1c,d,4] The rational selection and optimization of D/A building blocks allow the band gaps to be finely tuned, as well as the energy levels and light-absorption abilities of the designed LBG co-polymers.^[5] Moreover, the particular push–pull structure can reduce intrachain π – π stacking distances, and thus induce, improve charge-carrier mobility.^[6] By using this design strategy, the power conversion efficiencies (PCEs) of the PSCs reached 7–9% for a single junction and 9–11% for tandem device architectures with the newly developed LBG polymer materials.^[2f,7,8]

In addition to band-gap control and molecular energy level modulation, side-chain engineering has been receiving increasing attention for the design of high-performance photovoltaic polymers. Previously, alkyl side chains were introduced onto conjugated backbones as solubilizing groups to afford the prepared polymers with good solubility and processability.^[9] Generally, the solubility of the polymers can be improved by attaching longer alkyl side chains; however, the molecular packing, blend morphology, fullerene miscibility, and optoelectronic performance will also be influenced.^[9] In the last few years, branched alkyl chains have also been studied, including the length, size, and position of the branching point relative to the polymer backbone.^[10] In addition to the alkyl side chains, the





use of alkyl-substituted aromatic side groups on the polymer backbone has been demonstrated to extend the π conjugation from the backbone to the lateral substituents, leading to 2D conjugated systems.^[11, 12] The variable conjugated side chains have been introduced onto the D^[11] and A^[12] skeletons to process enhanced absorption, charge transport, and device performance. For example, Li et al. designed and prepared a series of polythiophenes with conjugated side chains of bi(phenylenevinylene),^[13] bi(thienylenevinylene),^[11a, 14] and phenothiazinevinylene;^[15] these exhibited broadened and strengthened absorption spectra, improved charge mobility, and enhanced PCEs. Hou et al. first introduced conjugated alkylthienyl side chains onto the benzodithiophene (BDT) skeleton, leading to a more planar configuration than that of BDT with alkoxyl side chains;^[11d] this had a positive effect on energy level modulation and π - π stacking properties between polymer main chains; hence improving solar cell performance.^[11] Ge et al. reported diketopyrrolopyrrole (DPP)-based co-polymers with furan side chains on the BDT core; these exhibited smaller optical band gaps, broader absorption ranges, and deeper HOMO energy levels than those of the corresponding alkoxyl-substituted counterparts.^[16] Recently, side chains composed of one or more thiophene units linked by single or double bonds were studied to further extend the π conjugation and raise the efficiency of related PSCs.^[17] It is notable that the rational choice of suitable side chains is very important for conjugated polymers to achieve high photovoltaic performance.^[18] However, no work has been done to consider the degree of branching and dimensionality at the same time. Thus, a systematic investigation of the side-chain engineering is needed to understand the structure-property relationship of D-A-type photovoltaic co-polymers.

Based on the above considerations, we present herein the synthesis and characterization of a series of BDT-quinoxaline (Q_x) conjugated co-polymers, PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ (Scheme 1), in which variable side chains with different degrees of branching and dimensionality have been attached onto the BDT skeleton. BDT is chosen as a weak electron-donating unit because of its structural symmetry and rigid fused aromatic system, which promotes enhanced electron delocalization and molecular packing.^[19] According to reports in the literature, a variety of BDTbased co-polymers have been designed and prepared with various electron acceptors, including benzothiadiazole (BT),^[2d, 11b, d] (BZ),^[8c, 11e, 19d] benzotriazole

DPP,^[20] thiazolothiazole (TTZ),^[21] thienopyrroledione (TPD),^{[17b][22]} and thieno[3,4-b]thiophene (TT),^[2c, 19b, 23] and substantial PCEs surpassing 7% had been achieved. Derivatives of Qx have been widely used as an acceptor unit for building D-A co-polymers because of the electron-withdrawing property of the imine nitrogen atoms.^[24] Recently, the incorporation of an electronwithdrawing fluorine atom onto the Qx skeleton has become more attractive.^[7b,25] The small size of the fluorine atom would not increase steric interactions; however, its strong electron-affinity nature is helpful for lowering the HOMO and LUMO energy levels to maintain almost the same optical band gap as their corresponding non-fluorinated analogues. $^{[2d,\,19d,\,26]}$ Fluorination would also induce molecular coplanarity and molecular packing through intra- and/or intermolecular interactions; $\!\!\!\!\!\!^{[8c,\,11b,\,25,\,27]}$ this would result in higher carrier mobilities and better morphology. From the viewpoints of the degree of branching and dimensionality studied herein, we would like to report the overall effect of side chains on the thermal stability, optical absorption, energy level, molecular packing, hole mobility, and photovoltaic performance of BDT-Q_x-based co-polymers. Although previous studies have been reported concerning alkyl, alkoxyl, and alkylthienyl side chains, there have not been any reports on a systematic investigation into the degree of branching and dimensionality of the side chains simultaneously with identical conjugated backbones. Polymer PBDTTL-BFQ, with 2D and linear conjugated side chains, demonstrated the best performance of up to 5.00% PCE, which could be of great importance for the future design and synthesis of polymer donor materials in photovoltaic applications.



Scheme 1. Design strategy and molecular structures of the co-polymers described herein.

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Results and Discussion

Synthesis and characterization

The molecular structures of the co-polymers and the synthetic routes to the monomers and co-polymers are shown in Schemes 1 and 2, respectively. All organic tin monomers, including monomer **BDTTB**, were synthesized according to our previously reported procedures.^[11b, 12] 4,7-Bibromo-5-fluoro-2,1,3-benzothiadiazole (**3**) was converted into the corresponding diamine compound (**4**) by means of a reductive reaction in the presence of Zn/acetic acid. Then, compound **5** was pre-



Scheme 2. Synthetic routes of the monomers and co-polymers. NBS = *N*-bromosuccinimide, dba = dibenzylidenea-cetone.

