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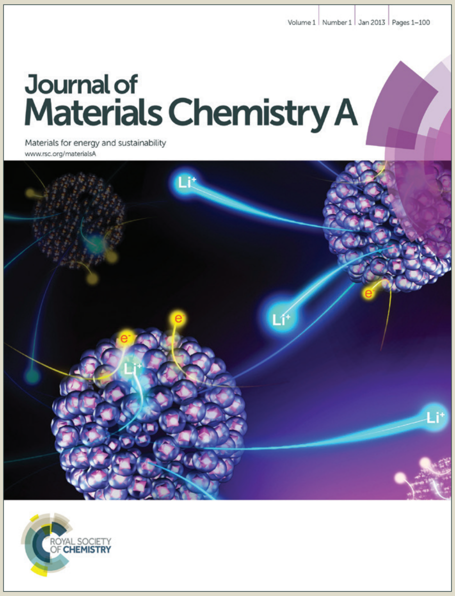

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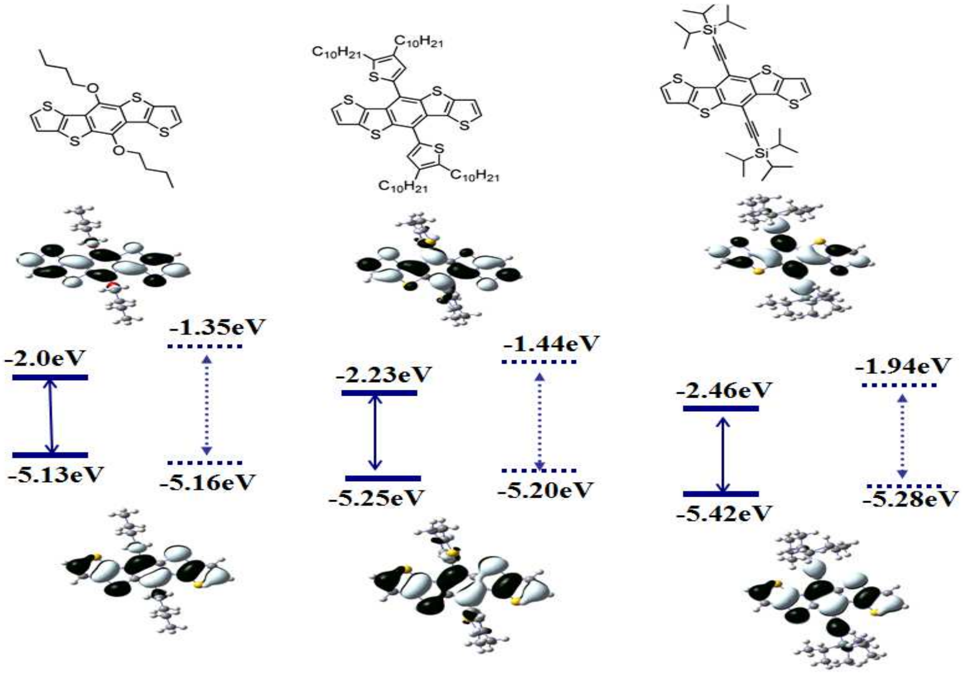
Graphical Abstract

Synthetic Controlling the Optoelectronic Properties of Dithieno[2,3-*d*:*2′*,*3′*-*d′*]benzo[1,2-b:4,5-b′]dithiophene-alt-diketopyrrolopyrrole Conjugated Polymers for Efficient Solar Cells

Shuo Sun, Peng Zhang, Jianfeng Li, Junfeng Tong, Jianlu Wang, Shujiang Zhang, Yangjun Xia*, Xiangjian Meng*, Duowang Fan and Junhao Chu

Systematic investigation of the optoelectronic properties of dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene derivatives (DTBDTs) and conjugated polymers derived from DTBDTs and di-ketopyrrolopyrrole derivatives are implemented. It have been demonstrated that, by changing the substituent groups on the DTBDT, the energy levels, optical band gaps and charge transporting properties *etc* of the DTBDTs and conjugated polymers derived from the DTBDTs and diketopyrrolopyrrole derivatives could effectively and rationally be tuned.



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Synthetic Controlling the Optoelectronic Properties of Dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene-*alt*-diketopyrrolopyrrole Conjugated Polymers for Efficient Solar Cells[†]

Shuo Sun[§a], Peng Zhang[§b], Jianfeng Li[b], Yuanke Li[b], Jianlu Wang[a], Shujiang Zhang[c], Yangjun Xia*[a,b], Xiangjian Meng*[a], Duowang Fan[b] and Junhao Chu[a]

We have demonstrated that, by changing the substituent groups on the dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (DTBDT), one could effectively and rationally tune the energy levels, optical band gaps and charge transporting properties *etc.* of the DTDBT derivatives (DTBDTs) and conjugated polymers (CPs) derived from the DTBDTs and diketopyrrolopyrrole (DPP) derivatives

Introduction

Since the discovery of the ultrafast photo-induced charge transfer between conjugated polymers (CPs) and fullerene,[1] the polymer bulk heterojunction photovoltaic cells (PVCs) have attracted much attention due to the potential application for large area, flexible, and low-cost solar cells.[2] Tremendous efforts such as the development of novel low band gap (LBG) CPs,[3–16] the optimization of the fabricating process[17] and modifying the morphology of the donor and acceptor blend etc,[18,19] have been devoted to improve the power conversion efficiencies (PCEs) of PVCs. Among them, the development of high performance donor-acceptor (D-A) type LBG CPs has been demonstrated to be the most vigorous approach to achieve the efficient PVCs, and many promising D-A type LBG CPs have been developed in the last decades.[3-16,20–30] The most attracting sample is benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT)-based CPs.[20–30] For instance, Huang and co-workers have reported a new and interesting BDT-based polymer (PBDT-DTNT) with naphtha[1,2-*c*:5,6-*c*]bis[1,2,5]thiadiazole as the new electron acceptor moieties exhibiting high PCEs up to 6.0-8.4%.[25,26] Hou and Yang *et al.* have demonstrated a series of LBG CPs based on BDT, and the PCEs of 5.63–8.4% have been achieved in the PVCs from the polymers.[27-29]

As a notable aromatic analogue of BDT, dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (DTBDT) not only shows similar HOMO level with BDT, but also holds larger coplanar core and extended conjugation length.[31-35] It was believed to provide advantageous properties for DTBDT-based CPs such as enhanced charge-carrier mobility, decreased band gaps and facilitated exciton separation into free charge carriers in contrast to BDT-based CPs.[33] In 2012, Hou *et al.* firstly reported a LBG CP (PDTT) based on 5,10-di(2-hexyldecyl-oxy)-DTBDT, and the PCE of 3.6% has been achieved in the PVCs from PDTT.[32] Lately, Yu *et al.* presented a series of LBG CPs based on 5,10-dialkyl-DTBDT (PTDBD2 *etc.*),[33] and Hou *et al.* demonstrated a polymer based on 5,10-di(5-(2-ethyl-hexylthieno-2-yl)-DTBDT (PDT-S-T).[34] And the PCEs of 7.3–7.6% have been achieved in the PVCs from PTDBD2 and PDT-S-T.[33,34] More recently, Kwon *et al.* have demonstrated that the flanking of DTBDT by alkylthieno-2-yl not only increased the charge-carrier mobilities, but also decreased the highest occupied molecular orbital (HOMO) levels of CPs based on alkylthieno2-yl-flanked DTBDTs, thus increasing the open circuit voltage (V_{oc}), short current density (J_{sc}) and PCEs of PVCs from the polymers as compared with those in the PVCs from the CPs based on alkyloxy-flanked DTBDTs.[35] However, the investigations of DTBDT-based CPs are still insufficient as compared with the well and intensive investigation of BDT-based CPs so far.

