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Synthesis and application of dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′] dithiophene in conjugated polymer†

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A feasible synthetic route to alkoxy-substituted DTBDT was designed and the first DTBDT-based polymer was prepared and applied in organic solar cells. The preliminary results indicate that the DTBDT unit can be used as a potential building block in organic semiconductor materials.

Linearly fused aromatic rings exhibit interesting properties and play important roles in the field of organic electronics,[1–4] especially in organic field-effect transistors (OFETs)[5–7] and organic solar cells (OSCs),[8–11] because of their superior charge transport properties due to their planar and well conjugated skeletons. For example, pentacene showed a mobility up to 35 cm^2 V^{-1} s^{-1} in an OFET,[12] which is one of the highest values in p-type OFETs; anthradithiophene (ADT) showed better stability, high hole mobility and great application potential in OFETs.[13–15] Fused aromatic units can also be used in photovoltaic polymers, and among linearly fused aromatic units, a broadly used and well-studied example is benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT).[16,17] Recently, many copolymers based on BDT and different conjugated units, such as thieno[3,4-*b*]thiophene (TT),[18,19] *N*-alkylthieno[3,4-*c*]pyrrole-4,6-dione (TPD)[20,21] and so on,[17] showed promising photovoltaic properties. Based on the development of organic semiconductor materials, it can be concluded that to introduce new building blocks into conjugated polymers is an important topic in material design for optoelectronic applications. In this work, a linearly fused conjugated unit, dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (DTBDT), was introduced as a new building block into conjugated polymers, the synthesis method and the basic properties of a new conjugated polymer based on DTBDT are investigated. The results indicate that the DTBDT unit can be used as a useful building block in new conjugated polymers.

In order to demonstrate the electronic structures as well as molecular energy levels of the linearly fused aromatic rings with representative structures, such as pentacene, ADT, DTBDT and

BDT, quantum chemistry calculations were performed by using the density functional theory (DFT) on the B3LYP/6-31G level.[22] As shown in Fig. 1, these four units show planar structures and the π-electrons are well delocalized along their backbones, however, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are different. Pentacene, ADT and DTBDT are all pentacyclic compounds, and the comparisons among them give information about the influence of the hetero atoms (sulfur) on molecular energy levels. The bandgaps of pentacene, ADT and DTBDT are 2.21 eV, 2.79 eV and 3.90 eV, respectively, indicating that the introduction of sulfur as hetero atom affects the bandgaps as well as the molecular energy levels of fused aromatic systems distinctly. Since BDT is a tricyclic molecule and DTBDT is a pentacyclic molecule, the conjugation length of DTBDT is obviously longer than that of BDT, and hence DTBDT exhibits a smaller bandgap than BDT. Interestingly, although DTBDT shows a lower LUMO level than BDT, it possesses a similar HOMO level compared to BDT. The results from DFT calculations indicate that DTBDT might be a potential building block to replace BDT in conjugated polymers.

Commonly, conjugated polymers, especially conjugated polymers based on fused aromatic rings, have rigid backbones and show strong intermolecular π–π stacking effects, and hence conjugated polymers without flexible side groups are insoluble. Therefore, in order to apply the DTBDT unit as a new building block in designing new conjugated polymers, a feasible synthetic approach to prepare DTBDT with alkoxy side groups and reactive functional groups was firstly developed in this work. By this synthetic route, the dibromide and the bis(tributylstannyl)-substituted derivatives of DTBDT with desired
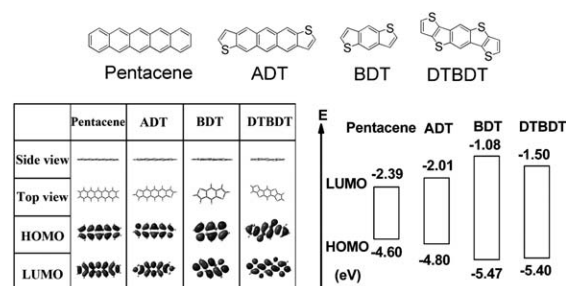
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Fig. 1 Molecular conformations and the frontier molecular orbitals of pentacene, ADT, BDT and DTBDT obtained from DFT calculations.

alkyl side groups can be easily prepared. In addition, the first DTBDT-based polymer, PDTT was synthesized, characterized and applied in OSCs. The optical, electrochemical, as well as the preliminary photovoltaic results of the OSCs based on this new polymer are provided. These results provide guidance on the molecular design of the conjugated polymers based on DTBDT unit.