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pared by a condensation reaction of **4** with 1,2-bis[3-(octyloxy)phenyl]ethane-1,2-dione.^[24,25] A Stille cross-coupling reaction of dibromide **5** with 2-(tributylstannyl)thiophene yielded intermediate **6**. Bromination of **6** with NBS in DMF afforded the target monomer **BFQ**. Co-polymers **PBDTAL-BFQ**, **PBDTAB-BFQ**, **PBDTTL-BFQ**, and **PBDTTB-BFQ** were then prepared through Stille coupling polymerization by using [Pd₂(dba)₃]/ P(o-tolyl)₃ as catalysts to give the co-polymers in good yields. The crude polymers were precipitated into methanol and filtered, followed by sequential Soxhlet extraction with methanol, hexane, and chloroform to remove byproducts and oligomers. The purified co-polymers were obtained from the chloro-

> form fraction precipitated into methanol again, filtered, and dried under vacuum for 24 h. The chemical structures of the resulting co-polymers were confirmed by ¹H NMR spectroscopy and elemental analysis. These polymers exhibit excellent filmcasting properties and good solubility in some common organic solvents, such as chloroform, THF, chlorobenzene (CB), and di-(DCB). chlorobenzene The number-average molecular weights (M_p) and polydispersity indices (PDIs) of these polymers were measured by gel permeation chromatography (GPC) by using THF as the eluent and polystyrene as the internal standard. The M_n values of **PBDTAL**-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ were determined to be 28, 8, 44, and 46 kDa, respectively, with PDIs in the range of 2.1-4.2.

> The thermal stability of conjugated polymers plays a very important role in PSCs. The thermal properties were investigated by thermogravimetric analysis (TGA). As shown in Figure 1a and Table 1, the degradation temperatures (T_d) of **PBDTAL**-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ with 5% weight loss were measured to be about 332, 326, 434, and 423 °C, respectively. From the results, it is easy to see that increasing the degree of branching of the side chains decreases the thermal stability of the relevant co-polymers. We also found that 2D conjugated side chains

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Figure 1. TGA and differential scanning calorimetry (DSC) curves of the copolymers.

Table 1. Molecular weights and thermal properties of the co-polymers.						
Co-polymers	Yield [%]	Mw ^[a] [kDa]	Mn ^[a] [kDa]	PDI ^[a]	τ _d ^[b] [°C]	
PBDTAL-BFQ	73	95	28	3.4	332	
PBDTAB-BFQ	78	17	8	2.1	326	
PBDTTL-BFQ	59	185	44	4.2	434	
PBDTTB-BFQ	78	101	46	2.2	423	
[a] Molecular weights and PDIs were determined by GPC in THF by using polystyrene as standards. [b] Opset decomposition temperature mea-						

sured by TGA under N₂.

based on alkylthienyl-substituted BDTs were much more stable than their alkoxyl-substituted analogues. Therefore, the thermal stability was mainly affected by the 2D conjugated side chains, and the branched alkyl side chains made a slightly

more negative difference. On the other hand, no endo- or exothermal signals were observed from DSC measurements in the range of 0–230 °C from the second heating run (Figure 1 b), which implied that these polymers were thermally robust. The data for molecular weights and thermal analysis are listed in Table 1.

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Optical properties

The UV/Vis absorption properties of the polymers were investigated in chloroform (10^{-5} M) and as thin solid films prepared by drop-casting on guartz slides from a 10 mg mL⁻¹ solution in chloroform. The corresponding absorption data of the co-polymers are summarized in Table 2. As shown in Figure 2, these polymers exhibit similar UV/Vis absorption spectra due to the consistency of their backbone structures. The first intense band ranges from $\lambda = 300$ to 480 nm and the second ranges from $\lambda = 500$ to 750 nm. The higher energy absorption band corresponds to the π - π * transition of the conjugated backbone, whereas the lower one should be attributed to ICT between the D (BDT) and A (Q_x) in the polymer backbone.^[4] Both in CHCl₃ and in the solid state, polymers PBDTAB-BFQ and PBDTTB-BFQ, with branched alkoxyl side chains, possess blueshifted absorption relative to that of the linear alkoxyl-substituted side-chain analogues. This is probably because the branched alkoxyl substituents in the BDT skeleton disrupt the planar conformation of the resulting co-polymers to some extent. Going from 1D alkoxyl side chains to 2D alkylthienyl side chains, the maximum peaks are redshifted greatly, which signifies the extension and delocalization of the π -electron system. Consequently, polymer PBDTTL-BFQ has a relatively good absorption at long wavelengths with the main peaks at $\lambda = 359$, 445, and 616 nm in solution and at $\lambda = 365$, 447, and 652 nm in the thin film. From the onset absorption edges, optical band-gap energies of the thin films were determined to be 1.75, 1.79, 1.70, and 1.74 eV for PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ, respectively. All of these copolymers had LBGs with broad absorption bands in the visible region, which implied the significance of harvesting more solar photons in their PSCs. The co-polymers with linear alkoxyl side chains have lower band gaps than those of co-polymers with branched alkoxyl side chains. Furthermore, replacing alkoxyl side chains with alkylthienyl side chains could efficiently reduce the band gaps of the relevant co-polymers; this implied that polymer PBDTTL-BFQ, with 2D conjugated linear side chains, should exhibit the best light-harvesting ability and would be expected to obtain high J_{sc} values in the fabricated PSCs.

Electrochemical properties

The energy levels are crucial for the selection of appropriate acceptors in BHJ PSCs.^[28] The HOMO and LUMO energy levels

Table 2. Optical and electrochemical data of the co-polymers.						
Co-polymers	Abs. λ_{\max}^{sol} [nm]	Abs. $\lambda_{\max}^{\text{film}}$ [nm]	<i>E</i> _g ^[a] [eV]	HOMO [eV]	LUMO [eV]	$E_{g}^{[b]}$ [eV]
PBDTAL-BFQ	417, 584	429, 627	1.75	-5.18	-2.90	2.28
PBDTAB-BFQ	408, 565	420, 584	1.79	-5.19	-2.88	2.31
PBDTTL-BFQ	359, 445, 616	365, 447, 652	1.70	-5.21	-3.08	2.13
PBDTTB-BFQ	355, 427, 580	360, 440, 598	1.74	-5.30	-3.05	2.25
[a] The optical band gap was estimated from the wavelength of the optical absorption edge of the co-polymer film. [b] The electrochemical band gap was calculated from the LUMO and HOMO energy levels.						