In this paper, we demonstrated that the optoelectronic properties of DTBDTs and the CPs derived from DTBDTs and DPP could effectively and rationally be tuned *via* the flanking of DTBDT by alkyloxy, 4,5-didecylthieno-2-yl, and trialkylsilylethynyl substituent groups. It was found that, HOMO levels of DTBDTs were deepened from –5.21 eV to –5.36 eV and then dropped to –5.65 eV, and HOMO levels of the three CPs based on the DTBDTs and DPP (named as PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16, respectively) were deepened from –5.13 eV to –5.19 eV and then dropped to –5.25 eV while the DTBDT were accordingly flanked by the alkyloxy, 4,5-didecylthineo-2-yl and tri-*iso*-propylsilylethynyl (TIPS) substituent groups. Meanwhile, it was also found that, the flanking of DTBDT by the TIPS substituent group provided PBT-TIPS-DPP-C16 exhibiting the lowest HOMO level, the narrowest band gap and comparatively higher mobility among the three DTBDTs-based CPs. As the consequences, the PVCs based on PBT-TIPS-DPP-C16 and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) blend show the highest V_{oc} (0.75 V *vs.* 0.62 V and 0.65 V), the highest J_{sc} (13.9 mA/cm^2 *vs.* 6.41 mA/ cm^2 and 12.79 mA/cm^2) and PCE (6.39% *vs.* 2.42% and 5.19%) in the optimized PVCs using PBT-TIPS-DPP-C16, PBT-HD-DPP-C16 and/or PBT-T-DPP-C12 as electron donor materials and $PC_{71}BM$ as electron acceptor materials, respectively. The PCE of 6.39% has been achieved in the PVCs from PBT-TIPS-DPP-C16 under 100 mW/cm^2 illumination (AM 1.5G).

Results and discussion

1. Synthesis and Structural Characterization of DTBDT Derivatives

Scheme 1 shows the synthetic routes for DTBDT derivatives. The dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene-5,10-dione (I) was synthesized as the optimized procedure in the reference (See ESI†).[35] The 5,10-di(alkyloxy)-DTBDT (IIa-d) were synthesized as the following procedure: the dione (I) was successively treated with zinc powder under the presence of NaOH aqueous solution and alkyl bromide to lead 5,10-di(alkyloxy)-DTBDT (IIa-d). The DTBDT-TIPS, DTBDT-TMS and DTBDT-T were synthesized as the following procedures: the dione (I) was treated with TIPS lithium, trimethylsilylethynyl (TMS) lithium or 4,5-didecylthieno-2-yl lithium, followed by reduction and dehydration with the tin dichloride and hydrochloric acid (10%) to generate DTBDT-TIPS, DTBDT-TMS and DTBDT-T, respectively. The 2,7-bis(trimethylstannyl)-5,10-di(2-hexyldecyloxy)-DTBDT (III), 2,7-di(trimethylstannyl)-5,10-bis(4,5-didecylthieno-2-yl)-DTBDT (IV) and 2,7-di(trimethylstannyl)-5,10-bis(tri-*iso*-propylsilylethynyl)-DTBDT (V) were synthesized as the following procedure: the IId, DTBDT-T and/or DTBDT-TIPS were firstly reacted with n-BuLi in anhydrous THF at 0 □, then the solution of trimethylstannyl chloride in anhydrous THF was added in one portion to lead compound III, IV and/or V in the yield of 53-60%, respectively. The structures of the compounds were confirmed by ^{1}H NMR (See ESI†), FBA-MS and elemental analyses.

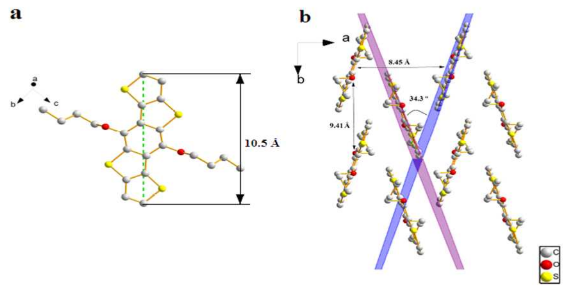
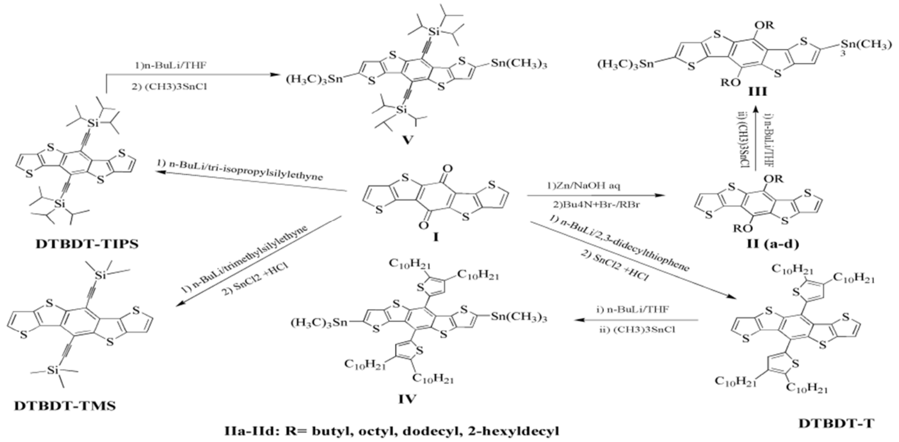


Figure. 1 Molecular structures (a) and the molecular packing diagram (b) in crystal with layered herringbone structure of 5,10-di(butyloxy)di-thieno[2,3-d:2′,3′-d′]benzo[1,2-b:4,5-b′]dithiophene

Four single crystals of the resulting DTBDT derivatives (DTBDT-C4, DTBDT-C8, DTBDT-C12 and DTBDT-TMS) were obtained from slow evaporation of the chloroform/*n*-hexane solution. Fig. 1 shows that 5,10-di-(butyloxy)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (DTBDT-C4) molecule exhibits the fully planar geometric structure. And the other molecules such as DTBDT-C8, DTBDT-C12 and DTBDT-TMS also exhibit the fully planar geometric structure (See ESI†, Fig. S1–S3, Table S1).The coplanar area of 21.0 Å^2 and the conjugation length of 10.5 Å for DTBDT-C4 core are larger than those for BDT (13.2 Å^2 and 7.0Å), respectively (See ESI†, Fig. S4, Table S2).[36] And the bonding geometry for extending the conjugated system through the two terminal unsubstituted α-positions of DTBDT-C4 is associated with the *ca*. 180° bend, which is similar to that of BDT (See ESI†, Fig. S5).[36] It was noted that different flanking substituent groups have little effect on geometry, conjugated plane area and conjugated length of central core of DTBDT-based compounds (See ESI†, Table S2).



