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A D–A copolymer of dithienosilole and a new acceptor unit of naphtho[2,3-*c*]thiophene-4,9-dione for efficient polymer solar cells†

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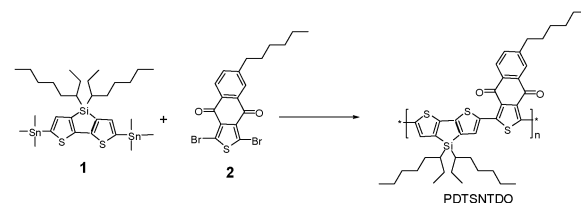
A strong electron-withdrawing unit, naphtho[2,3-*c*]thiophene-4,9-dione, was copolymerized with dithienosilole to get a D–A copolymer, PDTSNTDO, with a narrow bandgap and lower-lying HOMO level. The PCE of the PDTSNTDO-based device reached 5.21%, with a high open circuit voltage of 0.88 V.

Polymer solar cells (PSCs) offer great opportunities as renewable energy sources because of their unique advantages of being low cost, light-weight and having mechanical flexibility.^{1,2} PSCs are commonly composed of a photoactive blend layer of a conjugated polymer donor and a fullerene derivative acceptor sandwiched between a ITO positive electrode and a low work function metal negative electrode. At present, high power conversion efficiency (PCE) is the central concern of the studies on the PSCs and the key materials for improving the PCE of these devices are high-efficiency conjugated polymer donor^{3–5} and fullerene derivatives acceptor⁶ photovoltaic materials.

For the conjugated polymer donor materials, the issues we should consider in the molecular design are broad absorption spectra in order to enhance sunlight harvest for higher short circuit current (J_{sc}), an appropriately lower HOMO (the highest occupied molecular orbital) energy level to maximize the open circuit voltage (V_{oc}), and a higher hole mobility for higher J_{sc} and higher fill factor (FF) of the PSCs. Donor–acceptor (D–A) copolymerization has become an efficient strategy for obtaining low-band-gap conjugated polymers and modulating their electronic properties because of the easy tuning of their band-gap, absorption spectra and HOMO energy level by using different donor and acceptor units in the copolymers.^{7–14} In D–A copolymers, a number of electron donor units, such as fluorene,⁸ 2,7-carbazole,⁹ benzo[1,2-*b*:3,4-*b'*]dithiophene (BDT)^{10–15} and dithieno[3,2-*b*:2',3'-*d'*]silole (DTS),¹⁶ have been widely used in synthesizing high-efficiency polymer donor materials. In particular, DTS-based copolymers show a broad absorption, relatively lower HOMO energy level and higher hole mobility, which are attractive for the application as the

donor in PSCs. For example, Lu and Tao *et al.* recently synthesized a DTS-based copolymer that demonstrated a PCE as high as 7.3% when the polymer was used as the donor blended with PC₇₀BM.^{16b}

For the acceptor units used in D–A copolymers, benzothiadiazole is the most successful and popular acceptor unit.^{8–9,13} In addition, diketopyrrolopyrrole,^{17,18} thieno[3,4-*c*]pyrrole-4,6-dione^{11,16b,19} and thiazolothiazole^{16c} *etc.* have also been copolymerized with the appropriate donor units to get high performance copolymer donor materials. Here, aiming at extending the family of conjugated D–A copolymers and synthesizing new high-efficiency polymer photovoltaic materials, we introduced a new electron acceptor unit, naphtho[2,3-*c*]thiophene-4,9-dione (NTDO),²⁰ into the D–A copolymers. NTDO is easy to synthesize and possesses a relatively simple planar structure, which could be beneficial to the electron delocalization when it is incorporated into D–A copolymers. In addition, its relatively strong electron-withdrawing ability would lead to lower HOMO and LUMO (the lowest unoccupied molecular orbital) energy levels of the D–A copolymers, which is desirable for obtaining a higher open circuit voltage (V_{oc}) in the PSCs because the V_{oc} is proportional to the energy difference between the LUMO of the acceptor and the HOMO of the donor.²¹ The new acceptor unit was copolymerized with a DTS donor unit to get a D–A copolymer, PDTSNTDO (see Scheme 1). The polymer film shows a broad absorption with an absorption edge at 752 nm and lower HOMO energy level at –5.42 eV. The PSC based on PDTSNTDO as the donor and PC₇₀BM as the acceptor exhibits a higher PCE of 5.21%, with a high V_{oc} of 0.88 V, a short circuit current of 9.24 mA cm^{–2}, and a fill factor of 0.64 under the illumination of AM1.5, 100 mW cm^{–2}. The results indicate that the copolymer based on the new NTDO acceptor unit could be promising photovoltaic polymer donor materials for high-efficiency PSCs.



Scheme 1 The synthesis route and structure of PDTSNTDO. Reaction conditions: Pd(PPh₃)₄, toluene, 120 °C, 24 h.