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Figure 2. Normalized UV/Vis absorption spectra of the co-polymers in chloroform (a) and as thin solid films (b).

of the co-polymers were evaluated by cyclic voltammetry (CV) of their thin films. CV measurements were carried out on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s⁻¹, with a platinum wire counter electrode and an Ag/AgCl reference electrode in a 0.1 mol L⁻¹ solution of Bu₄NClO₄ in anhydrous, nitrogen-saturated CH₃CN. A platinum plate coated with a thin film of the studied co-polymer was used as the working electrode. The energy level of the Ag/AgCl reference electrode was calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) system (4.34 eV).^[29] The HOMO and LUMO energy values (in eV) were calculated by using Equations (1) and (2), respectively:

$$E_{\rm HOMO} = -e(E_{\rm onset,ox} + 4.34) \tag{1}$$

$$E_{\rm LUMO} = -e(E_{\rm onset,re} + 4.34) \tag{2}$$

in which $E_{\text{onset,ox}}$ and $E_{\text{onset,re}}$ are the onset oxidation and reduction potentials, respectively, versus Ag/AgCl.^[29]

As shown in Figure 3 a, all of these co-polymers exhibited reversible oxidation and reduction waves, which implied their potential to transport positive and negative charges. On the basis of the onset potentials, the HOMO and LUMO energy levels were estimated to be -5.18 and -2.90 eV for **PBDTAL-BFQ**, -5.19 and -2.88 eV for **PBDTAB-BFQ**, -5.21 and -3.08 eV for **PBDTTL-BFQ**, and -5.30 and -3.05 eV for **PBDTTB-BFQ**. The electrochemical band gaps were calculated



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Figure 3. a) Cyclic voltammograms of the co-polymers at a scan rate of 50 mV s^{-1} and b) the electronic energy level diagram of the co-polymers and phenyl-C₆₁-butyric acid methyl ester (PC₇₁BM).

to be 2.28, 2.31, 2.13, and 2.25 eV for PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ, respectively. The difference between the optical and electrochemical band gaps could be explained by the exciton binding energy of the copolymers and/or the interfacial barriers for charge injection.^{[24d][30]} The results indicated that the branched alkoxyl side chains were beneficial to deepen the HOMO energy levels, compared with the linear alkoxyl chains, which gave the copolymers desired high V_{oc} values for PSCs.^[31] On the other hand, the introduction of 2D alkylthienyl conjugated side chains could further lower the HOMO and LUMO energy levels, as well as the band gaps. This deep-lying HOMO level was attributed to the conformational distortion and enhanced aromatic population of the conjugated backbone caused by high steric hindrance.^[11g] To make a clear comparison, the electronic energy level diagrams of the co-polymers and PC71BM are described in Figure 3b. The LUMO gaps of 0.92-1.12 eV and HOMO gaps of 1.18-1.30 eV between the co-polymers and PC₇₁BM should provide a sufficient driving force to guarantee efficient exciton dissociation at the D-A interface, which would ensure energetically favorable electron transfer.^[32]

Theoretical calculations

To evaluate the degree of branching and dimensionality impacts of the side chains on the molecular architectures and electronic properties of the polymers, DFT calculations were performed to verify stationary points as stable states for the

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optimized conformations and single-point energies, at the B3LYP/6-31G(d) level.^[25] Three repeating units (trimers: BDTAL-BFQ, BDTAB-BFQ, BDTTL-BFQ, and BDTTB-BFQ) of the copolymers were studied as the model compounds for simulations of PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ. To simplify the calculations, long alkyl chains of dodecyl, 2-ethylhexyl, and 2-octyldodecyl groups were replaced by amyl and isoamyl groups because they did not significantly affect the equilibrium geometries or electronic properties.^[25] The HOMO and LUMO wavefunctions of the model compounds are shown in Figure 4. The calculated HOMOs featured extended delocalization along the entire conjugated backbones. The electron density mainly distributed in the middle part of the conjugated molecular skeleton, which was affected by both the donor and acceptor units. However, the LUMOs were mainly focused on the Q_x skeletons, resulting from the effect on the acceptor units. Compared with the HOMO and LUMO, the HOMO-1 and LUMO+1 seemed to be distributed from the middle part to two side parts, which implied that the internal charge transfers were possible in BDT-Q_x conjugated systems. Thus, LBGs of PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ would be obtained by these efficient internal charge-transfer processes from D segments to A segments. The HOMO and LUMO energy levels of PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ trimers were calculated to be -4.71/-2.51, -4.74/-2.53, -4.65/-2.48, and -4.66/-2.49 eV, respectively. The band gaps were then determined to be 2.20, 2.21, 2.17, and 2.17 eV. From

the calculation results, the effect of side chains on the band gaps was similar to those results obtained from CV and UV/Vis evaluations. The introduction of branched alkoxyl side chains will deepen the HOMO energy levels and increase the band gaps. On the contrary, changes to the dimensionality by conjugated side chains will decrease the band gaps, while keeping low-lying HOMO energy levels.

Crystallinity and hole mobility

The crystallinities and molecular ordering properties of the copolymer films were investigated by XRD analyses of the spincast films onto glass substrates. Figure 5 a shows the XRD patterns of the corresponding co-polymer films cast from solutions in CB. As shown in Figure 5a, all films displayed somewhat crystalline properties with two diffraction peaks in the ranges of 3-5 and 20-30°, which were related to the lamellar spacings (d₁) and the stacking distances (d_{π}) between coplanar conjugated polymers. For the alkoxyl-substituted co-polymers, co-polymer PBDTAB-BFQ with branched alkoxyl side chains exhibits higher crystallinity than that of **PBDTAL-BFQ**. The d_1 and d_{π} spacings were calculated to be 25.58 and 22.23 Å and 3.59 and 3.64 Å for PBDTAL-BFQ and PBDTAB-BFQ, respectively. The increased degree of branching would help to induce lamellar-like ordering of the resulting co-polymer, separated by the attached alkyl side chains. Conversely, branched alkyl side chains would prevent the face-to-face packing of the polymer backbones due to greater steric hindrance. After the introduc-



Figure 4. Molecular structures and optimized molecular orbital surfaces of the LUMO + 1, LUMO, HOMO, and HOMO - 1 for the model trimers, obtained by Gaussian 09 at the B3LYP/6-31G(d) level.

