Synthesis, characterization and photovoltaic applications of a low band gap polymer based on s-tetrazine and dithienosilole†‡

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A new copolymer of dithienosilole (DTS) and dithienyl-s-tetrazine (TTz), PDTSTTz, has been designed and synthesized. This solution processable polymer shows a low band gap, strong absorption and good thermal stability. Solar cells from the blend of this polymer with $PC_{71}BM$ showed power conversion efficiency (PCE) up to 4.2%.

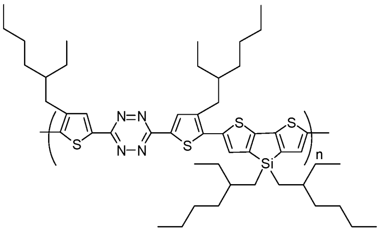
Solar energy is free, clean and sustainable, and is the ultimate energy source for the earth and human beings. The simplest way to utilize solar energy is to convert it to electricity using photovoltaic (PV) technology. Although PV technology has been developed for several decades, its share in the world electricity market is very low.[1] One of the main barriers to its wide application is the high cost. Polymer solar cells have attracted lots of research attention recently due to their low cost and easy industry production.[2] The key part of a polymer solar cell is the active layer, which is usually a blend of an electron donor, such as poly(3-hexylthiophene), P3HT, and an electron acceptor (a fullerene derivative). Ideally, these two materials form a bi-continuous bulk heterojunction (BHJ) structure with domain size at 10–20 nm scale.[3] P3HT is extensively studied as a donor material, however its power conversion efficiency (PCE) is limited at 4–5%, because of its large band gap and high-lying highest-occupied molecular orbital (HOMO), which result in limited light absorption and a low open circuit voltage (V_{oc}) of the PV devices.[4] Modified polythiophenes containing electron deficient units showed a reduced band gap and a low-lying HOMO, which can better cover the solar spectrum and offer the devices a higher V_{oc}. Based on this design strategy, devices with PCEs over 6% have been reported by several groups.[5]

In this communication, a new modified polythiophene, poly[2,6-(4,4′-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]silole)-alt-5,5′-(3,6-bis[4-(2-ethylhexyl)thienyl-2-yl]-s-tetrazine)], PDTSTTz (Scheme 1) is reported. This polymer is synthesized in a high yield, is thermally stable and solution-processable, and can act as an efficient donor material in PV devices.

We chose dithieno[3,2-*b*:2′,3′-*d*]silole (DTS) as electron rich unit because of its two distinctive advantages. First, the two σ*-orbitals of the silicon–carbon bonds will be effectively mixed with the π*-orbital of the butadiene fragment, affording a low-lying lowest-unoccupied molecular orbital (LUMO).[6] Second, silicon atom substitution can enhance interchain packing and improve the hole transport property of the polymer.[7] Meanwhile, s-tetrazine was introduced into the polymer backbone as an electron deficient unit for its high electron affinity.[8] Recent work on the electrochemically polymerized film of bis[5-(2,2′-bithienyl)-s-tetrazine] showed that incorporating a tetrazine unit into a polythiophene chain can effectively lower HOMO energy level and band gap.[9] To improve solubility and maintain a proper crystallization ability of the designed polymer, both DTS and TTz units were substituted with two short branched alkyl groups (2-ethylhexyl).

The synthesis of TTz monomer is shown in Scheme 2 and the detailed procedure is provided in the ESI.‡ Briefly, aldehyde group was introduced to the 5-position of 3-(2-ethylhexyl)-thiophene by a formylation reaction to give compound **1**, which was converted to nitrile through a two-step reaction with a total yield of 91%.[10] The nitrile **2** was reacted with hydrazine to form the relatively unstable dihydrotetrazine intermediate according to Pinner synthesis.[11] Without purification, this intermediate was aromatized by isoamyl nitrite to dithienyl-tetrazine **3** with a modest yield of 36%. The TTz monomer **4** was obtained by a simple bromination reaction. Finally, PDTSTTz was prepared by Stille coupling reaction of **4** with bis(trimethylstannane) of DTS. Gel permeation chromatography (GPC) study showed PDTSTTz has a number average molecular weight (M_n) of 22.1 kDa, and a polydispersity index (PDI) of 2.7.

s-Tetrazine derivatives are notorious for their instability and this feature inevitably restricts research interest.[8] In fact, some high nitrogen containing tetrazines have been studied as explosive materials.[12] Naturally, our first concern about this polymer is its stability. So it was examined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). As shown in Fig. 1, the polymer is stable up to 240 °C, with a weak transition appearing at 172 °C, probably attributable to the glass transition. Starting at 250 °C, a huge exothermal peak (centred at 280 °C) appeared. The TGA curve also



PDTSTTz

Scheme 1 Chemical structure of PDTSTTz.