IIa-IId: R= butyl, octyl, dodecyl, 2-hexyldecyl

Scheme 1 Synthetic routes of the DTBDT derivatives

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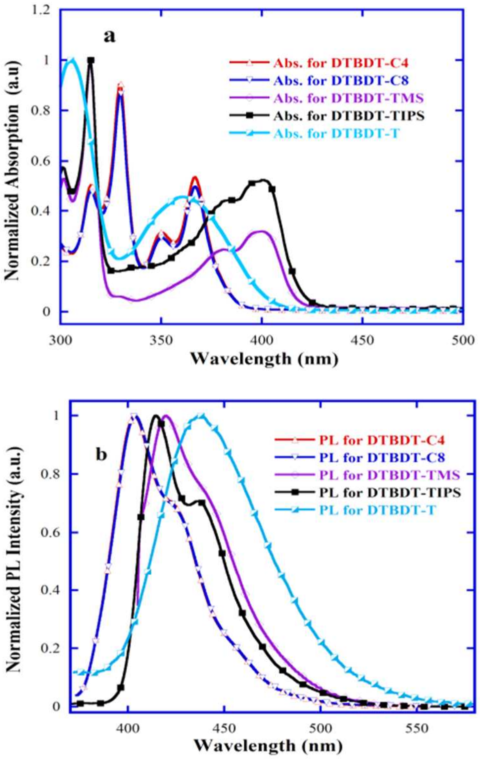

Figure. 2 Normalized absorption (a) and photoluminescence (b) spectra of DTBDT derivatives in dichloromethane solution

The UV-Vis absorption and photoluminescence (PL) spectra of 5,10-di(alkyloxy)-DTBDT (DTBDT-C4 and DTBDT-C8), DTBDT-TMS, DTBDT-TIPS and DTBDT-T are shown in Fig. 2a and Fig. 2b, respectively. The 5,10-di(alkyloxy)-DTBDT derivatives (DTBDT-C4 and DTBDT-C8) show absorption bands in the region of 300–395 nm with on-set band gap wavelength at 395 nm in dichloromethane (DCM) solution. The PL emission peaks of 5,10-di(alkyloxy)-DTBDT derivatives are at around 402 nm in DCM solution. The DTBDT-T shows absorption bands in the region of 300–410 nm with on-set band gap wavelength at 410 nm, and the PL emission peak of DTBDT-T is at 434 nm in DCM solution. The DTBDT-TMS and DTBDT-TIPS exhibit absorption bands in the region of 300–420 nm with on-set band gap wavelength at 420 nm. The PL emission peaks of DTBDT-TMS and DTBDT-TIPS are at 425 nm in DCM solution. The optical band gaps of 5,10-di(alkyloxy)-DTBDT (DTBDT-C4 and DTBDT-C8), DTBDT-T, DTBDT-TMS and DTBDT-TIPS in DCM solution are about 3.13 eV, 3.02 eV, 2.96 eV, 2.95 eV, respectively. As compared with the 5,10-di(alkyloxy)-DTBDT, the on-set band gap wavelengths and PL peaks of DTBDT-TMS, DTBDT-TIPS and DTBDT-T are red-shifted. It could be attributed to the promotion of π-orbital overlap between the trialkylsilylethynyl or 4,5-didecylthieno-2-yl moieties and the DTBDT core.

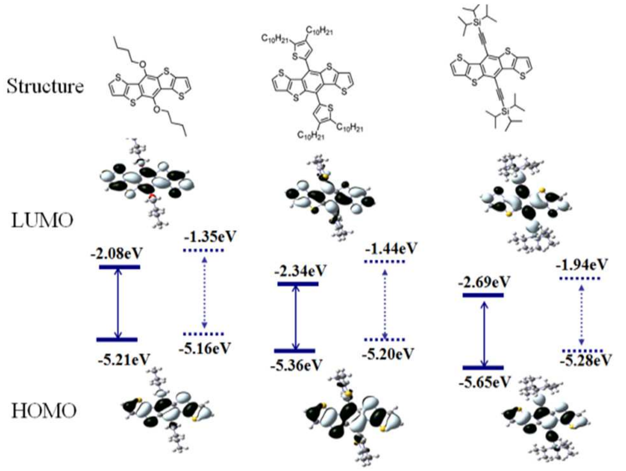

Figure. 3 HOMO and LUMO energy levels DTBDT derivatives determined by CV and optical band gap data (solid line) and computational calculation (dotted line)

The electrochemical behaviors of DTBDTs were investigated by cyclic voltammetry (CV) in a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in CH_3CN /DCM (1:1) with glass carbon and Ag/$AgNO_3$ electrode as the working and reference electrode, respectively. The first oxidation potential of 5,10-di(alkyloxy)-DTBDT derivatives (DTBDT-C4 and DTBDT-C8), DTBDT-T and DTBDT-TMS and DTBDT-TIPS, are about +0.55 V, +0.55 V, 0.79 V, +1.01 and 1.00 V, respectively (See ESI†, Fig. S6). The redox potential of ferrocene/ferrocenium (Fc/Fc^+) in the above-mentioned condition is +0.14 V, which is assumed to have an absolute energy level of -4.8 eV to vacuum for calibration (See ESI†, Fig. S7). So the HOMO levels of 5,10-di(alkyloxy)-DTBDT, DTBDT-T, DTBDT-TMS and DTBDT-TIPS are –5.21 eV, –5.36 eV, –5.66 eV and –5.65 eV, respectively (Fig. 3). It could be found that the HOMO levels of the DTBDTs were successively deepened as the DTBDT were accordingly flanked by alkyloxy, 4,5-didecylthieno-2-yl and trialkylsilyl-ethynyl substituent groups. The HOMO and the lowest unoccupied molecular orbital (LUMO) levels of DTBDT derivatives were also simulated by using density functional theory (DFT). The DFT calculations were performed using Gaussian 09 with a hybrid B3LYP correlation functional and a split valence 6-31G* basis set. And the optimized molecular geometries of the models and calculated HOMO and LUMO energy level are shown in Fig. 3. The calculated HOMO and LUMO levels of DTBDTs were

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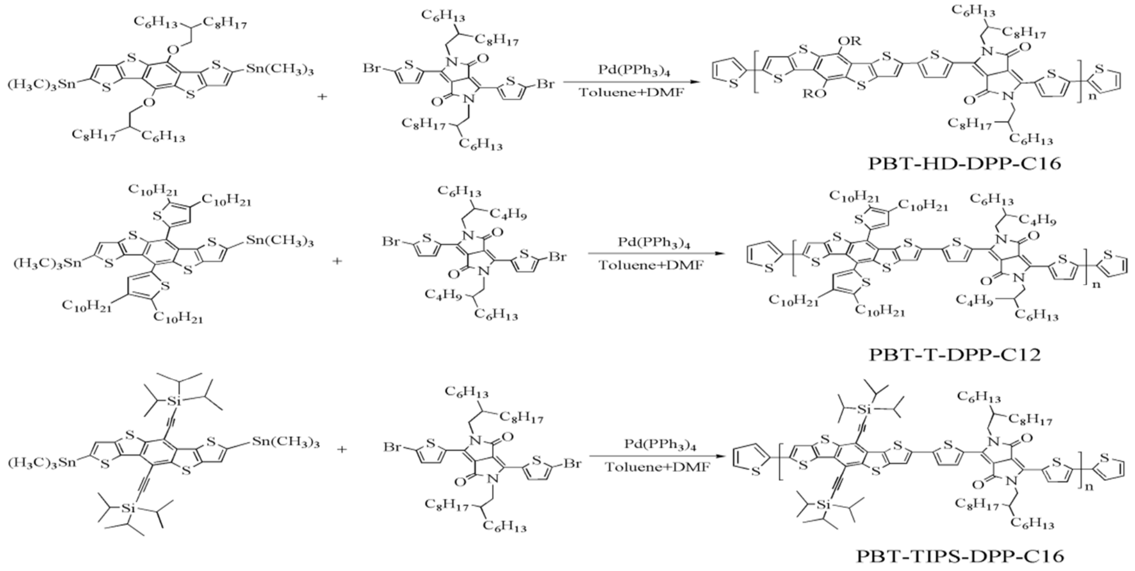
Table 1. Molecular weight, optical absorption, HOMO and LUMO energy levels, thermal decomposition temperature of **DTBDTs**-based polymer

Polymer	M_n (g/mol)	PDI	E_g[a] (eV)	E_{HOMO} (eV)	E_{LUMO}[b] (eV)	T_d (℃)
PBT-HD-DPP-C16	9,650	1.58	1.48	–5.13	–3.65	305.1
PBT-HD-DPP-C12	20,600	1.67	1.47	–5.19	–3.72	412.0
PBT-TIPS-DPP-C16	16,150	1.71	1.45	–5.25	–3.80	393.0

[a] optical band gap; [b] $E_{LUMO} = -(|HOMO| - E_g)$ (eV)



Scheme 2. Synthetic route of conjugated polymers derived from DTBDTs and DPP

also successively deepened while the DTBDT were accordingly flanked by alkyloxy, 4,5-didecylthieno-2-yl and TIPS substituent groups. All of the CV experimental and computational results confirmed that the HOMO energy levels of DTBDT derivatives could be fine tuned *via* the flanking the DTBDT with alkyloxy, trialkylsilylethynyl and alkylthieno-2-yl substituent groups. And the trialkylsilylethynyl–flanked DTBDT exhibited the lowest HOMO energy levels as compared with those for alkyloxy and alkyklthieno-yl flanked DTBDT. It should be contributed to the electron-withdrawing *sp* hybridization triple bond in trialkylsilylethynyl group in contrast to the electron-rich units such as alkyloxy an dalkylthieno-2-yl.