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Figure 5. a) J-V characteristics of co-polymer/PC₇₁BM-based hole-only devices measured at ambient temperature. b) XRD patterns of the co-polymer films on silicon wafers.

tion of alkylthienyl conjugated side chains, the crystalline properties of the 2D co-polymers decreased. The lamellar-like ordering and π - π stacking also seemed to decrease, however, the effect of the degree of branching was the similar to that of the alkoxyl-substituted analogues. As calculated from peaks (100) and (010), the d_1 and d_{π} spacings were determined to be 27.75 and 24.79 Å and 3.61 and 3.79 Å for **PBDTTL-BFQ** and **PBDTTB-BFQ**, respectively. Through comprehensive consideration of the XRD results, co-polymer **PBDTAB-BFQ** shows the best stacking properties, and thus, can be expected to process the highest carrier mobility.

Generally in PSCs, the J_{sc} value and fill factor (FF) are somewhat affected by the hole mobility of the polymer donor materials. Previous work showed that higher hole mobility would enable better hole transport within an active layer without large photocurrent loss caused by recombination of opposite charges.^[12, 20c, 33] The space-charge limited current (SCLC) method was widely employed to investigate the vertical carrier transport properties of the PSCs. To obtain a realistic simulation for PSCs, we chose blend films of co-polymer:PC71BM (1:1) to fabricate the hole-only devices and evaluate the hole mobility by using the SCLC method.[12,20c,33] The structure of the hole-only device was indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT)/polymer/MoO₃/Au, whereas the mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which was described by Equation (3), according to our previous work.^[12]

 $J = 9 \varepsilon_0 \varepsilon_r \mu_h V^2 / 8 d^3$

(3)

The voltage (V)-current density (J) curves of the fabricated hole-only devices of the co-polymer blends are shown in Figure 5b. According to Equation (3) and the results shown in Figure 5 b, the hole mobilities of PBDTAL-BFQ, PBDTAB-BFQ, **PBDTTL-BFQ**, and **PBDTTB-BFQ** are calculated to be 2.6×10^{-6} , 1.2×10^{-5} , 3.8×10^{-6} , and 4.7×10^{-6} cm²V⁻¹s⁻¹, respectively. The PBDTAB-BFQ film exhibited the highest hole mobility under the same conditions; this is attributed to the best crystallinity and molecular packing properties, as described by the XRD results. The other three blend films show similar hole mobilities at a level of 10^{-6} cm²V⁻¹s⁻¹. The results also indicated that the introduction of branched side chains was helpful for increasing the hole mobilities of the relevant co-polymers. By considering of the XRD results, π - π stacking may have a more important effect on the carrier mobility than lamellar stacking in our copolymers based on BDT and Q_x.

Photovoltaic properties

To investigate the effects of side chains on the photovoltaic properties of these co-polymers, BHJ PSC devices with a conventional configuration of ITO/PEDOT:polystyrene sulfonate (PSS)/polymer:PC71BM/Ca/Al and an inverted configuration of ITO/ZnO/poly({9,9-bis[3'-(N,N-dimethylamino)propyl]-2,7-fluorene}-alt-2,7-(9,9-dioctylfluorene)) dibromide (PFN) /polymer:PC71BM/MoO3/AI were fabricated and evaluated. PC71BM was chosen here instead of PC₆₁BM because of its significantly broader and stronger absorption in the visible region.^[34] The device fabrication processes are described in detail in the Experimental Section. The fabrication conditions were optimized by changing many parameters, including the choice of solvent, annealing conditions, blend ratio of the polymer and PC71BM, and processing additive effect. The active layers were finally spin-coated from the co-polymers and solutions of PC71BM in CB and the optimal weight ratio of co-polymer to PC₇₁BM was 1:1 (w/w) with 3% 1,8-diiodooctane (DIO) additive. DIO was chosen as the additive because it had a high boiling point of 168°C and good ability to solvate the PC₇₁BM acceptor, which was expected to afford an optimal film morphology for obtaining a high PCE.^[35] The addition of DIO would decrease the V_{oc} value of the related PSCs, which could be attributed to lowering of the charge-separated and charge-transfer-state energies during the addition process.^[36] Generally, all conventional devices with 3% DIO additive exhibit better performances than those of PSCs without any additives. On the other hand, the thermal annealing process had no positive effect on improving the photovoltaic performance in this work. All solar cell devices were evaluated under simulated 100 mW cm⁻², AM 1.5G illumination. The current density-voltage (J-V) curves are plotted in Figure 6a and b, and the photovoltaic data of V_{ocr} J_{scr} FF, and PCE are summarized in Table 3 for a clear comparison.

For conventional devices, the PSC based on **PBDTAL-BFQ** exhibited a V_{oc} of 0.64 V, a J_{sc} of 9.44 mA cm⁻², and an FF of 47.5%, resulting in a PCE of 2.86%. For polymer **PBDTAB-BFQ**, the V_{oc} value improved from 0.64 to 0.70 V, which was consis-

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Figure 6. *J*–*V* curves of co-polymer:PC₇₁BM (1:1) based PSCs with a conventional (a) and an inverted structure (b) under AM 1.5G illumination, 100 mW cm⁻². c) EQE curves of co-polymer:PC₇₁BM (1:1) based PSCs.

tent with the CV measurements, that is, PBDTAB-BFQ had a lower HOMO level than that of PBDTAL-BFQ. However, the J_{sc} and FF values dropped, which resulted in a lower PCE of 1.78%. Similar trends were found for PSCs based on PBDTTL-BFQ and PBDTTB-BFQ. The results indicated that the introduction of branched alkoxyl side chains could improve the V_{ocr} but decrease the J_{sc} and FF values of the PSCs. On the contrary, the introduction of 2D conjugated side chains would increase the $V_{\rm ocr}$ J_{scr} and FF values simultaneously, which would result in higher efficiencies than the alkoxyl-substituted analogues. PSCs based on the polymer of BDTTL-BFQ exhibited the highest V_{oc} of 0.79 V. Overall, devices composed of PBDTTB-BFQ showed the best performance of 4.80% PCE with a $V_{\rm oc}$ of 0.70 V, a $J_{\rm sc}$ of 11.87 mA cm⁻², and an FF of 57.5%, as a result of the significantly enhanced J_{sc} and FF values. Relative to conventional PSCs, inverted solar cell devices display better photo-

