

## NOTE

# Synthesis of thienoselenadiazole-containing conjugated copolymers and their application in polymer solar cells

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## INTRODUCTION

In recent years, polymer solar cells (PSCs) have attracted great attention due to the energy crisis all over the world. Compared with inorganic solar cells, PSCs have many advantages, such as light weight, solution processability, mechanical flexibility and low cost.<sup>1</sup> The state-of-the-art of PSCs are based on a fullerene-derivative acceptor, such as [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC<sub>71</sub>BM), and a conjugated polymer donor, such as poly(3-hexylthiophene) (P3HT).<sup>2</sup> Power conversion efficiency (PCE) of 4–5% has been achieved for P3HT/PCBM solar cells.<sup>3</sup> To obtain high-performance PSCs, a variety of low-bandgap conjugated polymers have been synthesized through donor–acceptor (D–A) copolymerization.<sup>4,5</sup> A number of electron-rich heterocycles, such as benzodithiophene (BDT),<sup>6</sup> dithieno[3,2-b:2',3'-d]silole (DTS)<sup>7</sup> and indacenodithiophene,<sup>8</sup> have been widely used as donor units, whereas benzothiadiazole,<sup>9</sup> thieno[3,4-c]-pyrrole-4,6-dione<sup>10</sup> and diketopyrrolo[3,4-c]-pyrrole-1,4-dione<sup>11</sup> have been used as acceptor units. Recently, remarkable progress has been made by using a new copolymer, PBDTTT-CE, yielding a high PCE up to 7.73%.<sup>12</sup> To further improve the device performance, some heavy-atom-containing heterocycles, such as Se- and Ge-containing heterocycles, have also been explored for developing novel D–A copolymers.<sup>13,14</sup> The influence of the selenium atom on the electron distribution and the charge transport property has been investigated.<sup>15</sup> Selenium shows a stronger heteroaromatic interaction than sulfur, and it may enhance the inter-chain interaction and free charge carrier transportation.<sup>16</sup> To the best of our knowledge, the novel selenium-heterocycle thienoselenadiazole, has never been synthesized and investigated as the building block for conjugated polymers. In this work, we report for the first time the synthesis of a thienoselenadiazole derivative 4,6-Bis(4'-hexylthiophen-2'-yl)thieno[3,4-c][1,2,5]selenadiazole (DTTSe) through the con-

densation of the 4,4''-dihexyl-3,4'-diamino-2,2':5',2''-terthiophene and SeO<sub>2</sub>. Furthermore, we synthesized two new Se-containing conjugated copolymers PBDTDTTSe and PDTSDTTSe by copolymerization of DTTSe with BDT and DTS. The optical, electrochemical and photovoltaic properties of the polymers were investigated.

## EXPERIMENTAL PROCEDURE

### Synthesis and characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance-400 spectrometer (Ettlingen, Germany). Mass spectra were measured by an Auto Flex III (MALDI-TOF) spectrometer (Bremen, Germany). The molecular weight of the polymers was measured by gel permeation chromatography, and polystyrene was used as a standard. Thermogravimetric analysis was performed on a Perkin-Elmer Diamond TG/DTA instrument (Waltham, MA, USA). Absorption spectra were measured on a SHIMADZU UV-1800 spectrophotometer (Kyoto, Japan). Cyclic voltammetry was conducted in a 0.1 mol l<sup>-1</sup> tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution using a glassy-carbon electrode coated with the polymer film as the working electrode, a Pt wire as the counter electrode and an Ag/Ag<sup>+</sup> electrode as the reference electrode. All potentials were corrected against Fc/Fc<sup>+</sup>. Tetrahydrofuran (THF) and toluene were dried over Na/benzophenone and freshly distilled before use. 2,5-Dibromo-3,4-dinitrothiophene (1),<sup>17</sup> 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexoxy)benzo[1,2-b:3,4-b']dithiophene (6),<sup>18</sup> and 4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethyltin)dithieno[3,2-b:2',3'-d]silole (7)<sup>18</sup> were synthesized according to the methods reported in the literature. 4,4'-Bis(2-ethylhexyl)-5,5'-dibromodithieno[3,2-b:2',3'-d]silole was purchased from Solarmer Materials (Beijing, China). The synthetic routes for the monomers and polymers are shown in Figure 1. The detailed synthetic procedures for 2, 3, 5 and PDTSDTTSe are described in the Supplementary Information. The detailed synthetic procedures for 4 and PBDTDTTSe are as follows: 4,6-Bis(4'-hexylthiophen-2'-yl)thieno[3,4-c][1,2,5]selenadiazole (4)<sup>19</sup> Compound 3 (0.5 g, 1.1 mmol) was dissolved in anhydrous tetrahydrofuran (20 ml) under N<sub>2</sub>. To the solution was added SeO<sub>2</sub> (0.4 g, 3.6 mmol). The mixture was then refluxed for 12 h. The reaction mixture was cooled to room temperature,

