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Effect of bifurcation point of alkoxy side chains on photovoltaic performance of 5-alkoxy-6-fluorobenzo[c][1,2,5]thiadiazole-based conjugated polymers

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ABSTRACT

Three novel copolymers (**PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2**) based on thieno[3,2-b]thiophene and 5-alkoxy-6-fluorobenzo-[c][1,2,5]thiadiazole (AFBT) bearing branched alkoxy chains with varied branching positions are synthesized. The influences of the bifurcation positions on intermolecular stacking, charge mobility, film morphology and photovoltaic performance are systematically investigated. 2D-GIWAXS analyses of the optimized polymer:PC$_{71}$BM blend films exhibit the crystallinity increases from **PTTAFBT-C0** to **PTTAFBT-C1** and **PTTAFBT-C2** is more prone to form the edge-on orientation than **PTTAFBT-C1**, which result in a dramatic difference in film morphologies. TEM image of **PTTAFBT-C1**:PC$_{71}$BM blend films exhibits a suitable morphology with favorable interpenetrating networks, which is in favor of high performance. The best PCE of 5.67% with a device configuration of ITO/ PEDOT: PSS/**PTTAFBT-C1**:PC$_{71}$BM/LiF/Al under AM 1.5G solar radiation (100 mW cm^{-2}) is achieved. These results indicate that higher PCE can be obtained by adjusting the bifurcation points of the branched side chains away from the polymer backbone.

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1. Introduction

Over the past decades, polymers have played an important role in photovoltaic community because of their simple synthesis, light weight, low cost and flexibility. For example, they have been used as the counter electrode, quasi-solid electrolyte or electrode separator in dye-sensitized solar cells [1–3], donor or acceptor materials in polymer solar cells (PSCs) and so on. Bulk heterojunction (BHJ) PSCs, consisting of electron-rich polymers as donor and electron-deficient fullerene derivatives as acceptor, have become the mainstream and most efficient device structure [4–10]. To date, power conversion efficiency (PCE) exceeding 10% for single junction BHJ PSCs has been achieved by several groups [11–15]. To obtain higher PCE, various influence factors on

photovoltaic performance have been investigated in detail [16–19]. Besides device engineering, the polymer structure has been recognized to be a very important factor in determining photovoltaic performance.

The active layer of PSCs is a blend of polymer donor and PCBM acceptor, high efficiency PSCs require the donor and acceptor to form interpenetrated networks in nanoscale. To form such morphology, the donor polymers should have a proper solubility as well as the ability to form ordered molecular packing in the solid state [20,21]. Hitherto, a large number of donor-acceptor (D-A) alternating conjugated polymers have been synthesized as the donor component of the active layer. Generally, solution-processable donor polymers comprise rod-like conjugated backbones and flexible alkyl side chains. Great efforts have been devoted to structural modification of conjugated backbones. The side chains are generally considered as little more than solubilizing groups. Recently, more and more reports have demonstrated that side chain engineering, such as manipulating different chain length [22–24], the side chain type (linear or branch) [25,26], orientation [27] and density [28,29] can significantly affect not only solubility, but also intermolecular interaction, molecular packing, crystallinity, thin-film morphology, charge-transport

property and then photovoltaic performance. For example, linear side chains will almost not influence molecular packing but sacrifice the solubility, while branched side chains are more favorable for solubility. However, the spacer length between branching point and polymer backbone may have a significant influence on the molecular ordering and intermolecular π-π interactions [30–33].

Here, our side chain engineering strategy utilizes the advantages of both branched and linear side chains, and the influence of polymer structures on photovoltaic performance is screened by moving the bifurcation point of the branched side chains away from the polymer backbone. We focused on benzo[c][1,2,5]thiadiazole (BT)-based D-A polymers and introduced a fluorine atom on the BT unit to lower the HOMO and LUMO energy levels of the resulting polymers to achieve higher open circuit voltage (V_{oc}), meanwhile introduced a flexible alkoxyl chain onto the same BT unit to increase solubility of polymers in common organic solvents [34]. A series of new thieno[3,2-*b*]thiophene and 5-alkoxy-6-fluorobenzothiadiazole (AFBT) based alternative copolymers (**PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2**) were designed and synthesized. As shown in Scheme 1, **PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2** comprise branched alkoxy chains with the bifurcation point located at different distance to the polymer backbone, which are zero, one and two methylene spacers, respectively. Our results have demonstrated that the bifurcation point position of the alkoxy chains has a significant effect on the intermolecular stacking, charge mobility, film morphology and device performance. As indicated by GIWAXS analysis of the optimized polymer: PC$_{71}$BM blend films, the crystallinity increased from **PTTAFBT-C0** to **PTTAFBT-C1**, and **PTTAFBT-C2** exhibited similar crystallinity to **PTTAFBT-C1**, whereas **PTTAFBT-C2** seems more prone to form the edge-on orientation than **PTTAFBT-C1** in the blend films. TEM investigations demonstrated that **PTTAFBT-C1**:PC$_{71}$BM blend films formed suitable morphology and favorable interpenetrating networks. A lot of fibril-like nanostructures with a diameter of ca. 10 nm appeared, providing separated channels for charge transportation in the active layer [21]. The best PCE of 5.67% with a

device configuration of ITO/PEDOT:PSS/**PTTAFBT-C1**:PC$_{71}$BM/LiF/Al under AM 1.5 G solar radiation (100 mW cm^{-2}) was achieved. These results indicate that utilizing the advantages of both branched and linear side chains, higher PCE can be obtained by tuning the distance of the bifurcation point to the polymer backbone.