The synthetic route of DTBDT using 4,8-bis((2-hexyldecyl)oxy)-benzo[1,2-b:4,5-b′]dithiophene (compound **1**) as starting material is presented in Scheme 1. In the first step of the synthetic route, compound **1** is brominated by liquid bromine using chloroform as solvent and compound **2** can be obtained in a quantitative yield. In the second step of the route, the bromine atoms on the 2 and 6 positions of compound **2** are exchanged by lithium atoms in tetrahydrofuran (THF) and then quenched by N-formylpiperidine with a yield of 90%. Then, compound **4** was easily obtained by using ethyl mercaptoacetate with compound **3** in N,N-dimethylformamide (DMF). Compound **5** was prepared by the hydrolysis of compound **4** by using 10% (aqueous solution) NaOH and used in the next step without further purification. The decarboxylation of compound **5** in quinoline using copper powder as catalyst at 180 °C gives compound **6** in 58% yield. It should be mentioned that the synthetic route consists of five steps with an overall yield of about 40%. The chemical structures of all novel compounds were clearly characterized by ^{1}H NMR and ^{13}C NMR spectra (See ESI†).

In order to explore the potential of DTBDT as a building block in molecular design of conjugated polymers, synthesis methods of two kinds of derivatives, dibromo-DTBDT and bis(trimethylstannyl)-DTBDT, were verified. We found that the protons on the 2 and 7 positions of the DTBDT unit have high reactivity so these two kinds of derivatives can be easily prepared. The dibromide and bis(tributylstannyl)-substituted derivatives were prepared using the following methods. As shown in Scheme 2, compound **7** and **8** can be obtained in high yields by similar methods as used in the synthesis of BDT derivatives.[16] Since the bis(trimethylstannyl)-substituted conjugated units are broadly used in the synthesis of conjugated polymers, herein compound **7** was copolymerized with a thieno[3,4-b]thiophene derivative (TT-C) to provide preliminary information of the DTBDT-based conjugated polymers. As shown in Scheme 2, the newly designed DTBDT-based polymer, named as PDTT, was synthesized by a Pd-catalyzed Stille coupling polycondensation. A yield of 70% was obtained and the polymer exhibits good solubility in commonly used organic solvents such as chloroform, toluene, xylenes and o-dichlorobenzene (o-DCB). The number-average molecular weight (M_n) of PDTT is 35.7 K with a polydispersity index (PDI) of
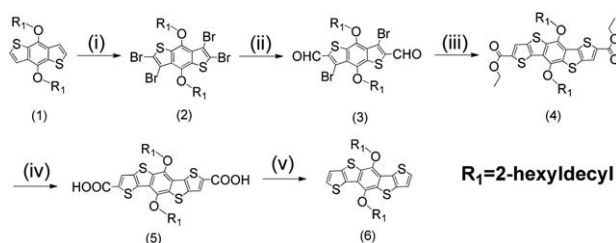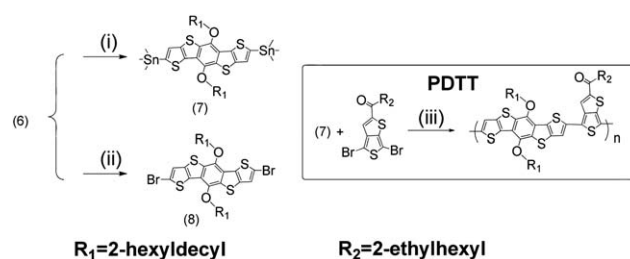
Scheme 2 Synthetic route of the functional DTBDT and the polymer: (i) LDA, THF, argon, −78 °C, 1 h, then trimethylchlorostannane, r.t. 0.5 h; (ii) NBS, CHCl₃, DMF, argon, 0 °C, 1 h. (iii) Pd(PPh₃)₄, toluene, DMF, 110 °C, 10 h, argon.

3.6, estimated by gel permeation chromatography (GPC) using THF as eluent. Thermal stability of PDTT was investigated by thermogravimetric analysis (TGA) (see Fig. S13 in ESI†). The onset point of the 5% weight loss temperature (T_d) is around 308 °C, indicating that thermal stability of PDTT is adequate for the application in optoelectronic devices. Based on the synthesis and characterization of PDTT, it can be concluded that the alkoxy-substituted DTBDT can be prepared in a good overall yield and a solution processable conjugated polymer based on DTBDT can be synthesized by Pd-catalyzed polycondensation and shows good thermal stability, hence DTBDT can be seen as a potential building block in the design of conjugated polymers.

