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Alkyl chain engineering on a dithieno[3,2-*b*:2′,3′-*d*]silole-alt-dithienylthiazolo[5,4-*d*]thiazole copolymer toward high performance bulk heterojunction solar cells†

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A new copolymer of dithienosilole and dithienylthiazolo[5,4-*d*]thiazole with a hexyl side chain on the 4-position of thiophene units was designed and synthesized. Polymer solar cells based on the polymer as a donor and PC$_{70}$BM as an acceptor demonstrated a power conversion efficiency up to 5.88% with a high fill factor of 71.6%.
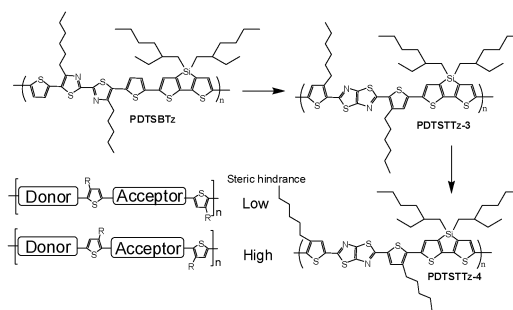
Bulk heterojunction (BHJ) polymer solar cells (PSCs) based on *p*-type conjugated polymers as donors and *n*-type fullerene derivatives as acceptors have been intensively studied in recent years for the generation of affordable, clean, and renewable energy.[1] Advantages of the BHJ PSCs include low-cost fabrication of large-area devices, light weight, mechanical flexibility, and easy tunability of chemical properties of the polymer materials.

It has been realized that an ideal polymer donor in PSCs should exhibit broad absorption with high absorption coefficient in the visible region, high hole mobility, suitable energy level matching to the fullerene acceptor, and appropriate compatibility with the fullerene acceptor to form a nanoscale bicontinuous interpenetrating network. All these specific design criteria can offer high values of short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and a fill-factor (FF) of the PSCs, all of which are related to the power conversion efficiency (PCE).[2,3] One feasible approach towards broadening the visible absorption and tuning the energy levels is to design alternating donor–acceptor (D–A) copolymers, in which the orbital mixing of the donor moiety and the acceptor moiety provides a means for narrowing the bandgap and tuning the energy levels of conjugated polymers.[4–20]

Recent studies have identified several design rules for developing high efficiency D–A copolymer photovoltaic donor materials,[3,4,15–17] such as (i) proper combination of D–A units to keep efficient orbital mixing, namely weak donor–strong acceptor combinations or medium donor–medium acceptor combinations; (ii) planarity of the whole backbone to ensure effective D–A conjugation. Here we demonstrate a successful example of enhancing the photovoltaic properties of the D–A copolymer donor materials by improving the planarity of the polymer main chain *via* simply changing the side chain position on the polymer main chain.

Our group recently developed a D–A copolymer based on a medium donor dithienosilole (DTS) unit and a medium acceptor bithiazole (BTz) unit,[18] **PDTSBTz** (see Scheme 1, named as P3 in ref. 18). **PDTSBTz** demonstrated an optical bandgap of 1.85 eV with a film absorption edge at 670 nm, and exhibited a hole mobility of 3.07×10^{-4} cm^2 V^{-1} s^{-1}. PCE of the PSCs based on **PDTSBTz** as a donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC$_{70}$BM) as an acceptor reached 2.86% under the illumination of AM1.5G, 100 mW cm^{-2}.[18] Compared with bithiazole, thiazolothiazole (TTz) has a more rigid and coplanar fused ring.[19] Thus within the structure motif of **PDTSBTz**, replacement of the BTz unit with TTz affords a more planar copolymer of **PDTSTTz**.[20] Due to enhanced backbone planarity and stronger π-stacking, **PDTSTTz** exhibits an order higher hole mobility of 3.56×10^{-3} cm^2 V^{-1} s^{-1} and a 15 nm red-shifted film absorption than **PDTSBTz**. These improved photo-physical properties account for an enhanced PCE up to 5.59% with a J_{sc} of 11.9 mA cm^{-2} and a V_{oc} of 0.77 V for the PSC based on **PDTSTTz**/PC$_{70}$BM. In addition to using the rigid and coplanar fused ring in the D–A copolymers, the position of alkyl side chains at D–A linkage is another important and recently