Table 3. Performance of the PSCs tested under AM 1.5G simulated illumination.						
Co-polymers	<i>V</i> _{oc} [V]	$J_{\rm sc} [{ m mA}{ m cm}^{-2}]$	FF [%]	PCE [%]		
PBDTAL-BFQ ^[a]	0.64	9.44	47.5	2.86		
PBDTAL-BFQ ^[b]	0.66	7.94	67.9	3.55		
PBDTAB-BFQ ^[a]	0.70	7.63	33.2	1.78		
PBDTAB-BFQ ^[b]	0.70	7.51	45.8	2.41		
PBDTTL-BFQ ^[a]	0.70	11.87	57.5	4.80		
PBDTTL-BFQ ^[b]	0.74	10.91	70.0	5.00		
PBDTTB-BFQ ^[a]	0.79	5.71	47.9	2.16		
PBDTTB-BFQ ^[b]	0.88	4.71	63.9	2.64		
[a] Data obtained by using a conventional configuration of ITO/PE- DOT:PSS/polymer:PC ₂₁ BM/Ca/AI. [b] Data obtained by using an inverted						

configuration of ITO/ZnO/PFN/polymer:PC71BM/MoO3/Al.

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voltaic performances and longer ambient stability because a more stable, high work-function metal electrode is used and the acidic PEDOT:PSS layer is replaced by other stable anode buffer layers.^[20c, 27, 37] As shown in Figure 6b, the inverted devices based on PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ exhibit PCEs of 3.55, 2.41, 5.00, and 2.64%, respectively. The efficiencies of all inverted PSCs are larger than their corresponding conventional devices; this is mainly due to the increased V_{oc} and FF values. The significantly increased V_{oc} and FF values should be attributed to the improved interface between the active layer and ITO electrode and decreased work functions of ITO by ZnO layer, which might supply efficient electron collection and decrease electron-hole recombination.^[7c, 38]

In conventional and inverted PSCs, the PBDTTL-BFQ devices exhibited the best photovoltaic performance, which was further verified by external quantum efficiency (EQE) evaluations and surface morphology studies of the active blend films. The EQE curves of the PSCs fabricated under optimal conditions are provided in Figure 6 c. The PBDTTL-BFQ device had a higher maximum EQE value of 51 % at $\lambda =$ 460 nm than those devices based on PBDTAL-BFQ, PBDTAB-BFQ, and PBDTTB-BFQ. Moreover, the PBDTTL-BFQ device exhibited a significantly broader spectral response range, within $\lambda = 300-750$ nm, compared with those based on the other three co-polymers; this is in good agreement with optical absorption spectra of the thin solid films, as discussed in the section on optical properties. Accordingly, the PBDTTL-BFQ devices should show a larger photocurrent and a higher overall PCE than the other devices. The surface morphology of polymer:PC71BM film was also investigated by using AFM. The AFM height (left) and phase (right) images are shown in Figure 7. The average surface roughnesses (R_a) measured from the topographic images were 1.79, 2.98, 2.53, and 3.84 nm for PBDTAL-BFQ, PBDTAB-BFQ, PBDTTL-BFQ, and PBDTTB-BFQ, respectively, blend films cast from CB with ratios of 1:1 (by adding 3% DIO). The phase images of the active blending films show uniform D-A interpenetrating networks with appropriate domain sizes. As shown in Figure 7, the domain sizes of the PBDTTB-BFQ:PC71BM active layer are a little bigger. The lowest J_{sc} value of the PBDTTB-BFQ device was probably caused by the poor phase

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required to obtain high FF and J_{sc} values in the PSCs.^[39] Herein, the large difference in absorption may play a more significant role on the photovoltaic properties than that of the carrier mobility.

Conclusion

We used Stille coupling polymerization to prepare a series of new conjugated polymers featuring BDT donors, with different side chains, co-polymerized with monofluorinated Q_x moieties. Our results showed that subtle changes to the degree of branching and dimensionality of the side chains altered their molecular coplanarity and the electron state of the related co-polymers, which simultaneously influenced their thermal stability, optical band gap, energy levels, and molecular packing of the resulting co-polymers. The linear and 2D conjugated structures of the side chains were helpful at increasing the thermal stabilities and optical absorptions of the relevant co-polymers. Moreover, the introduction of 2D alkylthienyl conjugated side chains could lower the HOMO and LUMO energy levels, whereas the branched alkoxyl side chains were beneficial at deepening the HOMO energy levels compared with the linear alkoxyl chains. The increased degree of branching would also help to induce lamellar-like ordering of the resulting co-polymers; however, the branched alkoxyl side chains would prevent face-to-face packing of the polymer backbones.

Figure 7. AFM topographic images of the film blends (polymer:PC₇₁BM = 1:1, w/w): PBDTAL-BFQ (a,b), PBDTAB-BFQ (c,d), PBDTTL-BFQ (e,f), and PBDTTB-BFQ (g,h). Image size: $5 \times 5 \ \mu m^2$.

separation and narrow, low spectral response, as discussed above. Although the morphology of the **PBDTAB-BFQ**:PC₇₁BM layer was also comparable to that of **PBDTTL-BFQ**:PC₇₁BM, its related PSCs could not achieve high performance, although the blended film had the highest hole mobility, as determined from the SCLC evaluation. The hole mobility could be influenced by morphology, field, recombination, or carrier density in the photoactive layer under the operating conditions. Our results proved that high hole mobility alone could not guarantee high device performance; substantial carrier mobility was The 2D conjugated side chains would decrease the crystalline properties of the co-polymers. The photovoltaic results indicated that the introduction of branched alkoxyl side chains could improve the V_{ocr} , but decrease the J_{sc} and FF values of the PSCs. On the contrary, the introduction of 2D conjugated side chains would increase the V_{ocr} J_{scr} and FF simultaneously, which would result in higher efficiencies than their alkoxyl-substituted analogues. Finally, PSCs based on the polymer **BDTTL-BFQ** exhibited the highest V_{oc} of 0.88 V. Overall, the **PBDTTB-BFQ** devices showed the best performance of 5.00% PCE with a V_{oc}

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of 0.74 V, a J_{sc} of 10.91 mA cm⁻², and an FF of 70.0%, which resulted from the significantly enhanced J_{sc} and FF values. This work demonstrates a good example for tuning the thermal stability, absorption range, energy level, charge transport, and photovoltaic properties of the designed co-polymers by side-chain engineering of the degree of branching and dimensionality, which can offer a simple and effective method to improve the efficiency of PSCs.