2. Synthesis and Characterization of the Conjugated Polymers

To investigate the influence of the flanking DTBDT by the substituent groups such as alkyloxy, 4,5-didecylthieno-2-yl and/or TIPS on the optoelectronic properties of DTBDTs-based CPs, three kinds alternating LBG CPs with 5,10-di(2-hexyldecyloxy)-DTBDT, 5,10-bis(4,5-decylthieno-2-yl)-DTBDT and/or 5,10-bis(TIPS)-DTBDT as electron donor moieties and DPP as electron acceptor moieties, were synthesized and named as PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16, respectively (Scheme 2). The number-average molecular weights of the resulting polymers such as PBT-HD-DPP-C16, PBT-T-DPP-C12, PBT-TIPS-DPP-C16 are ranging from 9.65 kDa to 20.06 kDa, and the polydisperse indexes from 1.58 to 1.71 (Table 1). The decomposed temperature ($T_{d,}$, 5% weight-loss) of the polymers are ranging from 305.1□ to 412.0□ (See ESI†, Fig. S8 and Table 1).

The UV-Vis absorption spectra of the polymers in solid thin film were monitored on a UV-2550 spectrophotometer. The normalized absorption spectra of PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16 in solid thin film were presented in Fig. 4a. As shown in Fig. 4a, the PBT-HD-DPP-

C16 shows two absorption peaks at 405 nm and 750 nm with shoulder absorption peak at around 675 nm. The PBT-T-DPP-C12 and PBT-TIPS-DPP-C16 show similar absorption spectra except that the absorption peaks at the short wavelength are blue-shifted, and the absorption peaks at long wavelength were red-shifted. The on-set band gap wavelengths and optical band gaps of PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16, are around 837 nm and 1.48 eV for PBT-HD-DPP-C16, 844 nm and 1.47 eV for PBT-T-DPP-C12, 855 nm and 1.45 eV for PBT-TIPS-DPP-C16 (Fig. 4a, Table 1).

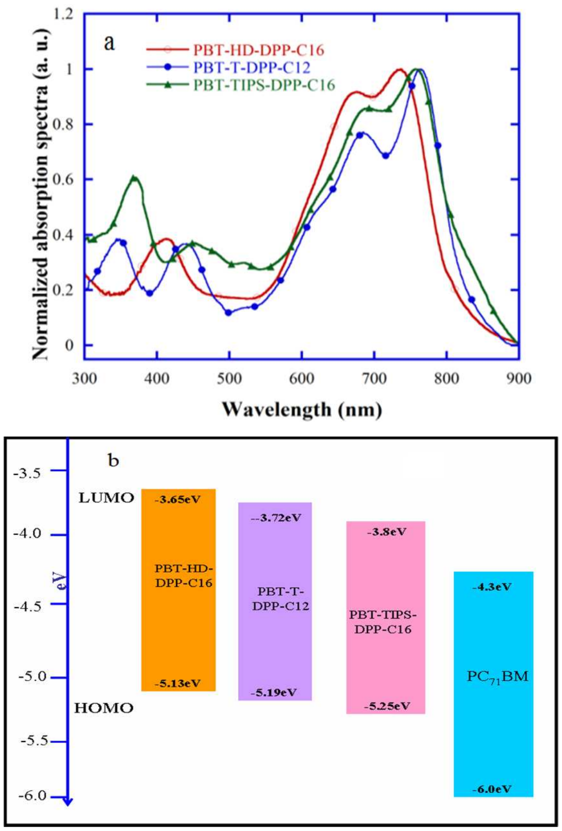


Figure. 4 Normalized absorption spectra (a) and the energy level diagram of alternating DTBDTs-based conjugated polymers and $P_{71}CBM$ (b)

The electrochemical behaviors of the polymer films were investigated by CV in a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with glass carbon and $Ag/AgNO_3$ electrode as the working and reference electrode, respectively. The onset oxidation potential of PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16 are respectively around +0.42 V, +0.48 V and +0.54 V (See ESI†, Fig. S9.) The redox potential of Fc/Fc^+ in the above-mentioned condition is +0.09 V, which is assumed to have an absolute energy level of -4.8 eV to vacuum for calibration (See ESI†, Fig. S10.). the HOMO and LUMO levels calculated by empirical formulas ($E_{\text{HOMO}} = -(E_{\text{ox}} + 4.71)$ (eV) and $E_{\text{LUMO}} = -(|\text{HOMO}| - E_g)$ (eV)),[38] were are –5.13 eV and –3.65 eV for PBT-HD-DPP-C16, –5.19 eV and –3.72 eV for PBT-T-DPP-C12 and –5.25 eV and –3.80 eV for PBT-TIPS-DPP-C16 (Table 1, Fig. 4b). It could be clearly found that the HOMO and LUMO levels of the CPs were successively deepened as the DTBDT were accordingly flanked by alkyloxy, 4,5-didecyl-thieno-2-yl and TIPS substituent groups.

Photovoltaic properties of the polymers were investigated by fabricating PVCs with a configuration of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al. Chlorobenzene (CB) was used as solvent, and 1,8-diiodoctane (DIO) was used as solvent additives in the fabrication of the PVCs. Initially, the blending weight ratios of the PBT-HD-DPP-C16/$PC_{71}BM$, PBT-T-DPP-C12/$PC_{71}BM$ and PBT-TIPS-DPP-C16/$PC_{71}BM$ were optimized from 1:1 to 1:1.5. The photovoltaic parameters of PVCs are summarized in Table 2, and the *J/V* characteristics of the PVCs are plotted in Fig. 5a. It can be seen that the optimum ratio of PBT-HD-DPP-C16/$PC_{71}BM$, PBT-T-DPP-C12/$PC_{71}BM$ and PBT-TIPS-DPP-C16/$PC_{71}BM$ were 1:1.5. Under the optimal donor/acceptor, the PVCs based on PBT-HD-DPP-C16 shows a PCE of 2.42% V_{oc} of 0.62 V, J_{sc} of 6.41 mA/cm^2 and fill factor (FF) the PVCs based on PBT-T-DPP-C12 shows a PCE of 5.19% with V_{oc} of 0.65 V, J_{sc} of 12.61 mA/cm^2 and FF of 63.7%，and the PVCs based on PBT-TIPS-DPP-C16 shows a PCE of 6.39% with V_{oc} of 0.75 V, J_{sc} of 13.9 mA/cm^2 and FF of 61.3%. The V_{oc} of PVCs based