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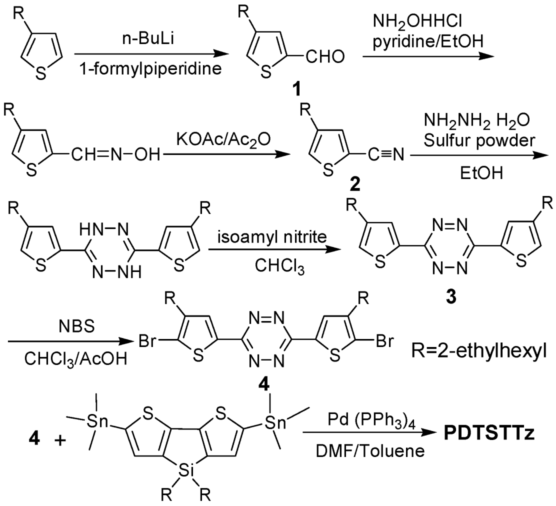
‡ Electronic supplementary information (ESI) available: Instruments, experimental details of the synthesis of monomer and polymer, NMR, CV, device fabrication and characterization. See DOI: 10.1039/c0cc02766a



Scheme 2 Synthesis route for the preparation of PDTSTTz.

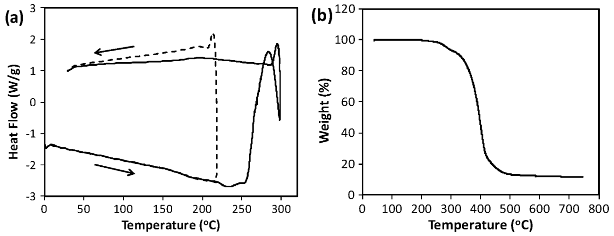


Fig. 1 Thermal analysis of PDTSTTz at a scan rate of 10 °C min^{-1} in nitrogen: (a) DSC curves of second scan after heating to 220 °C in the first scan (dashed line: 0–220 °C, solid line: 0–300 °C); (b) TGA curve.

showed a stage with weight loss of 6% at ~280 °C. It was found yellow liquid remained in the DSC pan after the scan to 300 °C. All these results indicated that the polymer main chain was broken due to the decomposition of s-tetrazine moieties with the exclusion of nitrogen gas like most s-tetrazine small molecules.[12] Considering that there are dozens of tetrazine units in a single polymer chain, this stability is remarkable. It is believed the fully conjugated structure effectively lowers its energy level and consequently improves its stability.

PDTSTTz showed high absorption both in solution and as a film. Its molar absorptivity ($\varepsilon_{\max}$, M^{-1} cm^{-1}) is 4.67×10^4 and 4.61×10^4 in toluene and in $CHCl_3$, corresponding to high weight absorptivity (ε_w, mL g^{-1} cm^{-1}) of 5.27×10^4 and 5.21×10^4 respectively. This was tentatively explained by the small size of the tetrazine, compared with other electron deficient units.[2] The UV absorption spectra of PDTSTTz are shown in Fig. 2. A symmetric peak was observed in hot *o*-dichlorobenzene solution with maximum absorption at 541 nm. This peak moved to 565 nm with the appearance of a shoulder at about 630 nm in cold solution. In solid film, this shoulder peak grew stronger with the main absorption peak moved to 579 nm. Such a change of UV absorption usually indicates a longer effective conjugation length due to the formation of a larger planar structure and stronger inter- or intra-chain π–π stacking in cold solution and in the solid state.[13]

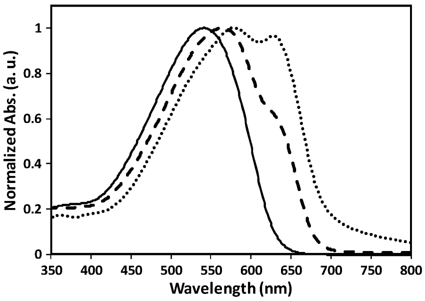


Fig. 2 UV absorption spectra of PDTSTTz in dilute *o*-dichlorobenzene solution at 60 °C (solid line), at ambient temperature (dashed line) and as a thin film (dotted line).

The polymer solution was coated on a platinum electrode to form a thin film for a cyclic voltammetry (CV) test. The CV curve shows the oxidation onset at 0.89 V and the reduction onset at −0.73 V, resulting in the HOMO and LUMO energy levels of −5.29 and −3.67 eV, according to a previously established empirical equation.[14] This result indicates a low electrochemical band gap (1.62 eV), which agrees very well with its optical band gap (1.65 eV). It should be noted that the reduction peak is much smaller than the oxidation peak (see ESI‡). This phenomenon is also found for the carbon analogue of this polymer.[15] The reason for the smaller reduction peak is currently under investigation.