Experimental Section

Measurements and characterization

NMR spectra were collected on a Bruker ARX 400 NMR spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed on a Carlo Erba 116 elemental analyzer. Molecular weights of the co-polymers were determined by using a Waters 1515 GPC instrument with chloroform as the eluent and polystyrene as a standard. TGA was conducted on a TA Instrument Model SDT Q600 simultaneous TGA/ DSC analyzer at a heating rate of 10°C min⁻¹ under a N₂ flow rate of 90 mLmin⁻¹. UV/Vis spectra were obtained on a Cary 300 spectrophotometer. CV measurements were made at room temperature on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1} , with a platinum wire counter electrode and an Ag/AgCl reference electrode in an anhydrous nitrogen-saturated solution of Bu₄NClO₄ in acetonitrile (0.1 molL⁻¹). The redox couple of Fc/Fc⁺ was used as an external standard. The co-polymers were coated on the platinum plate working electrodes from dilute solutions in chloroform. XRD patterns of the polymers were recorded on a Philips X-ray diffractometer operated in reflection geometry at 30 mA, 40 kV with $Cu_{K\alpha}$ radiation. The AFM measurements were performed on a Veeco Nanoscope V microscope in tapping mode.

PSC device fabrication and characterization

Conventional PSCs were fabricated with ITO glass (15 Ω cm⁻²) as the anode, Ca/Al as the cathode, and the active layer of the copolymer and PC71BM as the photosensitive layer. After spin-coating a 35 nm layer of PEDOT:PSS (Baytron P VP AI 4083) onto the precleaned ITO substrate, the photosensitive layer was subsequently prepared by spin-coating the solution (and adding 3% DIO) of the co-polymer and PC71BM (w/w) in CB on the ITO/PEDOT:PSS electrode. For the inverted devices, a ZnO thin film (about 40 nm) was deposited on the surface of ITO glass. The ZnO layer was pretreated with UV-ozone for 10 min and the conjugated polyelectrolyte of PFN (5 nm) was spin-coated on top of the ZnO layer. The photoactive layer was then spin-coated on top of this layer from a solution in CB (containing 3% DIO). Subsequently, about 10 nm MoO₃ and 100 nm Ag were deposited in turn through shadow masks by thermal evaporation. The device area was 0.04 cm². The I-V characterization of the devices was carried out on a computer-controlled Keithley 236 Source Measurement system. The EQE values were measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830 DSP) during illumination with monochromatic light from a xenon lamp. A solar simulator was used as the light source, and the light intensity was monitored by using a standard Si solar cell. The thickness of the films was measured by using a Dektak 6 M surface profilometer. All fabrication and characterization processes, except for the EQE measurements, were conducted in a glove box.

Materials

All chemicals were purchased as reagent grade from Aladdin, Adamas, Aldrich, Alfa Aesar, and Acros Chemical Co., and used without further purification. All solvents were freshly distilled immediately prior to use. 4,8-Dehydrobenzo[I,2-*b*:4,5-b']dithiophene-4,8-dione (1), 4,7-dibromo-5-fluoro[2,1,3]benzothiadiazole (3) and the four organic tin monomers were synthesized according to procedures reported previously.^[11b, 12]

4,8-Bis[5-(2-octyldodecyl)-2-thenyl]benzo[1,2-b:4,5-b']dithiophene (2)

2-(2-Octyldodecyl)thiophene (3.64 g, 10 mmol) in anhydrous THF (15 mL) was added to a three-necked, round-bottomed flask equipped with a condenser. When the solution was cooled to 0°C under an argon atmosphere, n-butyllithium (4.4 mL, 11 mmol, 2.5 м in hexane) was added dropwise. The reactant solution was then heated to 50 °C and kept at the same temperature for 2 h. Then, 4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (0.55 g, 2.5 mmol) in anhydrous THF (10 mL) was added dropwise. The mixture was stirred at 50 °C overnight, and then cooled to ambient temperature. SnCl₂·H₂O (4.5 g, 20 mmol) in HCl (8 mL; 10%) was added, and the mixture was stirred for another 2 h. Then ice water was added and extracted with dichloromethane. The combined extracts were dried over anhydrous MgSO₄ and evaporated. The crude product was purified by column chromatography (SiO₂, petroleum ether) to give 2 as a light-yellow oil (0.98 g, 42.8%). ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (d, J = 5.7 Hz, 2 H; ArH), 7.47 (d, J=5.7 Hz, 2H; ArH), 7.32 (d, J=3.5 Hz, 2H; ArH), 6.91 (d, J=3.5 Hz, 2H; ArH), 2.88 (d, J=6.6 Hz, 4H; -CH₂-), 1.75 (m, 2H; -CH-), 1.43-1.20 (m, 64H; -CH₂-), 0.93–0.86 ppm (m, 12H; -CH₃); ¹³C NMR (100 MHz, CDCl₃): $\delta = 145.7$, 139.0, 137.2, 136.5, 127.7, 127.4, 125.4, 124.1, 123.4, 40.0, 34.7, 33.4, 32.0, 30.0, 29.7, 29.69, 29.66, 29.4, 26.7, 22.7, 14.2 ppm; elemental analysis calcd (%) for C₅₈H₉₀S₄: C 76.08, H 9.91; found: C 76.05, H 9.96.