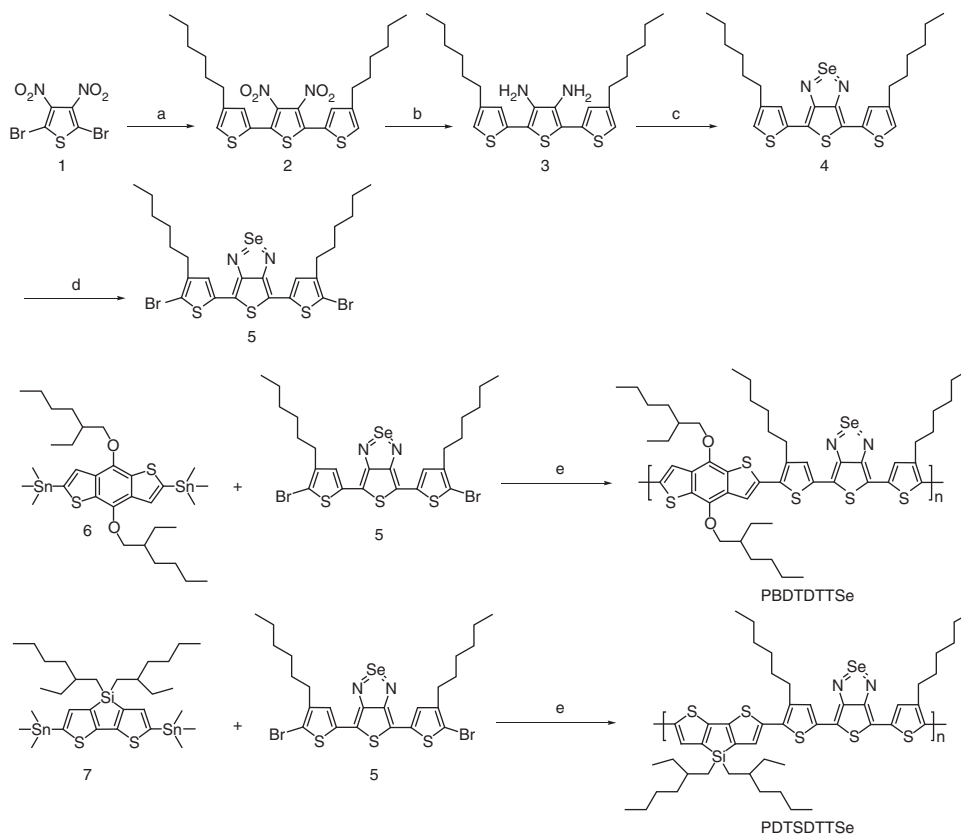
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**Figure 1** Synthetic routes for the monomers and copolymers. Reagents and conditions: (a) 3-hexyl-5-tributylstannyl-thiophene, THF, Pd(PPh<sub>3</sub>)<sub>4</sub>, 24 h; (b) SnCl<sub>2</sub>, HCl, EtOH, 18 h; (c) SeO<sub>2</sub>, THF, reflux for 12 h, under N<sub>2</sub>; (d) Br<sub>2</sub>, AcOH, 40 °C, 36 h and (e) Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, under argon.