All these features including good thermal stability, strong absorbance in the visible range and low band gap, make PDTSTTz an ideal donor material for polymer solar cells. Solar cell devices were fabricated with a general structure of ITO/PEDOT-PSS (45 nm)/PDTSTTz:$PC_{71}BM$ (90 nm)/LiF (1 nm)/Al (100 nm). Here $PC_{71}BM$ was chosen to compensate the absorption valley around 400 nm of the polymer (Fig. 2). Indeed, a strong and flat absorbance from 350 to 650 nm was observed from the blend of PDTSTTz with $PC_{71}BM$ (Fig. 3). The total absorption (1−reflectance) curve of the finished device showed about 90% light was absorbed by the active layer in the 450 to 650 nm range. PV devices with three different PDTSTTz/$PC_{71}BM$ weight ratios were tested to optimize the balance of electron and hole transporting. The active layers were spin coated at 80 °C from *o*-dichlorobenzene solutions. Diiodooctane (2.5% v/v) was added as a processing additive to control the phase separation. The effective area of the polymer solar cells was 50 mm^2 to avoid the size effect of small devices.[16] Other details on device fabrication and characterization are provided in ESI.‡ The current density–voltage (*J*–*V*) curves are shown in Fig. 4 and the relevant data are

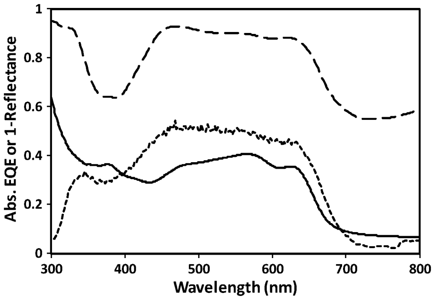


Fig. 3 UV absorption spectra (solid line), total absorption (1−reflectance, dashed line) of PDTSTTz:$PC_{71}BM$ blend at 1:2 weight ratio and external quantum efficiency curve (dotted line) of the corresponding devices.

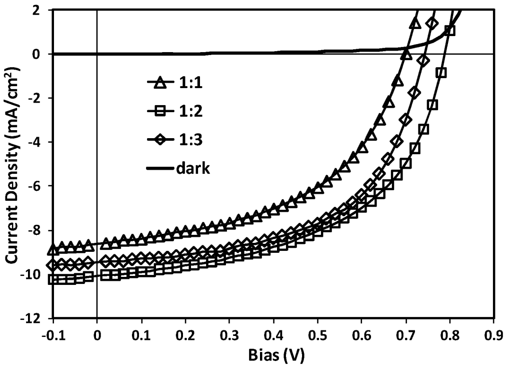


Fig. 4 *J–V* curves of the solar cell devices under illumination of AM 1.5 G, 100 mW cm^{-2} from PDTSTTz/PC$_{71}$BM blend with the weight ratio of 1 : 1, 1 : 2, and 1 : 3. The solid line is the dark current from the 1 : 2 device.

Table 1 Summary of devices performance of PDTSTTz/PC$_{71}$BM at different weight ratio

PDTSTTz : PC$_{71}$BM	V_{oc}/V	J_{sc}/mA cm^{-2}	FF (%)	PCE (%)
1 : 1	0.69	8.6	50.8	3.0
1 : 2	0.79	10.1 (9.7)[a]	52.5	4.2 (4.0)[a]
1 : 3	0.75	9.5	55.8	3.9

[a] EQE calibrated data.

summarized in Table 1. Devices with 1 : 2 PDTSTTz/PC$_{71}$BM weight ratio showed the best result with V_{oc} of 0.79 V, J_{sc} of 10.1 mA cm^{-2}, PCE of 4.2% and modest FF of 52.5%. Interestingly, the 1 : 3 devices gave the highest FF of 55.8%, which usually means better phase separation and more efficient charge dissociation. External quantum efficiency (EQE) measurement of the 1 : 2 devices demonstrated a high photo to electron conversion efficiency of ~50% in the 450 to 650 nm range (Fig. 3). The integration of the EQE curve gives calibrated J_{sc} of 9.7 mA cm^{-2}, which is 4% less than the data from the *J–V* curve, indicating minor spectral mismatch. Although our devices show lower J_{sc} and PCE than those of the best DTS based materials because of the slightly large band gap,[7b] the performance of our devices is better than that of most other DTS containing conjugated polymers,[17] due to the high electron affinity of the tetrazine unit, which leads to lower HOMO level and higher V_{oc}.

In conclusion, we have designed and synthesized a new DTS and TTz backboned copolymer, PDTSTTz. It shows good thermal stability, low band gap and strong absorbance from 450 to 700 nm. A preliminary device test based on the blend of PDTSTTz with PC$_{71}$BM gives very promising results with PCE up to 4.2%. Further improvement of the device performance is possible by fine tuning the device fabrication process. All these make PDTSTTz a promising candidate for future polymer solar cell applications.

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