The Ultraviolet-visible (UV-vis) absorption spectra of the copolymer in solution state and as a solid thin film are shown in Fig. 2a. In a dilute chloroform solution, PDTT displays an absorption band from 500 to 780 nm with a peak at 690 nm. The main absorption band of the solid film is broader than that of the solution. The onset absorption of the polymer at long wavelength direction is located at ∼780 nm, corresponding to an optical bandgap (E_g^{opt}) of 1.59 eV. Electrochemical cyclic voltammetry (CV) is employed to measure the molecular energy levels of conjugated polymers.[23] Based on the CV curve as shown in Fig. 2b, it is found that PDTT shows the onset points of p-doping and n-doping processes at 0.44 V and −1.76 V, respectively, corresponding to a HOMO level of −5.15 eV and a LUMO level of −2.95 eV. In comparison with the analogue based on PBDTTT–C (ref. 19) composed of BDT and TT-C, PDTT exhibits a similar absorption edge as well as the HOMO level. Considering the great success of BDT-based polymers in OSCs, DTBDT-based polymers might have great potential in the applications of photovoltaic cells.
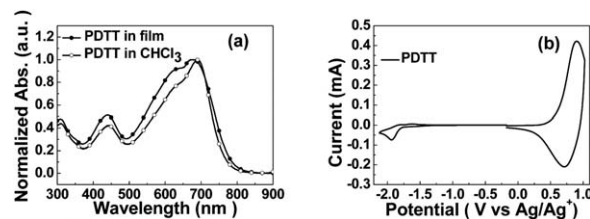

Scheme 1 Synthetic routes of DTBDT: (i) Br₂, CHCl₃, overnight; (ii) n-BuLi, THF, argon, −78 °C, 0.5 h then N-formylpiperidine, r.t. 1 h; (iii) ethyl mercaptoacetate, DMF, K₂CO₃, argon, 60 °C, overnight; (iv) NaOH (10% aqueous solution), methanol, THF, reflux, overnight; (v) Cu, quinoline, 180 °C, 1 h.

Fig. 2 (a) UV-vis absorption spectra of PDTT in a dilute chloroform solution and in spin-coated thin film. (b) Cyclic voltammogram of PDTT drop cast on a glassy carbon working electrode in 0.1 M Bu₄NPF₆ in CH₃CN at a scan rate of 50 mV s⁻¹.

One of the most important and successful applications of conjugated polymers based on fused aromatic building blocks is in OSCs. Therefore, in order to investigate the photovoltaic properties of PDTT, OSC devices were fabricated and characterized. Herein, a typical OSC device structure ITO/PEDOT:PSS/PDTT:PC$_{71}$BM/Ca/Al was employed to get preliminary information on PDTT's photovoltaic properties. First of all, different D/A ratios (PDTT/PC$_{71}$BM, wt/wt), 1 : 1 and 1 : 2, were scanned using a 10 mg mL^{-1} concentration (calculated for the polymer) and we found that the optimum D/A ratio of OSC devices is 1 : 1, when o-DCB was used as the processing solvent for the preparation of the active layers. The current density–voltage (J–V) curves of the solar cells under the illumination of AM 1.5G are shown in Fig. 3a. It can be seen that for the device with a D/A ratio of 1 : 1, the open circuit voltage (V_{oc}), the short circuit current (J_{sc}) and the fill factor (FF) are 0.75 V, 6.80 mA cm^{-2} and 44%, respectively, resulting in a power conversion efficiency (PCE) of 2.24%. Moreover, addition of 3% (v/v) diiodooctane (DIO) as solvent additive[24,25] can further enhance the efficiency to 3.64% with an improved J_{sc} of 9.85 mA cm^{-2}. The external quantum efficiency (EQE) curve of the enhanced OSC device is shown in Fig. 3b. The response range of the device covers almost the whole visible wavelength range with a maximum of 46% at 473 nm. The relatively low EQE value suggested that better device performance can be expected by further optimization, such as polymer structure design, thermal annealing, solvent annealing, and the choice of different additives. The integral current density based on the EQE curve is ~9.9 mA cm^{-2}, which is quite similar to the result from the J–V measurements. Moreover, the hole mobility of the active layer of the enhanced device was measured by the space-charge-limited-current (SCLC) method,[26] and the hole mobility can be estimated to be 1.57×10^{-3} cm^2 V^{-1} s^{-1}.