2,6-Bis(tributyltin)-4,8-bis[5-(2-octyldodecyl)-2-thenyl]benzo[1,2-b:3,4-b']dithiophene (BDTTB)

A solution of 2 (0.92 g, 1.0 mmol) in anhydrous THF (20 mL) was added to a three-necked, round-bottomed flask. The mixture was cooled to 0°C under an argon atmosphere. n-Butyllithium (1.0 mL, 2.5 mmol, 2.5 m in hexane) was added dropwise and the solution was stirred for 2 h at ambient temperature. The mixture was cooled to 0°C, and tributyltin chloride (0.96 g, 3.0 mmol) was added slowly. The mixture was stirred at 0 $^\circ\text{C}$ for 30 min, and then slowly warmed to room temperature. After the solution was stirred overnight, deionized water (50 mL) was added to terminate the reaction. The mixture was then extracted with diethyl ether, and the combined organic layers were dried over anhydrous MgSO₄. After removing the desiccant, the filtrate was concentrated. The crude product was finally purified by column chromatography (SiO₂, petroleum ether, containing 1% triethylamine) to give BDTTB as a yellow oil (0.61 g, 41 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.30 (t, J = 13.4 Hz, 2H; ArH), 7.35 (d, J=3.4 Hz, 2H; ArH), 6.89 (d, J=3.5 Hz, 2H; ArH), 2.89 (d, J=6.6 Hz, 4H; ArH), 1.80-1.70 (m, 2H; -CH-), 1.68-1.47 (m, 12H; -CH2-), 1.45-1.20 (m, 76H; CH2-), 1.15 (t, 12H; -CH₂-), 0.94–0.80 ppm (m, 30 H; -CH₃); ¹³C NMR (100 MHz, CDCl₃): $\delta =$ 145.2, 143.2, 141.5, 138.3, 137.3, 131.6, 127.5, 125.3, 122.2, 34.8, 33.4, 32.0, 30.1, 29.8, 29.8, 29.5, 29.4, 29.2, 29.1, 29.0, 27.6, 27.5, 27.3, 27.1, 26.8, 22.8, 14.2, 13.8, 10.9, 8.8 ppm; elemental analysis calcd (%) for C₈₂H₁₄₂S₄Sn₂: C 65.94, H 9.58; found: C 65.96, H 9.62.

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3,6-Dibromo-4-fluoro-1,2-phenylenediamine (4)

Under the protection of argon, compound **3** (1.0 g, 3.2 mmol), zinc powder (2.5 g, 12 mmol), and glacial acetic acid (30 mL) were added to a round-bottomed flask. The mixture was heated at reflux for 3 h. After cooling to room temperature, a solution of NaOH (10%) was added until the pH became alkaline. The mixture was then extracted with diethyl ether (4×100 mL). The combined extracts were washed with a solution of NaOH and then deionized water, and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure to give **4** as a brown solid (0.72 g, 79%). The product was used in the next step directly with no further purification.

5,8-Dibromo-6-fluoro-2,3-bis(3-octyloxyphenyl)quinoxaline (5)

Compound **4** (1.5 g, 5.28 mmol), 1,2-bis(3-octyloxyphenyl)-ethane-1,2-dione (2.47 g, 5.28 mmol), and glacial acetic acid (30 mL) were added to a round-bottomed flask. Under the protection of argon, the mixture was briefly warmed to 50 °C, and then stirred at room temperature for 2 h. The precipitate was collected by filtration, washed with ethanol, and dried to afford compound **4** as a white solid (2.8 g, 74%). ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 8.0 Hz, 1H; ArH), 7.24–7.21 (m, 4H; ArH), 7.17 (t, *J* = 7.1 Hz, 2H; ArH), 6.94 (m, 2H; ArH), 3.86 (t, *J* = 6.6 Hz, 4H; -O-CH₂-), 1.73 (m, 4H; -CH₂-), 1.42–1.29 (m, 20H; -CH₂-), 0.89 ppm (t, *J* = 6.9 Hz, 6H; -CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 160.6, 159.1, 158.0, 154.5, 153.2, 139.5, 139.0, 138.9, 136.3, 129.4, 124.3, 123.3, 123.0, 122.6, 122.5, 116.7, 116.5, 115.8, 68.1, 31.9, 29.3, 29.2, 26.1, 22.7, 14.2 ppm; elemental analysis calcd (%) for C₃₆H₄₃Br₂FN₂O₂: C 60.51, H 6.07, N 3.92; found: C 60.48, H 6.05, N 3.98.

2,3-Bis(3-octyloxyphenyl)-6-fluoro-5,8-di(thiophen-2-yl)quinoxaline (6)

A mixture of 5 (0.64 g, 0.90 mmol), tributyl(2-thienyl)stannane (0.84 g, 2.25 mmol), [Pd(PPh₃)₂Cl₂] (25 mg, 0.036 mmol), and degassed toluene (10 mL) was heated at reflux overnight. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO2, petroleum ether/dichloromethane = 3:2) to give **6** as a yellow solid (0.54 g, 83.6%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.01$ (d, J = 13.3 Hz, 2H; ArH), 7.89 (dd, J =3.7, J=1.0 Hz, 1H; ArH), 7.58–7.54 (m, 2H; ArH), 7.37 (d, J= 11.52 Hz, 2H; ArH), 7.26-7.19 (m, 6H; ArH), 6.94 (m, 2H; ArH), 3.91 (t, J=6.6 Hz, 4H; -O-CH₂-), 1.75 (m, 4H; -CH₂-), 1.44–1.29 (m, 20H; -CH₂-), 0.90 ppm (t, J = 6.9 Hz, 6H; -CH₃-); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 161.1$, 160.2, 159.09, 159.05, 158.6, 157.7, 153.6, 152.0, 151.6, 151.6, 150.6, 139.8, 139.7, 139.6, 139.5, 139.4, 139.3, 137.3, 136.92, 136.89, 134.8, 134.3, 133.7, 133.6, 132.2, 132.1, 131.81, 131.77, 130.3, 130.2, 130.1, 129.8, 129.3, 129.24, 129.20, 129.16, 129.02, 128.99, 127.4, 127.0, 126.7, 126.6, 126.4, 122.9, 122.79, 122.75, 122.6, 117.1, 116.8, 116.7, 116.6, 116.52, 116.49, 116.4, 116.1, 115.82, 115.76, 115.72, 68.3, 68.1, 31.9, 29.4, 29.3, 29.21, 29.18, 26.11, 26.09, 22.7, 14.2 ppm; elemental analysis calcd (%) for C44H49FN2O2S2: C 73.30, H 6.85, N 3.89; found: C 73.29, H 6.88, N 3.92.