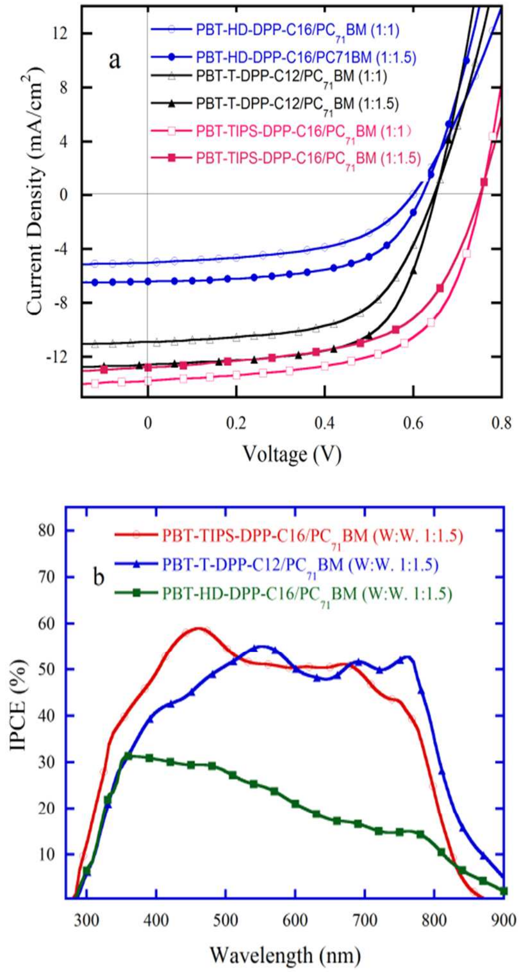


Figure 5. J/V characteristics (a) and EQE curves (b) of PVCs based on the DTBDTs-based conjugated polymers:$PC_{71}BM$

Table 2 Photovoltaic parameters of PVCs from DTBDTs-based polymers

polymer	Weight ratio	DIO (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	$J^{\mathrm{Integral}}_{\mathrm{sc}}$ (mA/cm^2)	FF (100%)	η (100%)
PBT-HD-DPP-C16/PC$_{71}$BM	1:1	3	0.60	5.01	—	52.1	1.57
PBT-HD-DPP-C16/PC$_{71}$BM	1:1.5	3	0.62	6.41	6.25	60.9	2.42
PBT-T-DPP-C12/PC$_{71}$BM	1:1	3	0.65	11.01	—	58.3	4.17
PBT-T-DPP-C12/PC$_{71}$BM	1:1.5	3	0.65	12.61	13.21	63.4	5.19
PBT-TIPS-DPP-C16/PC$_{71}$BM	1:1	3	0.75	12.79	—	58.2	5.59
PBT-TIPS-DPP-C16/PC$_{71}$BM	1:1.5	3	0.75	13.9	13.5	61.3	6.39

$J^{\mathrm{Integral}}_{\mathrm{sc}}$ intergral current density calculated by IPCEs data

on the DTBDTs-based CPs are successively increased while the DTBDT were accordingly flanked by the alkyloxy, 4,5-didecylthieno-2-yl and TIPS substituent groups. It could be attributed to the deepening of the HOMO levels of DTBDTs-based CPs, thus successive enlarging of the differences between the LUMO energy level of PC$_{71}$BM and HOMO energy levels of the polymers (See ESI†, Fig. 4b. and Fig. S11), while the DTBDT were accordingly flanked by the alkyloxy, 4,5-didecylthieno-2-yl and TIPS substituent groups.

The incident photon to charge carrier efficiency (IPCE) curves of the PVCs with the optimal donor/acceptor weight ratio are presented in Fig. 5b. The PVCs based on PBT-HD-DPP-C16 and PBT-T-DPP-C12 exhibited photo-response ranging from 280 nm to 890 nm, except that the IPCE of the PVCs based on PBT-HD-DPP-C16 is quite lower in the whole range than that of the PVCs based on PBT-T-DPP-C12. The PVCs based on PBT-T-DPP-C12 showed the photo-response ranging from 280 nm to 860 nm. According to the IPCEs of the PVCs, the integral current density values of the PVCs based on PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16, are 6.25 mA/cm^2, 13.21 mA/cm^2 and 13.50 mA/cm^2, respectively. The mismatch between the integral current densities and the J_{sc} values of the PVCs obtained from J-V measurement is within 5% (Table 2). It indicated that J_{sc} obtained from J-V measurements in this study are reliable.

To elucidate the mechanism by which the J_{sc} of the PVCs from PBT-T-DPP-C12 and PBT-TIPS-DPP-C16 is dramatically enhanced as compared with that of the PVCs from PBT-HD-DPP-C16, the hole mobility in the blends of polymers and PC$_{71}$BM are measured and analyzed by using the space-charge limited current (SCLC) method.[28] The hole mobilities of PBT-HD-DPP-C16/PC$_{71}$BM, PBT-T-DPP-C12/PC$_{71}$BM and PBT-TIPS-DPP-C16/PC$_{71}$BM were found to be 8.5×10^{-6} cm^2 V^{-1} s^{-1}, 1.78×10^{-4} cm^2 V^{-1} s^{-1} and 1.33×10^{-4} cm^2 V^{-1} s^{-1}, respectively(See ESI†, Fig. S12, Table S3). It could be found that the hole mobilities in the blends PBT-T-DPP-C12/PC$_{71}$BM and PBT-TIPS-DPP-C16/PC$_{71}$BM are two orders of magnitude greater than that in the blend of PBT-HD-DPP-C16/PC$_{71}$BM. The higher J_{sc} of PVCs based on PBT-T-DPP-C12/PC$_{71}$BM and PBT-TIPS-DPP-C16/PC$_{71}$BM should be owing to the higher hole mobilities in the blends of PBT-T-DPP-C12/PC$_{71}$BM and PBT-TIPS-DPP-C16/PC$_{71}$BM as compared with that in the bland of PBT-HD-DPP-C16/PC$_{71}$BM.

Conclusion

In this paper, we demonstrated that the optoelectronic properties of DTBDTs and CPs derived from DTBDTs and DPP could effectively and rationally be tuned *via* the flanking of DTBDT by alkyloxy, 4,5-didecylthieno-2-yl, and trialkylsilylethynyl substituent groups. The HOMO levels of DTBDTs were deepened from –5.21 eV to –5.36 eV and then dropped to –5.66 eV, and HOMO energy levels of the CPs based on DTBDTs (PBT-HD-DPP-C16, PBT-T-DPP-C12 and PBT-TIPS-DPP-C16) were deepened from –5.13 eV, –5.19 eV and then dropped to –5.25 eV while the DTBDT were accordingly flanked by the alkyloxy, 4,5-didecylthieno-2-yl and TIPS substituent groups. Meanwhile, it was also found that, the flanking of DTBDT by TIPS substituent group provided PBT-TIPS-DPP-C16 exhibiting the lowest HOMO level, the narrowest band gap and comparatively high mobility among the three DTBDTs-based CPs. As the consequences, the PVCs based on PBT-TIPS-DPP-C16 and PC$_{71}$BM blend show the highest V_{oc}, the highest J_{sc} and PCEs in the optimized PVCs using PBT-TIPS-DPP-C16, PBT-HD-DPP-C16 and/or PBT-T-DPP-C12 as electron donor materials and PC$_{71}$BM as electron acceptor materials, respectively. In more general terms, we have shown that, by changing the substituent groups on the DTBDT, one can rationally tune the energy levels, optical band gap and charge transporting properties *etc.* of the CPs based on DTBDTs. And the TIPS-flanked DTBDT is a more valuable electron donor blocks for the CPs in the application photovoltaic devices as compared with the alkyloxy-flanked DTBDT and 4,5-didecylthieno-2-yl-flanked DTBDT.