2. Results and discussion

2.1. Material synthesis and characterization

The syntheses of monomers (**AFBT-C0**, **AFBT-C1** and **AFBT-C2**) and copolymers (**PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2**) are outlined in Scheme 1. Originating from commercially available 4,5-difluorobenzene-1,2-diamine, 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**3**) was prepared according to the literature procedures [35]. The treatment of compound **3** with heptadecan-9-ol, 2-decyltetradecan-1-ol and 3-decyltridecan-1-ol under Williamson etherification conditions with potassium *tert*-butoxide as the base and tetrahydrofuran (THF) as the solvent at 60 °C afforded **AFBT-C0**, **AFBT-C1** and **AFBT-C2**, respectively, in yields of 52–70%. **PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2** were synthesized by Pd-catalyzed Stille coupling between **AFBT-C0**, **AFBT-C1** or **AFBT-C2** and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene in yields of 76–85%. **PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2** were soluble in o-dichlorobenzene (DCB) at elevated temperature. Molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) at 80 °C using chlorobenzene (CB) as an eluent and polystyrenes as the calibration standards and the results are summarized in Table 1. Number-average molecular weights (M_n) and polydispersity index (PDI) were measured to be 24.8 kg/mol and 2.94 for P**TTAFBT-C0**, 42.5 kg/mol and 2.81 for **PTTAFBT-C1**, and 30.2 kg/mol and 4.81 for **PTTAFBT-C2**. Thermo gravimetric analysis (TGA) indicated that all polymers are of good thermal stability with the decomposition temperature (5% weight loss) up to 280, 332 and 322 °C for **PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2**, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min. There was no obvious glass transition for three polymers in differential scanning calorimetry (DSC) curves under nitrogen atmosphere at a heating rate of 10 °C/min in the range of 70–250 °C.

2.2. Optical properties

UV−vis absorption spectra of **PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2** recorded in DCB solutions and as films are shown in Fig. 1. These three polymers exhibited similar absorption features in dilute DCB solutions at room temperature due to the same π-conjugated backbones. A low energy absorption band ranged from 500 to 750 nm with two peaks at around 625 and 680 nm was observed, which can be attributed to the intramolecular charge transfer (ICT) from thieno[3,2-b]thiophene to benzothiadiazole units. The long wavelength absorption peak at 680 nm was related to the aggregation of polymer backbones. For all polymers, this
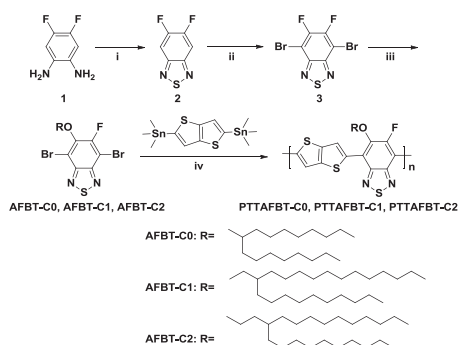
Scheme 1. Synthesis of monomers and copolymers. Reagents and conditions: (i) aniline, SOCl₂, toluene, 100 °C; (ii) NBS, H₂SO₄, room temperature; (iii) KOBu^t, alkanol, THF, 60 °C; (iv) Pd(PPh₃)₄, toluene/DMF (5:1 by volume), reflux.

Table 1
The optical and electronic properties of **PTTAFBT-C0**, **PTTAFBT-C1** and **PTTAFBT-C2**.

Polymer	M_n/M_w [Kg/mol][a]	PDI	T_d [°C][b]	λ_{max} solution [nm][c]	λ_{max} film [nm]	$E_{g,opt}$ [eV][d]	HOMO/LUMO [eV]
PTTAFBT-C0	24.8/73.1	2.94	280	625,680	628,690	1.63	−5.47/−3.84
PTTAFBT-C1	42.5/119.5	2.81	332	626,684	628,688	1.69	−5.54/−3.85
PTTAFBT-C2	30.2/145.4	4.81	322	625,684	626,686	1.68	−5.48/−3.80

[a] M_n, M_w and PDI of polymers were determined by GPC calibrated with polystyrene standards in chlorobenzene at 80 °C.

[b] T_d is the 5% weight-loss temperature of the polymer under inert atmosphere.

[c] Measured at 25 °C.

[d] Energy levels calculated from the absorption band edge of the copolymer film according to equations $E_{g,opt}=1240/\lambda_{edge}$ and $E_{LUMO}=E_{HOMO}+E_{g,opt}$.