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Scheme 1 Molecular structures of the polymer analogues along with the effect of the alkyl sidechain position on the planarity.
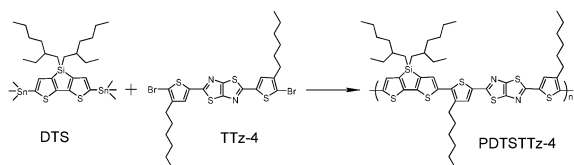
Scheme 2 Synthesis route of **PDTSTTz-4**.

identified issue employed to improve the planarity of the D–A copolymers. For example, the 4-position anchoring of alkyl chains on the flanking thiophene units in di-2-thienyl-2,1,3-benzothiadiazole has negligible impact on the steric hindrance relative to that of 3-position anchoring.[16] Inspired by these findings, in this work we moved the alkyl chains on thiophene units from the 3-position to the 4-position under the motif of **PDTSTTz** (Scheme 1), to reduce the steric hindrance and further improve its photovoltaic performance. For the convenience of discussion, the copolymers with hexyl substitution on 3- and 4-positions of thiophene units in **PDTSTTz** are named as **PDTSTTz-3** and **PDTSTTz-4** respectively (see Scheme 1). Interestingly, the synthesized copolymer **PDTSTTz-4** does adopt a more planar structure, which possesses an even higher hole mobility of *ca.* 7.8×10^{-2} cm^2 V^{-1} s^{-1} and a reduced band gap of 1.76 eV in comparison with **PDTSTTz-3**. PCE of the PSCs based on **PDTSTTz-4** as a donor and PC$_{70}$BM as an acceptor reached 5.88% with a high fill factor of 71.6%.

The polymer **PDTSTTz-4** was synthesized by the Stille coupling reaction as shown in Scheme 2. The polymer is soluble in chlorinated solvents, such as chloroform, chlorobenzene and dichlorobenzene, and exhibited a number-average molecular weight (M_n) of 6.3K, with a narrow polydispersity index of 1.47. Thermogravimetric analysis (TGA) demonstrated a good thermal stability of the polymer with a 5% weight-loss temperature at 317 °C (see Fig. S1 in ESI†).

Fig. 1 shows the absorption spectra of **PDTSTTz-4** in solution and film. The polymer solution demonstrates an absorption peak at *ca.* 540 nm, as shown in Fig. 1(a). With the decrease of temperature from 80 °C to 0 °C, the absorption peak red-shifted and a new shoulder peak at around 650 nm appeared. A thermal chromic phenomenon was observed with the color of the polymer solution changed from red to purple when the temperature was decreased from 80 °C to 0 °C, which agrees with the absorption spectral change. The results
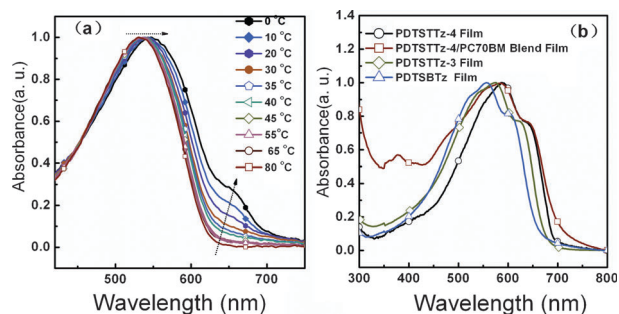
indicate that the main chain of the polymer turned to a more planar structure or some aggregation of the polymer main chains occurred during the decrease of temperature. The absorption spectrum of the polymer film is significantly red-shifted (see Fig. 1b) in comparison with that of the polymer solution. Interestingly, the absorption spectrum of **PDTSTTz-4** film is red-shifted by *ca.* 20 nm than that of **PDTSTTz-3** film (see Fig. 1b), indicating a more planar structure of **PDTSTTz-4** than **PDTSTTz-3** due to reduced steric hindrance in **PDTSTTz-4**. In addition, a sharp shoulder peak can be observed at *ca.* 670 nm in the absorption spectrum of the **PDTSTTz-4** film, which has a similar peak shape but red-shifted in comparison with that of **PDTSTTz-3** film. The absorption edge of **PDTSTTz-4** film is at 706 nm, corresponding to a bandgap of 1.76 eV which is reduced in comparison with 1.81 eV for **PDTSTTz-3** film and 1.85 eV for **PDTSBTz** film.[18] The X-ray diffraction pattern of the pristine polymer film exhibits two diffraction peaks at $2\theta = 5.16°$ and 21.16°, corresponding, respectively, to an interlayer *d*-spacing of 17.13 Å and a π–π stacking distance of 4.27 Å (see Fig. S2 in ESI†). DSC thermogram of **PDTSTTz-4** (see Fig. S3 in ESI†) shows a small endothermic peak at 109 °C which could be ascribed to side chain melting. The results imply that **PDTSTTz-4** possesses highly ordered polymer chains and densely packed side chains, which should benefit to higher hole mobility and better photovoltaic performance of the polymer.