Experimental Section

1. Materials

All reagents, unless otherwise specified, were obtained from Aldrich, Acros and TCI Chemical Co., and used as received. All the solvents were further purified under a nitrogen flow. Dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene-5,10-dione (I) was synthesized as the procedure reported[35] in the reference (See ESI†). 3,6-Bis(5-bromothineno-2-yl)-*N*,*N*′-bis(2-hexyl-decyl)-1,4-dioxopyrrolo[3,4-c]pyrrole and 3,6-bis(5-bromo-thineno-2-yl)-*N*,*N*′-bis(2-butyloctyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole were synthesized as the reported procedure.[39]

2. General Methods

^{1}H NMR spectra and ^{13}C NMR were recorded on a Breuker DRX 400 and JEOL ECS-400 spectrometer operating at 400 MHz and were referred to tetramethylsilane. FAB-MS were obtained on VG ZAB-HS. Single-crystal X-ray diffraction data were collected at 296 K on a BRUKER SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The polymerization reactions were carried on a mono-microwave system (NOVA, PreeKem Scientific Instruments Co.) Analytical GPC was performed using a Waters GPC 2410 in tetrahydrofuran (THF) relative to polystyrene standards. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.) Thermal gravimetric analysis (TGA) was conducted on a TGA 2050 (TA instruments) thermal analysils system under a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min. UV-visible absorption spectra were measured on a UV-2550 spectrophotometer (Shimadzu. Co.). The cyclic voltammetry (CV) of the DTBDTs were measured on CHI 660 electrochemical workstation (Shanghai Chenhua Co.) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN) and dichloromethane (V:V, 1:1) with glass carbon and Ag/$AgNO_3$ electrode as the working and reference electrode, respectively. The cyclic voltammetry of DTBDTs-based CPs were measured similar condition with the CV measurement of DTBDTs, except that acetonitrile was only used as solvent. All the CV measurements of the DTBDTs and CPs based on DTBDTs were calibrated with Fc/Fc^+.

3. Preparation and Characterization of the Photovoltaic Solar Cells

A patterned indium tin oxide (ITO) coated glass with a sheet resistance of 10–15 Ω/square was cleaned by a surfactant scrub, followed by a wet-cleaning process inside an ultrasonic bath, beginning with de-ionized water, followed by acetone and *iso*-propanol. After oxygen plasma cleaning for 5 min, a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-casted onto the ITO substrate and then dried by baking in a vacuum oven at 80 ºC overnight. The active layer, with a thickness in the 70–80 nm range, was then deposited on top of the PEDOT:PSS layer by spin-casting from the chlorobenzene solution containing PBT-HD-DPP-C16/$PC_{71}BM$ (W/W, 1:1, 1:1.5), PBT-T-DPP-C12/$PC_{71}BM$ (W/W, 1:1, 1:1.5) and PBT-TIPS-DPP-C16/$PC_{71}BM$ (W/W, 1:1, 1:1.5). Then a 8 nm calcium and a 100 nm aluminium layer were evaporated with a shadow mask under vacuum of $(1–5)\times10^{-5}$ Pa. The overlapping area between the cathode and anode defined a pixel size of device of 0.1 cm^2. The thickness of the evaporated cathode was monitored by a quartz crystal thickness/ratio monitor (SI-TM206, Shenyang Sciens Co.). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere in a nitrogen drybox (Etelux Co.) containing less than 1 ppm oxygen and moisture. The power conversion efficiencies (PCEs) of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (Air mass 1.5 global) condition using a solar simulator (XES-70S1, San-EI Electric Co.) with irradiation of 100 mW·cm^{-2}. The current density–voltage (*J*–*V*) characteristics were recorded with a Keithley 2400 source-measurement unit. The spectral responses of the devices were measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Bejing 7-star Opt. In. Co.). A calibrated silicon detector was used to determine the absolute photosensitivity.

4. Synthesis of DTBDT Derivatives

5,10-Di(butyloxy)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (IIa), In a 50 mL flask, the dione of I (0.5 g, 1.5 mmol), zinc powder (0.39 g, 6.0 mmol), and 15 mL distilled water were added. After the mixture was stirred for 15 minutes, 3 g of NaOH was added, and the solution was refluxed for 1 h. Then, 1-bromobutane (2.47 g, 18.0 mmol) and a catalytic amount of tetrabutylammonium bromide (Bu_4NBr) were added, and the solution was refluxed overnight. After the reaction mixture was cooled to ambient temperature, the resulted solution was poured into cold water and hydrochloric acid (20 mL) was added to the mixture for adjusting the pH (~3.0). Then the mixture was extracted with chloroform and the organic phase was dried with anhydrous Na_2SO_4. After removing solvent under reduced pressure, the crude product was purified over a silica gel column using petroleum ether/$CHCl_3$ (3:1, v/v) as an eluent. Compound IIa (0.40 g, yield 59%) was obtained as white powder. M.p.: 179–181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.56 (d, 2H), 7.32 (d, 2H), 4.26 (t, 4H), 2.05–1.98 (m, 4H), 1.41–1.34 (m, 4H), 0.86 (t, 6H). Anal. Calcd for: $C_{22}H_{22}O_2S_4$: C, 59.16; H, 4.96. Found: C, 59.10; H, 4.90.

5,10-Di(octyloxy)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (IIb). Compound IIb was synthesized as the procedure of IIa with yield of 76% except that the 1-

bromobutane was substituted as 1-bromooctance. M.p.: 89–91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.56 (d, 2H), 7.32 (d, 2H), 4.26 (t, 4H), 2.05–1.98 (m, 4H), 1.65–1.58 (m, 4H), 1.46–1.30 (m, 16H), 0.90 (t, 6H). Anal. Calcd for: $C_{30}H_{38}O_2S_4$: C, 64.47; H, 6.85. Found: C, 64.38; H, 6.79.

5,10-Di(dodecyloxy)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4, 5-*b*′]dithiophene (IIc). Compound IIc was synthesized as the procedure of IIa except that the 1-bromobutane was substituted as 1-bromododecane, and IIc was obtained as pale solid with yield of 83%. M.p.: 72–73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.56 (d, 2H), 7.32 (d, 2H), 4.34 (t, 4H), 2.05–1.98 (m, 4H), 1.65–1.57 (m, 4H), 1.45–1.36 (m, 32H), 0.88 (t, 6H). Anal. Calcd for: $C_{38}H_{54}O_2S_4$: C, 68.01; H, 8.11. Found: C, 68.00; H, 8.05.

5,10-Di(2-hexyldecyloxy)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1, 2-*b*:4,5-*b*′]dithiophene (IId). Compound IId was synthesized as the procedure of IIa, except that the 1-bromobutane was substituted as 1-bromo-2-hexyldecane, and IId was obtained as yellow oil with yield of 78%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.56 (d, 2H), 7.32 (d, 2H), 4.22 (d, 4H), 2.12–2.06 (m, 2H), 1.71–1.64 (m, 4H), 1.58–1.55 (m, 6H), 1.53–1.28 (m, 8H), 1.39–1.31 (m, 30H), 0.89 (t, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 143.55, 135.93, 132.10, 130.15, 125.26, 122.56, 115.74, 39.38, 32.04, 31.22, 30.19, 29.86, 29.76, 24.49, 27.00, 26.95, 22.84, 22.81, 14.27, 14.25. $C_{46}H_{70}O_2S_4$: C, 70.53; H, 9.01. Found: C, 70.40; H, 8.95.

5,10-Bis(2-trimethylsilylethynyl)dithieno[2,3-*d*:2′,3′-*d*′]-benzo[1,2-*b*:4,5-*b*′]dithiophene (**DTBDT-TMS**). To a solution of trimethylsilylacetylene (0.6 g, 6.1 mmol) in 20 mL anhydrous THF, 3.0 mL of n-BuLi in hexance (2.5M, 7.5 mmol) was added dropwise at 0℃. Then 0.5 g (1.5 mmol) of diketone I suspended in 10 mL THF was added in one portion. The mixture was refluxed over night under argon atmosphere. Tin dichloride (1.0 g, 4.4 mmol) and hydrochloric acid (10%, 5 mL) were added in the solution. After the reaction was carried for another 2 h, the cooled solution was poured into 100 mL distilled water, and extracted with DCM for three times. The combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford yellow solid. The resulted yellow solid was purified by chromatography to give yellow needle crystalline solid (0.45 g, yield, 60 %). M.p.: 286–288 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.61 (d, 2H), 7.37 (d, 2H), 0.44 (s, 18H). Anal. Calcd for: $C_{24}H_{22}S_4Si_2$: C, 58.25; H, 4.48. Found: C, 58.21; H, 4.40.