Tapping-mode atomic force microscopy (AFM) and transmission electron microscopy (TEM) were employed to investigate the morphological properties of the pure polymer film and polymer/PC$_{71}$BM blended films processed by different conditions. As shown in the ESI,† the pure polymer film processed from o-DCB shows a root mean square (RMS) roughness of 4.51 nm in the topography and irregular domains in the phase image. In the blended film processed by o-DCB with a D/A ratio of 1 : 1, regular fibril domains (~25 nm in width) are formed in the phase image (see Fig. 4b) and the RMS roughness of the film is 2.19 nm. Severe phase separation occurs when the D/A ratio of the blended film increased to 1 : 2, i.e. the film shows small size dark regions (40 nm) in Fig. 4c, while huge dark domains (>150 nm) are observed in Fig. 4f. These huge domains would be unfavorable to realize efficient exciton diffusion and hence limit the current density of the photovoltaic device. Therefore, the
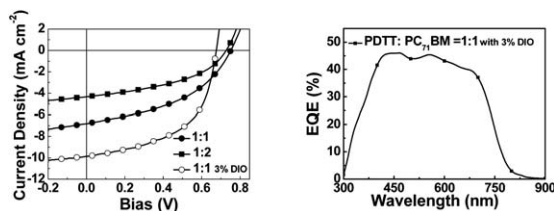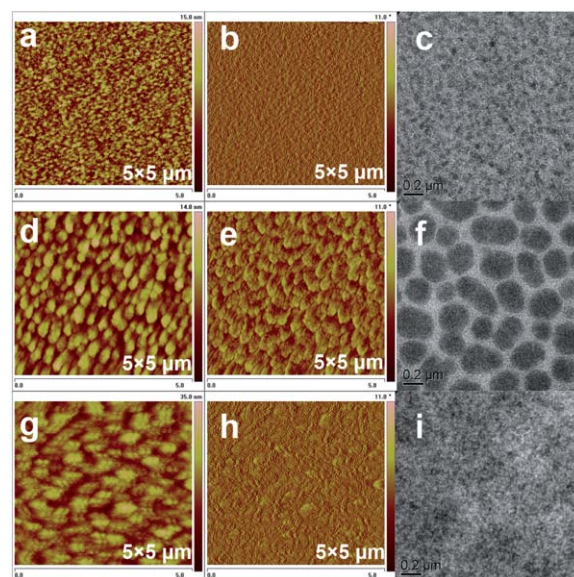

Fig. 4 AFM topography (a, d and g), phase (b, e, h) and TEM (c, f and i) images of polymer:PC$_{71}$BM (1 : 1) (a, b and c), polymer:PC$_{71}$BM (1 : 2) (d, e and f) and polymer:PC$_{71}$BM (1 : 1 with 3% (v/v) DIO additive) (g, h and i).

device with D/A ratio = 1 : 2 shows the lowest current density as shown in Table 1. Interestingly, when DIO was used as additive during the spin-coating process, the phase image (see Fig. 4h) looks very different to the film processed with pure o-DCB (Fig. 4b). The fibril pattern in Fig. 4b changed to irregular islands in Fig. 4h, while little change can be distinguished from the TEM images (from Fig. 4c and 4i). As shown in Fig. 4b, the surface is mainly occupied by fibril domains which are composed of the polymer, while in Fig. 4h, the surface is partially occupied by dark color areas, which should be ascribed to the PC$_{71}$BM phase. This observation indicates that the surface composition distribution of the blended film may be changed by the addition of DIO. More specifically, when DIO was used during the spin-coating process, PC$_{71}$BM can be enriched on the surface. As is known, enriched PC$_{71}$BM at the interface between the active layer and the metal cathode will lower the barrier and thus facilitate charge collection.[27] Therefore, after adding 3% DIO (v/v), the vertical composition/phase separation might be optimized, so higher J_{sc}, better FF and thus better PCE can be realized.

In conclusion, we developed a feasible synthetic route to alkoxy-substituted DTBDT. Since the dibromide and bis(tributylstannyl)-substituted derivatives of DTBDT can be easily prepared, this unit can be used as a versatile building block in conjugated semiconductor materials. The first DTBDT-based polymer, PDTT, was synthesized to give an example for the DTBDT-based polymers. Based on the

Fig. 3 a) J–V curves of the OSC devices based on PDTT under illumination of AM 1.5G, 100 mW cm^{-2}. (b) EQE curve of the photovoltaic cells with PDTT : PC$_{71}$BM = 1 : 1 with 3% (v/v) DIO as additive as the active layer.

Table 1 Photovoltaic results based on PDTT:PC$_{71}$BM

Polymer	D : A (wt/wt)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
PDTT	1 : 1	6.80	0.75	0.44	2.24
	1 : 2	4.34	0.73	0.44	1.39
	1 : 1[a]	9.85	0.68	0.54	3.64

[a] With 3% DIO additive (v/v).

study in this work, we found that PDTT exhibits excellent solubility in some commonly used solvents, good thermal stability, a broad absorption band and appropriate molecular energy levels. The best OSC device based on PDTT showed a PCE of 3.64% and a broad response band covering the whole visible region with a medium quantum efficiency. Based on these findings, the study in this work suggests that DTBDT should be a promising building block in organic electronic materials, and furthermore DTBDT-based polymers have great potential for applications in the organic photovoltaic field.

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