The hole mobility of the polymer was measured by the space charge-limited current (SCLC) method with a device structure of ITO/PEDOT : PSS/polymer : PC$_{70}$BM/Au. A high hole mobility of *ca.* 7.8×10^{-2} cm^2 V^{-1} s^{-1} was obtained for the blend of the polymer and PC$_{70}$BM (see Fig. S4 in ESI†), which is one order higher than that (3.56×10^{-3} cm^2 V^{-1} s^{-1}) of **PDTSTTz-3**.[20] The electronic energy levels of **PDTSTTz-4** were measured by electrochemical cyclic voltammetry.[21] The HOMO and LUMO are −5.04 and −3.41 eV, respectively, calculated from the onset oxidation and reduction potentials of the polymer (see Fig. S5 in ESI†).

The photovoltaic properties of **PDTSTTz-4** were investigated using PC$_{70}$BM as the acceptor in BHJ devices with a device structure of ITO/PEDOT : PSS/**PDTSTTz-4** : PC$_{70}$BM/Ca/Al. PC$_{70}$BM was chosen as the acceptor because it possesses strong absorption in the visible region from 440 to 530 nm,[22] as shown in the absorption spectrum of the blend in Fig. 1b. The active layer was spin-coated at 100 °C from *o*-dichlorobenzene solution at 2800 rpm, and thermochromism is visible in the solvent evaporation and film solidification within several seconds, corresponding to the reorganization of the polymer chains to polymer rich domains. Details on device fabrication and characterization are provided in the ESI.†

The photovoltaic performance of the PSC devices was optimized by changing the **PDTSTTz-4** : PC$_{70}$BM weight ratio

Fig. 1 (a) Absorption spectra of **PDTSTTz-4** in dichlorobenzene at various temperatures; (b) absorption spectra of **PDTSTTz-4** in films cast without blending (○), blended with PC$_{70}$BM (1 : 1.3, □) along with the film absorptions of PDTSTTz-3 (◇) and PDTSBTz (△) for comparison.

Table 1 Effect of the **PDTSTTz-4**/PC$_{70}$BM blend ratio on the photovoltaic performance of the PSCs based on PDTSTTz-4/PC$_{70}$BM