5,10-Bis(2-tri-*iso*-propylsilylethynyl)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (DTBDT-TIPS). Compound DTBDT-TIPS was synthesized as the procedure of DTBDT-TMS, and DTBDT-TIPS was obtained as white solid with yield of 65%. M.p.: 218–220 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.62 (d, 2H), 7.38 (d, 2H), 1.37–1.28(m, 42H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 144.48, 138.98, 133.84, 130.76, 13.08, 120.04, 111.21, 105.41, 101.87, 18.94, 11.52. Anal. Calcd for: $C_{36}H_{46}S_4Si_2$: C, 65.20; H, 6.99. Found: C, 65.21; H, 7.05. FAB-MS: 663.

5,10-Bis(4,5-didecylthieno-2-yl)dithieno[2,3-*d*:2′,3′-*d*′]be-nzo[1,2-*b*:4,5-*b*′]dithiophene (DTBDT-T). To a solution of 2,3-didecylthiophene (2 g, 5.5mmol) in 40 mL anhydrous THF, n-BuLi (2.5 M in hexane, 2.2 mL) was added dropwise under the ice bath. Then the mixture was reacted for another 3 h at 50 ℃ and cooled to ambient temperature, and the solution was added in one portion to the solution of diketone I (0.54 g, 1.6 mmol) suspended in 20 mL THF and refluxed over night under argon atmosphere. Then tin dichloride dihydrate (2.0 g, 8.8 mmol) and hydrochloric acid (10%, 10 mL) was added in the solution. After the reaction was carried for another 2 h, the solution was poured into 100 mL distilled water, and extracted with DCM for three times. The combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulted yellow solid was purified by chromatography to give light yellow solid (1.16 g, yield, 69.5%). M.p.: 76–78 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm):7.37 (d, 2H), 7.23(d, 2H), 7.07 (s, 2H), 2.88 (t, 4H), 2.65(t, 4H), 1.78–1.68 (m, 8H), 1.47–1.25 (m, 56H), 0.87 (t, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 143.19, 141.46, 139.09, 138.62, 133.85, 132.23, 130.55, 130.09, 129.33, 124.07, 119.81, 32.02, 30.91, 29.83, 29.78, 29.74, 29.72, 29.58, 29.56, 29.49, 29.41, 28.45, 22.80, 14.23. Anal. Calcd for: $C_{62}H_{90}S_6$: C, 72.45; H, 8.83. Found: C, 72.32; H, 8.90. FAB-MS, 1028.

2,7-Bis(trimethylstannyl)-5,10-di(2-hexyldecyloxy)-dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiphene (III). IId (1.57 g, 2.0 mmol) was dissolved in 40 mL of anhydrous THF and cooled in an ice bath under nitrogen atmosphere. 1.2 mL n-butyllithium solution (2.5M in hexanes) was added dropwise. And the solution was kept in ice bath for 0.5 h and at ambient temperature for 0.5 h under vigorous stirring, respectively. The mixture was cooled in the ice bath again and trimethyltin chloride solution (1.22 g, 6.2 mmol) was added and kept in the ice bath for another 0.5 h. Then the solution was stirred at ambient temperature overnight. The mixture was quenched with 20 mL water and extracted with hexanes. The organic extraction was dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The compound was purified by neutral alumina column chromatography to yield III as colorless oil (1.1 g, yield, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.45 (s, 2H), 4.22 (d, 4H), 2.01–2.07 (m, 2H), 1.76-1.64 (m, 2H), 1.62–1.69 (m, 46H), 0.88 (t, 12H). 0.49 (t, 18H). Anal. Calcd for:$C_{52}H_{86}O_2S_4Sn_2$: C, 56.32; H, 7.82. Found: C, 56.42; H, 7.81.

2,7-Di(trimethylstannyl)-5,10-bis(4,5-didecylthien-2-yl)-dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (IV). DTBDT-T (1.03 g, 1.0 mmol) was dissolved in 20mL of anhydrous THF and cooled in an ice bath under nitrogen atmosphere. 1.0 mL n-butyllithium solution (2.5 M in hexanes) was added dropwise, and the solution was kept in the ice bath for 0.5 h and at ambient temperature for 0.5 h under vigorous stirring. The mixture was cooled in an ice bath again and trimethyltin chloride solution (0.61 g, 3.1 mmol) was added into the reaction mixture and kept in the ice bath for another 0.5 h. Then the solution was stirred at ambient temperature overnight. The mixture was quenched with 5 mL distilled water and extracted with hexanes. The organic extraction was dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulted solid was recrystallized in *iso*-propanol for four times to yield IV as colorless needles (0.72 g, yield, 53%). M.p.: 106–108 ºC. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 7.25 (s, 2H), 7.09 (s, 2H), 2.89 (t, 4H), 2.65 (t, 4H), 1.79–1.69 (m, 8), 1.48–1.28 (m, 56H), 0.88 (t, 12H), 0.43 (t, 18H). Anal. Calcd for: $C_{68}H_{106}S_6Sn_2$: C, 60.35; H, 7.89. Found: C, 60.22; H, 7.80.

2,7-Di(trimethylstannyl)-5,10-bis(2-tri-iso-propylsilyl-ethynyl)dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (V). DTBDT-TIPS (1.33 g, 2.0 mmol) was dissolved in 40 mL of anhydrous THF and cooled in an ice bath under nitrogen atmosphere. 1.2 mL n-butyllithium solution (2.5M in hexanes) was added dropwise, and the solution was kept in the ice bath for 0.5 h and ambient temperature for 0.5 h under vigorous stirring. The mixture was cooled in a dry ice bath again and trimethyltin chloride solution (1.22 g, 6.1 mmol) was added and kept at the ice bath for another 0.5 h. Then the solution was stirred at ambient temperature overnight. The mixture was quenched with 5 mL water and extracted with hexanes. The organic extraction was dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulted solid was recrystallized in *iso*-propanol for four times to yield V as colorless needles (1.1 g, yield, 56%). M.p.: 212–213 ºC. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 7.54 (s, 2H), 1.37–1.28 (m, 42H), 0.43 (t,18H). Anal. Calcd for: $C_{42}H_{62}S_4Si_2Sn_2$: C, 51.02; H, 6.32. Found: C, 51.58; H, 6.40.

5. Synthesis of the polymers

Synthesis of PBT-HD-DPP-C16. A mixture of toluene (6 mL) and *N*,*N*-dimethylformamide (DMF, 0.5 mL) was added to a 55 mL microwave tube containing III (333.1 mg, 0.3 mmol), 3,6-bis(5-bromothineno-2-yl)-*N*,*N*′-bis(2-hexyldecyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole (271.3 mg, 0.3 mmol) and Pd(PPh$_3$)$_4$ (4.0 mg) in a glove box with moisture and oxygen under 1 ppm. Then the tube was subjected to the following reaction conditions in a microwave reactor: 120 °C for 5 min, 140 °C for 5 min and 160 °C for 20 min. At the end of polymerization, the polymer was end-capped with 2-tributylstannylthiophene and 2-bromo-thiophene to remove bromo and trimethystannyl end groups. The mixture was then poured into methanol. The precipitated material was collected and extracted with ethanol, acetone, hexane and toluene in a Soxhlet extractor. The solution of the copolymer in toluene was condensed to 20 mL and then poured into methanol (500 mL). The precipitation was collected and dried under vacuum overnight (yield: 75%). M_n = 9650 g/mol with a polydisperse index (PDI) of 1.58. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 9.01 (br, 2H), 7.40 (br, 2H), 7.01 (br, 2H), 4.22 (br, 2H), 3.97 (br, 2H), 2.03-0.84 (m, br, 124).