filtered and dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography with petroleum ether/chloroform (1:1) as the eluent. The product **4** was obtained as a sticky dark red oil (0.33 g, yield: 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (p.p.m.): 7.78 (d, 2H), 7.43 (d, 2H), 2.59–2.65 (m, 4H), 1.56–1.65 (m, 4H), 1.26–1.34 (m, 12H), 0.88 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (p.p.m.): 178.57, 163.22, 144.01, 139.82, 136.55, 131.06, 30.55, 29.32, 29.19, 27.84, 21.54, 13.06. MALDI-TOF-MS for C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>S<sub>3</sub>Se [M + Li<sup>+</sup>]: 529.1. Poly[4,8-diethylhexyloxybenzo[1,2-b;3,4-b]dithiophene-alt-4,6-bis(4'-hexylthiophen-2'-yl)thieno[3,4-c][1,2,5]selenadiazole} (PBDTDTTSe). To a solution of **5** (120 mg, 0.18 mmol) and **6** (136 mg, 0.18 mmol) in toluene (20 ml) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (11 mg, 0.009 mmol), under Ar. The reaction mixture was then heated to reflux for 12 h. The mixture was cooled to room temperature and precipitated by addition of methanol (200 ml). The solid was filtered and subjected to a Soxhlet extractor. The solid was successively extracted with methanol, hexane, and chloroform. The polymer was recovered from the chloroform fraction as a red solid (110 mg, yield 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (p.p.m.): 7.84 (s, 2H), 7.66 (s, 2H), 4.23 (d, 4H), 2.85 (d, 4H), 1.26–1.88 (m, 34H), 0.83–1.09 (m, 18H). Poly[4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole-alt-4,6-bis(4'-hexylthiophen-2'-yl)thieno[3,4-c][1,2,5]selenadiazole} (PDTSDTTSe) PDTSDTTSe was synthesized according to the same procedure as PBDTDTTSe, using monomer **7** (164 mg, 0.22 mmol) and **5** (150 mg, 0.22 mmol) as the starting materials. PDTSDTTSe was obtained as a deep red solid (50 mg, yield: 24%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (p.p.m.): 7.71 (s, 2H), 7.23 (s, 2H), 2.74 (d, 4H), 1.60 (d, 4H), 0.64–1.45 (m, 52H). Figures S1–S5 in Supplementary Information show the NMR spectra for compound **2**, **3**, **4**, **5**, PBDTDTTSe, and PDTSDTTSe. Mass spectrum for compound **4** can be found in Supplementary Information.

#### Fabrication and characterization of solar cells

Solar cells with the typical structure of ITO/PEDOT:PSS/Polymer: PC<sub>71</sub>BM (1:1)/Ca/Al were fabricated under similar conditions as follows: The ITO glass

was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, and then treated in an ultraviolet-ozone chamber for 15 min. Then PEDOT:PSS (poly(3,4-ethylene dioxithiophene):poly(styrene sulfonate)) (Clevios P Al 4083, Leverkusen, Germany) was filtered through a 0.45 μm filter and spin coated at 4000 r.p.m. for 30 s on the ITO glass. Subsequently, the PEDOT:PSS film was baked at 140 °C for 10 min in the air. The blend solution of PBDTDTTSe or PBDTDTTSe and PC<sub>71</sub>BM in 1,2-dichlorobenzene (*o*-DCB) (12 mg ml<sup>-1</sup>) was then spin coated (800 r.p.m. for 60 s) on top of the PEDOT:PSS layer. Thermal annealing was then performed at 110 °C for 10 min. The devices were completed by thermal evaporation of Ca(10 nm)/Al(100 nm) as cathodes with an area of 7.57 mm<sup>2</sup> in a pressure of ca. 10<sup>-6</sup> Pa. Device characterization was done in the air under simulated AM1.5G irradiation (86 mW cm<sup>-2</sup>) using a xenon-lamp-based solar simulator (Newport, North Billerica, MA, USA) calibrated with a standard single-crystal Si photovoltaic cell.