Weight ratio (w : w)	V_{oc}/V	J_{sc}/mA cm^{-2}	FF (%)	PCE (%)
1 : 0.8	0.72	10.38	64.7	4.83
1 : 1	0.71	10.86	68.0	5.24
1 : 1.3	0.73	11.25	71.6	5.88
1 : 2	0.70	9.97	68.1	4.75
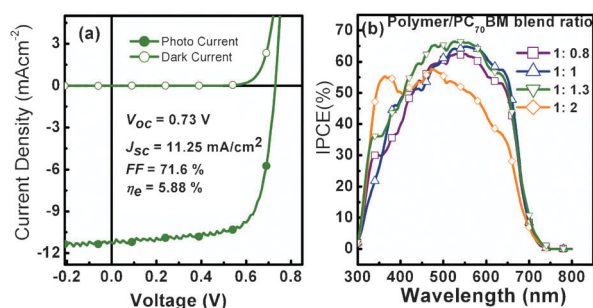
Fig. 2 (a) *J–V* curve of the PSC based on PDTSTTz-4 : PC$_{70}$BM (1 : 1.3, w/w) under the illumination of AM 1.5 G, 100 mW cm^{-2}. (b) The IPCE spectra of the PSCs under different polymer/PC$_{70}$BM weight ratios.

and thickness of the active layer. Table 1 lists and compares the photovoltaic data of the PSCs with the weight ratio from 1 : 0.8 to 1 : 2 under the illumination of AM1.5G, 100 mW cm^{-2}. Obviously, a 1 : 1.3 weight ratio seems to be the optimal ratio to form the interpenetrated networks for effective charge separation and transportation. The effect of the active layer thickness on the photovoltaic performance of the PSCs is shown in Table S1 in ESI.† It can be seen that 80 nm is the optimized thickness. *J*$_{sc}$ of the PSCs can be further improved to 11.7 mA cm^{-2} with a thicker active layer of 110 nm, but the PCE dropped to 5.40% due to a decreased FF of 66.9% and a lower *V*$_{oc}$ of 0.69 V.

Fig. 2a shows a typical *J–V* curve of the PSC based on **PDTSTTz-4** : PC$_{70}$BM under the optimized conditions. The PCE of the PSC reached 5.88% with a *V*$_{oc}$ of 0.73 V, a *J*$_{sc}$ of 11.25 mA cm^{-2} and a FF of 71.6%. The FF of 71.6% is a high value in the PSCs with the D–A copolymers as donors, which indicates that the charge flow in the device is well-balanced and no significant recombination loss occurs within the active material under this condition.[23] Thus from a PCE of 2.85% for **PDTSBTz** toward a PCE of 5.88% for **PDTSTTz-4**, our results highlighted the importance of rigid units and planarity backbone for developing high efficiency polymers. To better understand the structure–properties relationship among the three polymers **PDTSBTz**, **PDTSTTz-3** and **PDTSTTz-4**, the photophysical and photovoltaic properties of the three polymers were collected in Table S2 in ESI.†

Fig. 2b shows the incident-photon-to-converted-current efficiency (IPCE) of the PSCs based on **PDTSTTz-4** : PC$_{70}$BM with different weight ratios. In the IPCE spectra, the contribution of the fullerene component in the photocurrent generation process is readily observed by the presence of a peak at around 350 nm, while the polymer donor contributes the photocurrent in the range of 450–700 nm. Due to a balanced contribution of the fullerene acceptor and the polymer donor, the IPCE curve exhibits a broad response covering 300–700 nm, with ~60% from 400 to 650 nm, thus a high short-circuit current density (*J*$_{sc}$) of 11.25 mA cm^{-2} was obtained for the PSC based on **PDTSTTz-4** : PC$_{70}$BM with a weight ratio of 1 : 1.3.

In conclusion, through the 4-position alkyl side chain engineering on a DTS-alt-TTz copolymer, polymer **PDTSTTz-4** was obtained, with a lower band gap of 1.76 eV and a high hole

mobility of *ca.* 7.8 × 10^{-2} cm^2 V^{-1} s^{-1}. The PSC based on **PDTSTTz-4**/PC$_{70}$BM (1 : 1.3, w/w) demonstrated a high PCE of 5.88% with a *V*$_{oc}$ of 0.73 V, a *J*$_{sc}$ of 11.25 mA cm^{-2} and a FF of 71.6%. The results indicate that **PDTSTTz-4** is a promising polymer donor for future application of PSCs.

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