Synthesis of PBT-T-DPP-C12. The PBT-T-DPP-C12 was synthesized as the procedure of PBT-HD-DPP-C16, except that the polymerization was carried out with IV of 406.0 mg (0.3 mmol), 3,6-bis(5-bromothineno-2-yl)-*N*,*N*′-bis(2-butyloctyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole of 237.7 mg (0.30 mmol). Yield: 85%. M_n = 20600 g/mol with PDI of 1.67. ^{1}H NMR (CDCl$_3$, 400 MHz),δ (ppm): 9.00 (br, 2H), 7.25 (br, 2H), 7.00 (br, 2H), 6.91 (br, 2H), 3.99 (br, 2H), 2.90 (br, 2H), 2.64 (br, 2H), 1.56-0.81 (m, br, 122).

Synthesis of PBT-TIPS-DPP-C16. The PBT-TIPS-DPP-C16 was synthesized as the procedure of PBT-HD-DPP-C16, except that the polymerization was carried out with V of 296.6 mg (0.3 mmol), 3,6-bis(5-bromothineno-2-yl)-*N*,*N*′-bis(2-hexyldecyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole of 271.3 mg (0.3 mmol). Yield: 85%. M_n = 16150 g/mol with PDI of 1.71. H NMR (CDCl$_3$, 400 MHz), δ (ppm): 9.11 (br, 2H), 7.00 (br, 2H), 6.71 (br, 2H), 4.32 (br, 2H), 1.67-0.78 (m, br, 104).

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1. N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474–1476.
2. G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**,1789–1791.
3. T. Kietzke, H. -H. Hörhold and D. Nehe, *Chem. Mater.,* 2005, **17**, 6532–6537.
4. M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem. Int. Ed.,* 2003, **42**, 3371–3375.
5. Q. Zhou, Q. Hou, L. Zheng, X. Deng, G. Yu, Y. Cao, *Appl. Phys. Lett.*, 2004, **84**, 1653–1655.
6. L. Liu, C.-L. Ho, W.-Y. Wong, K.-Y. Cheung, M.-K. Fung, W.-T. Lam, A. B. Djurišić and W.-K. Chan, *Adv. Funct. Mater.*, 2008, **18**, 2824–2833.
7. M.-H. Chen, J. Hou, Z. Hong, G. Yang, S. Sista, L. -M. Chen and Y. Yang, *Adv. Mater.,* 2009, **21**, 4238–4242.

8. F. Huang, K. -S. Chen, H. -L. Yip, S. K. Hau, O. Acton, Y. Zhang, J. Luo and Alex K.-Y. Jen, *J. Am. Chem. Soc.*, 2009, **131**, 13886–13887.
9. N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, **19**, 2295–2300.
10. E. Wang, L. Wang, L. Lan, C. Luo, W. Zhuang, J. Peng and Y. Cao, *Appl. Phys. Lett.*, 2008, **92**, 033307.
11. C. Duan, W. Cai, F. Huang, J. Zhang,, M. Wang, T. Yang, C. Zhong, X. Gong and Y.Cao, *Macromolecules*, 2010, **43**, 5262–5268.
12. W.-Y. Wong, X.-Z. Wang, Z. He, A. B. DjuriŠiĆ, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S. K. Mak and W.-K. Chan, *Nat. Mater.*, 2007, **6**, 521–527.
13. R. C. Coffin, J. Peet, J. Rogers and G. C. Bazan, *Nat. Chem.*, 2009, **1**, 657–661.
14. Y. Xia, Y. Li, Y. Zhu, J. Li, P. Zhang, J. Tong, C. Yang, H. Li and D. Fan, *J. Mater. Chem. C*, 2014, **2**, 1601–1604.
15. Y. Xia, Y. Gao, Y. Zhang, J. Tong, J. Li, H. Li, D. Chen and D. Fan, *Polymer*, **2013**, 54, 607–613.
16. Z. Ma, D. Dang, Z. Tang, D. Gedefaw, J. Bergqvist, W. Zhu, W. Mammo, M. R. Andersson, O. Inganäs, F. Zhang and E. Wang, *Adv. Energy Mater.*, 2013, doi: 0.1002/aenm.201301455.
17. J. Peet, M. L. Senatore, A. J. Heeger and G. C. Banzan, *Adv. Mater.*, 2009, **21**, 1521–1527.
18. J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Mose, A. J. Heeger and G. C. Banzan, *Nat. Mater.*, 2007, **6**, 497–500.
19. L. Ye , S. Zhang, W. Ma, B. Fan, X. Guo, Y. Huang, H. Ade and J. Hou, *Adv. Mater.*, 2012, **24**, 6335–6341.
20. T.-Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.-R. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding and Y. Tao, *J. Am. Chem. Soc.*, 2011, **133**, 4250–4253.
21. J. Hou, H. -Y. Chen, S. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 16144–16145.
22. Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799.
23. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135–E138.
24. Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591–595.
25. M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang and Y. Cao, *J. Am. Chem. Soc.*, 2011, **133**, 9638–9641.
26. T. Yang, M. Wang, C. Duan, X. Hu, L. Huang, J. Peng, F. Huang and X. Gong, *Energy. Environ. Sci.*, 2012, **5**, 8208–8214.
27. L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angew. Chem.,* 2011, **123**, 9871–9876.
28. L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li and Y. Yang, *Nat. Photonics*, 2012, **6**, 180–185.
29. Y. Huang, X. Guo, F. Liu, L. Huo, Y. Chen, T. P. Russel, C. C. Han, Y. Li and J. Hou, *Adv. Mater.*, 2012, **24**, 3383–3389.
30. Z. Ma, E. Wang, M. E. Jarvid, P. Henriksson, O. Inganäs, F. Zhang and M. R. Andersson, *J. Mater. Chem.* 2012, **22**, 2306–2314.
31. P. Gao, D. Beckmann, H. N. Tsao, X. Feng, V. Enkelmann, M. Baumgarten, W. Pisula and K. Müllen, *Adv. Mater.*, 2009, **21**, 213–216.
32. Y. Wu, Z. Li, X. Guo, H. Fan, L. Huo and J. Hou, *J. Mater. Chem.*, 2012, **22**, 21362–21365.
33. H. J. Son, L. Lu, W. Chen, T. Xu, T. Zheng, B. Carsten, J. Strzalka, S. B. Darling, L. X. Chen and L. Yu, *Adv. Mater.*, 2012, **25**, 838–843.
34. Y. Wu, Z. Li, W. Ma, Y. Huang, L. Huo, X. Guo, M. Zhang, H. Ade and J. Hou, *Adv. Mater.*, 2013, **25**, 3449–3455.
35. H.-J. Yun, Y. -J. Lee, S. -J.Yoo, D. S. Chung, Y. -H. Kim and S. -K. Kwon, *Chem. Eur. J.*, 2013, **19**, 13242–13248.
36. K. Takimiya, Y. Konda, H. Ebata, N. Niihara and T. Otsubo, *J. Org. Chem.*, 2005, **70**, 10569–10571.
37. J. Pommerehne, H. Vestweber, W. Guss, R. F. Mark, H. Bässles, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551–554.
38. D.M. de Leeuw, M.M.J. Simenon, A.R. Brown and R.E.F.Einerhand, *Synth. Met.*, 1997, **87**, 53–59.
39. Y. Li, S. P. Singh and P. Sonar, *Adv. Mater.*, 2010, **22**, 4862–4866.