#### RESULTS AND DISCUSSION

The general synthetic routes for the monomers and copolymers are outlined in Figure 1. The key annulation reaction for thienoselenadiazole was realized by condensation of thiophene diamine **3** and SeO<sub>2</sub> for the first time. The thienoselenadiazole **4** was obtained in 58% yield and was characterized by spectroscopic methods. The MALDI-TOF mass spectrum of **4** afforded the expected molecular ion peak plus one lithium ion. The numbers and the intensity of the isotope peaks of the spectrum are also in good agreement with that of the simulated one (see Supplementary Information). The thienoselenadiazole-containing copolymers were synthesized by the Stille coupling reaction. The two copolymers PBDTDTTSe and PDTSDTTSe have good solubility in common organic solvents, such as chloroform and 1,2-dichlorobenzene. Molecular weights determined by gel permeation chromatography are 1.87 × 10<sup>4</sup> and

$1.32 \times 10^4$  for PBDDTTSe and PDTSDTTSe, respectively. The PDI for PBDDTTSe and PDTSDTTSe are 1.82 and 1.49, respectively.

Thermogravimetric analysis results show that the decomposition temperatures for PBDDTTSe and PDTSDTTSe are 317 and 224 °C, respectively. In comparison to other D–A-conjugated polymers, the decomposition temperatures for PBDDTTSe and PDTSDTTSe are relatively low, which might be due to the instability of the thienoselenadiazole heterocycle. Even so, the thermal stability of the two copolymers is good enough for solar cell applications.

The optical properties of the polymers were investigated by UV-vis absorption spectroscopy in chloroform solutions and in films. As shown in Figure 2, the absorption spectra of PBDDTTSe in solution and in film both show two absorption peaks, located at  $\sim 400$  and  $\sim 480$  nm, respectively. On the contrary, the spectra of PDTSDTTSe show only one peak at  $\sim 500$  nm in both solution and film. The absorption maximum for PDTSDTTSe is more red-shifted in comparison with PBDDTTSe due to the stronger electron-donating ability of the DTS moiety. The spectra of the two polymer films are broader than that of their solutions due to the aggregation of the polymer chains in the solid state. The absorption edges of PBDDTTSe and PDTSDTTSe films are at 609 and 620 nm, suggesting bandgaps of 2.04 and 2.00 eV, respectively.

Cyclic voltammetry was carried out for estimating the HOMO (highest occupied molecular orbital) levels, the LUMO (lowest unoccupied molecular orbital) levels and the bandgaps of the polymers, according to the following equations:<sup>20</sup>