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PDTSNTDO was synthesized by a Stille coupling reaction between 4,4-bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d'*]silole (**1**) and 1,3-dibromo-6-hexylnaphtho[2,3-*c*]thiophene-4,9-dione (**2**) in refluxing toluene under Ar in the presence of Pd(PPh₃)₄ as the catalyst for 24 h, as shown in Scheme 1. Monomer **1** was synthesized according to ref. 16 and the synthesis route of monomer **2** is shown in Scheme S1 in the electronic supplementary information (ESI†). The polymer possesses good solubility in common organic solvents, such as chloroform, toluene and *o*-dichlorobenzene. The molecular weight of the polymer was measured by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The number-average molecular weight and weight-average molecular weight of PDTSNTDO are 11.7 kDa and 16.3 kDa, respectively, and its polydispersity index (PDI) is 1.39. Thermogravimetric analysis (TGA) reveals that the onset temperature with 5% weight-loss (*T*_d) of PDTSNTDO is 321 °C, which indicates that the thermal stability of the polymer is good enough for its application in PSCs. The glass transition temperature of PDTSNTDO is 158 °C, which is measured by the differential scanning calorimetry (DSC) of PDTSNTDO, as shown in Fig. S1†.

Fig. 1 shows the ultraviolet-visible (UV-vis) absorption spectra of the polymer diluted solution in chloroform and film spin-coated on quartz substrates. The PDTSNTDO solution displays a broad absorption band in the wavelength range 400–700 nm, with the absorption maxima at 607 nm. The visible absorption band of the PDTSNTDO film is 22 nm red-shifted than that of the polymer solution. The absorption maximum of the polymer film is at 629 nm, with the absorption band edge at 752 nm. The optical band gap (*E*_g) of the polymer film calculated from the absorption band edge is 1.65 eV. The *E*_g of PDTSNTDO is obviously reduced in comparison to that of 1.81 eV^{16c} for the copolymer of DTS with the acceptor unit of bithienyl thiazolothiazole (bTTTz) and 1.73 eV^{16b} for the copolymer of DTS with the acceptor unit of thieno[3,4-*c*]pyrrole-4,6-dione (TPD), indicating that NTDO is a stronger acceptor unit than bTTTz and TPD.

The HOMO and LUMO energy levels of conjugated polymers are crucial for the application as photovoltaic materials in PSCs, and they can be measured from the onset oxidation and onset reduction potentials by electrochemical cyclic voltammetry. Fig. 2 displays the cyclic voltammogram of PDTSNTDO film. The onset oxidation potential (ϕ_{ox}) is 0.71 V vs. Ag/Ag⁺ and the onset reduction potential (ϕ_{red}) is −1.25 V vs. Ag/Ag⁺.

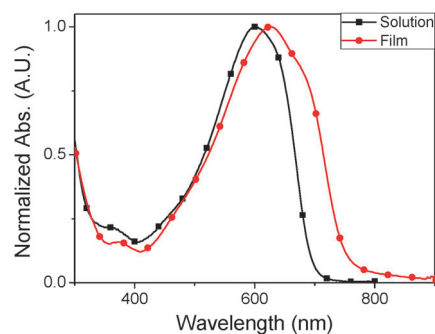


Fig. 1 Absorption spectra of PDTSNTDO in chloroform solution and in solid film.

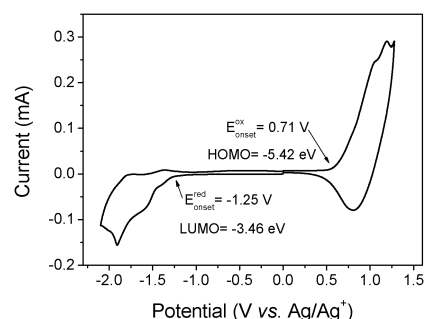


Fig. 2 A cyclic voltammogram of the PDTSNTDO film on glassy carbon electrode in 0.1 mol L^{−1} Bu₄NPF₆ acetonitrile solution at a scan rate of 100 mV s^{−1}

The HOMO and LUMO energy levels of the polymer are −5.42 eV and −3.46 eV respectively, calculated from ϕ_{ox} and ϕ_{red} according to the equations of HOMO = $-\epsilon(\phi_{ox} + 4.71)$ (eV) and LUMO = $-\epsilon(\phi_{red} + 4.71)$ (eV).²² The HOMO energy level of the polymer is significantly deeper than most of the conjugated polymer donor materials. The deeper HOMO level implies that the polymer should be more stable against oxidization, which will enhance the device stability. The deeper HOMO level is beneficial to a higher *V*_{oc} for the PSCs with the polymer as the donor.²¹

The photovoltaic properties of PDTSNTDO were investigated by fabricating the PSC devices with a structure of ITO/PEDOT: PSS/PDTSNTDO:PC₇₀BM/Ca/Al, where PDTSNTDO was used as the donor and PC₇₀BM was used as the acceptor in the photoactive layer of the devices. The active layer was prepared by spin-coating the blend solution of PDTSNTDO and PC₇₀BM in *o*-dichlorobenzene and its thickness is *ca.* 85 nm. The Ca/Al electrode was deposited onto the active layer by vacuum evaporation under 3 × 10^{−4} Pa. The effective area of the device is 4 mm². The characterization of the current density–voltage (*J*–*V*) curve was done in an inert nitrogen atmosphere and the external quantum efficiencies (EQEs) of the devices without encapsulation were measured in air.