5,8-Bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-octyloxy-phenyl)quinoxaline (BFQ)

Compound **5** (0.81 g, 1.1 mmol) was dissolved in DMF (20 mL) at room temperature. After *N*-bromosuccinimide (NBS,

0.45 g,2.5 mmol) was added to the solution, the mixture was heated at 50 °C for 24 h. The solution was cooled to room temperature and poured into a mixture of deionized water (150 mL) and dichloromethane (150 mL). The organic layer was separated and washed with deionized water several times. The solution was dried over anhydrous MgSO₄, and concentrated by reduced pressure distillation. The residue was finally purified by column chromatography (SiO₂, petroleum ether/dichloromethane = 3:1) to give monomer BFQ as an orange solid (0.65 g, 66%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.78$ (d, J = 13.7 Hz, 1H; ArH), 7.71 (d, J = 3.6 Hz, 1H; ArH), 7.54 (s, 1H; ArH), 7.51 (s, 1H; ArH), 7.43 (d, J=4.1 Hz, 2H; ArH), 7.23–7.19 (m, 2H; ArH), 7.11 (d, J=4.1 Hz, 1H; ArH), 7.07 (t, 3H; ArH), 6.98 (m, 2H; ArH), 4.04 (q, 4H; -O-CH₂-), 1.81 (m, 4H; -CH₂-), 1.54–1.27 (m, 20 H; -CH₂-), 0.90 ppm (t, J=6.9 Hz, 6 H; -CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 159.8, 159.43, 159.40, 157.3, 151.8, 150.43, 150.40, 139.03, 138.97, 137.54, 137.51, 137.2, 137.1, 133.4, 133.3, 133.1, 130.6, 130.5, 130.0, 129.8, 128.9, 128.7, 125.7, 123.1, 123.0, 118.4, 117.9, 117.8, 117.4, 117.3, 115.7, 115.6, 115.14, 115.06, 114.98, 114.8, 68.39, 68.36, 31.9, 29.54, 29.45, 29.38, 26.3 ppm; elemental analysis calcd (%) for C₄₄H₄₇Br₂FN₂O₂S₂: C 60.14, H 5.39, N 3.19; found: C 60.12, H 5.43, N 3.24.

PBDTAL-BFQ

2,6-Bis(tributyltin)-4,8-bis(dodecyloxy)benzo[1,2-b:3,4-b]dithiophene (0.3282 g, 0.2883 mmol), monomer BFQ (0.2526 g, 0.2883 mmol), and degassed toluene (12 mL) were added to a two-necked flask. After being degassed with argon several times, [Pd₂(dba)₃] (5.5 mg, 2 mol%) and P(o-tol)₃ (7.3 mg, 8%) were added and the solution was degassed with argon several times again. The reaction solution was subsequently heated to 110°C for 20 h. Tributylstannylthiophene (23.7 mL) was added to the reaction and then after 2 h, 2bromothiophene (7.5 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. The reactant mixture was slowly dropped into methanol (400 mL) to allow precipitation of the crude polymer. The precipitate was filtered, and washed with methanol and hexane in a Soxhlet apparatus to remove oligomers and catalyst residue. Finally, the co-polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol again. The polymer PBDTAL-BFQ was then collected as a dark-purple solid (0.267 g, 73%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.5-6.5$ (m, 15 H; ArH), 4.6–3.3 (m, 8 H; -O-CH₂-), 2.5–0.5 ppm (m, 76H); elemental analysis calcd (%) for $(C_{78}H_{99}O_4N_2S_4F)_n$: C 73.43, H 7.82, N: 2.20; found: C 70.22, H 8.03, N 2.27.

PBDTAB-BFQ

Co-polymer **PBDTAB-BFQ** was obtained as a dark-purple solid in a yield of 78% from the reaction of 2,6-bis(tributyltin)-4,8-bis(2-eth-ylhexyloxy) benzo[1,2-*b*:3,4-*b*]dithiophene with monomer **BFQ**, similar to the procedure described for co-polymer **PBDTAL-BFQ**. ¹H NMR (400 MHz, CDCl₃): δ = 8.4–6.5 (m, 15 H; ArH), 4.5–3.5 (m, 8H; -O-CH₂-), 2.5–0.5 ppm (m, 64 H); elemental analysis calcd (%) for (C₇₀H₈₃O₄N₂S₄F)_n: C 72.25, H 7.19, N 2.41; found: C 68.49, H 7.24, N 2.15.

PBDTTL-BFQ

Co-polymer **PBDTTL-BFQ** was obtained as a dark-purple solid in a yield of 59% from the reaction of 2,6-bis(tributyltin)-4,8-bis(5-do-decyl-2-thenyl) benzo[1,2-*b*:3,4-*b*]dithiophene with monomer **BFQ**, similar to the procedure described for co-polymer **PBDTAL-BFQ**. ¹H NMR (400 MHz, CDCl₃): δ =9.0–5.5 (m, 19H; ArH), 4.4–3.5 (m,

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4H; -O-CH₂-), 3.3–2.6 (m, 4H; -CH₂-), 2.3–0.5 ppm (m, 76H); elemental analysis calcd (%) for $(C_{86}H_{103}O_2N_2S_6F)_n$: C 73.36, H 7.37, N 1.99; found: C 73.85, H 7.60, N 2.24.

PBDTTB-BFQ

Co-polymer **PBDTTB-BFQ** was obtained as a dark-purple solid in a yield of 78% from the reaction of monomer **BDTTB** with monomer **BFQ**, similar to the procedure described for co-polymer **PBDTAL-BFQ**. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.8-6.5$ (m, 19H; ArH), 4.2–3.5 (m, 4H; -O-CH₂-), 3.3–2.6 (m, 4H; -CH₂-), 2.2–0.5 ppm (m, 108H); elemental analysis calcd (%) for (C₁₀₂H₁₃₅O₂N₂S₆F)_n: C 75.04, H 8.34, N 1.72; found: C 75.15, H 8.32, N 1.90.

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X. Xu, Y. Wu, J. Fang,* Z. Li, Z. Wang, Y. Li, Q. Peng*

Side-Chain Engineering of Benzodithiophene-Fluorinated Quinoxaline Low-Band-Gap Copolymers for High-Performance Polymer Solar Cells



PBDTAL-BFQ (PCE=5.00%)

Bit on the side: By considering the degree of branching and dimensionality simultaneously, a systematic investigation of side-chain engineering was performed to explore the effect on the thermal stability, optical absorption, energy levels, molecular packing, and photovoltaic properties of the resulting co-polymers (see figure).

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