Firstly, we optimized the device performance of the PSCs by changing the weight ratio of PDTSNTDO to PC₇₀BM from 1 : 1 to 1 : 3 and the results are listed in Table 1. It can be seen that the PSC with the weight ratio for PDTSNTDO:PC₇₀BM of 1 : 2 showed the best PCE of 5.21% under the illumination of AM1.5G, 100 mW cm^{−2}, and the average PCE of 50 devices reached 4.9(±0.3)%. The device with the weight ratio of 1 : 1 demonstrated a slightly lower PCE at 5.13% due to a slightly lower fill factor (FF). But the PCE of the PSC with the PDTSNTDO:PC₇₀BM weight ratio of 1 : 3 decreased to 3.31% due to a significantly lower short circuit current (*J*_{sc}) and FF.

Fig. 3 shows a typical current density–voltage (*J*–*V*) curve of the PSC based on PDTSNTDO:PC₇₀BM (1 : 2, w/w) under

Table 1 The photovoltaic performance of the PSCs based on PDTSNTDO:PC₇₀BM with different weight ratios, under the illumination of AM1.5G, 100 mW cm^{−2}

Active layer	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mA cm ^{−2})	FF (%)	PCE (%)
PDTSNTDO:PC ₇₀ BM = 1 : 1	0.89	9.57	60.3	5.13
PDTSNTDO:PC ₇₀ BM = 1 : 2	0.88	9.24	64	5.21
PDTSNTDO:PC ₇₀ BM = 1 : 3	0.88	6.39	58.8	3.31

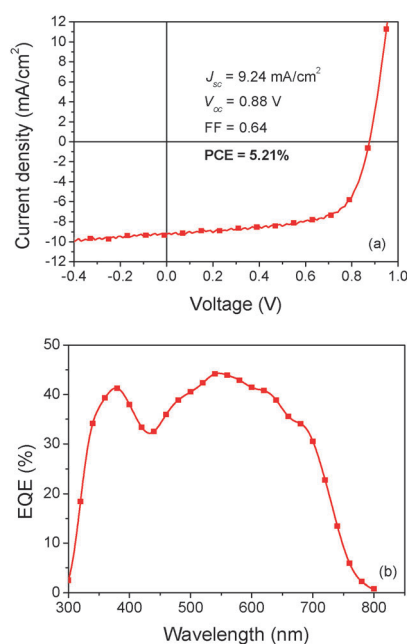


Fig. 3 (a) The I - V curve of the PSC based on PDTSTNTDO:PC₇₀BM (1:2, w/w) under the illumination of AM 1.5G, 100 mW cm⁻². (b) The EQE of the PSC based on PDTSTNTDO:PC₇₀BM (1:2, w/w).

the illumination of AM 1.5, 100 mW cm⁻², and the EQE plot of the PSC. The device demonstrated a PCE of 5.21% with a V_{oc} of 0.88 V, a J_{sc} of 9.24 mA cm⁻² and a FF of 0.64. The relatively high V_{oc} of 0.88 V of the PSC should be due to the lower-lying HOMO energy level of PDTSTNTDO, as discussed previously. The EQE curve of the device covered a broad wavelength range of 350–750 nm with a maximum EQE value of 45% at 541 nm, which indicates that the absorptions of the PDTSTNTDO donor and the PC₇₀BM acceptor all contribute to the photo-electronic conversion. The current density derived from integration of the EQE curve over the AM1.5 spectra is 9.10 mA cm⁻², which is consistent with the J_{sc} value (9.24 mA cm⁻²), if we consider a little degradation of the device performance during the EQE measurement in air.

In conclusion, a new acceptor unit of 1,3-dibromo-6-hexylnaphtho[2,3-*c*]thiophene-4,9-dione (NTDO) was utilized to synthesize D-A copolymer PDTSTNTDO with 4,4-bis(2-ethylhexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d'*]silole (DTS) donor unit for application as donor materials in PSCs. PDTSTNTDO shows good solubility in common organic solvents, a broad visible absorption at 400–750 nm, a narrow bandgap of 1.65 eV and a lower-lying HOMO energy level at -5.42 eV. The PSCs based on PDTSTNTDO:PC₇₀BM (1:2, w/w) showed a PCE of 5.21% with a high V_{oc} of 0.88 V, a J_{sc} of 9.24 mA cm⁻² and a FF of 0.64, under the illumination of AM1.5G, 100 mW cm⁻². The results indicate that the copolymer based on the new NTDO acceptor unit could be a promising photovoltaic polymer donor material for high-efficiency PSCs.

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