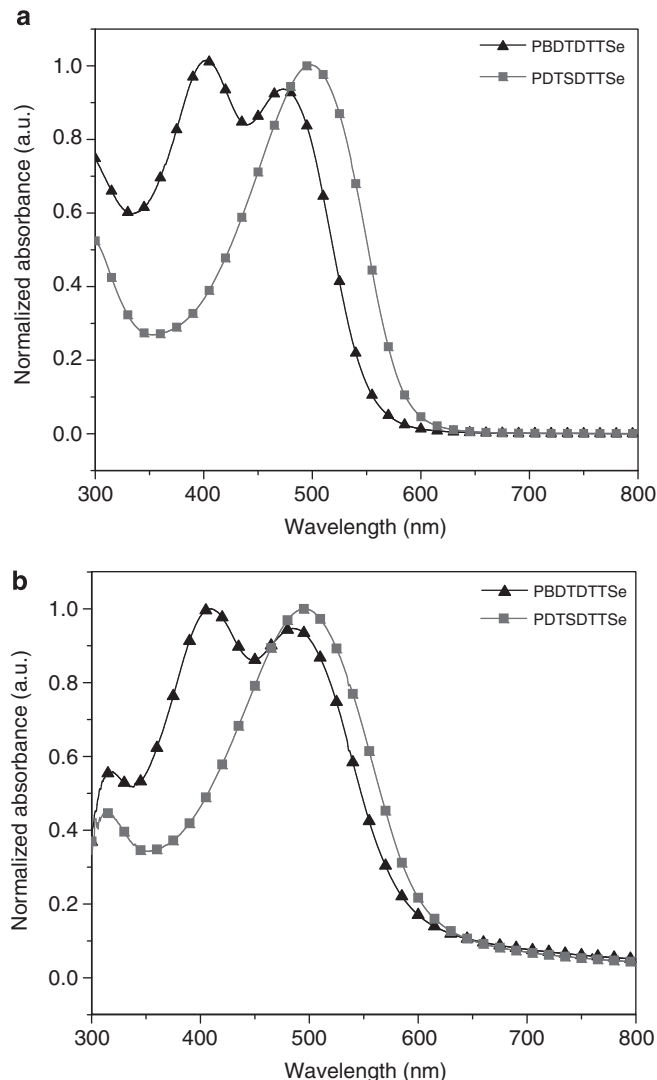
$$E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{on}} + 4.8) \text{ (eV)}$$

$$E_{\text{LUMO}} = -e(E_{\text{red}}^{\text{on}} + 4.8) \text{ (eV)}$$

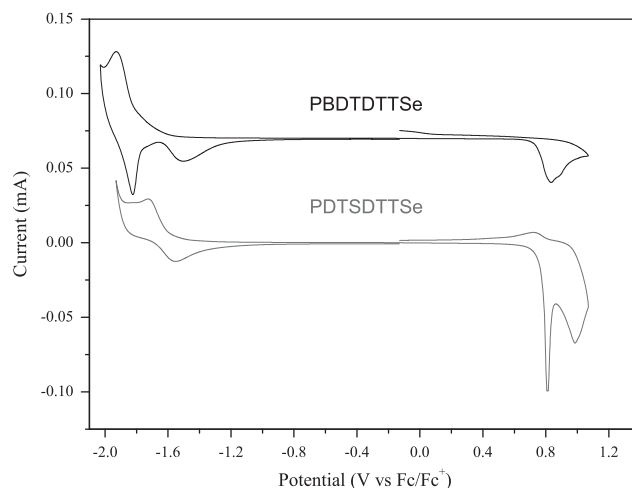
$$E_{\text{g}}^{\text{cc}} = E_{\text{LUMO}} - E_{\text{HOMO}} \text{ (eV)}$$

The cyclic voltammograms of the two polymers are shown in Figure 3. The electrochemical data are listed in Table 1. The onset reduction potentials ( $E_{\text{red}}^{\text{on}}$ ) of PBDDTTSe and PDTSDTTSe are  $-1.62$  and  $-1.51$  V, respectively, and the onset oxidation potentials ( $E_{\text{ox}}^{\text{on}}$ ) are  $0.71$  and  $0.70$  V, respectively. Both polymers exhibit relatively deep HOMO energy levels ( $-5.51$  and  $-5.5$  eV) suggesting that they are stable against oxidation and may lead to a high open-circuit voltage ( $V_{\text{oc}}$ ) of the solar cells, because  $V_{\text{oc}}$  is proportional to the energy difference between the HOMO of the donor and LUMO of the acceptor.

Solar cells with a configuration of ITO/PEDOT:PSS/Polymer:PC<sub>71</sub>BM/Ca/Al were fabricated and tested under simulated AM1.5G irradiation ( $86 \text{ mW cm}^{-2}$ ). The corresponding open-circuit voltage ( $V_{\text{oc}}$ ), short-circuit current density ( $J_{\text{sc}}$ ), fill factor and PCE of the cells are listed in Table 2. Cells based on PBDDTTSe:PC<sub>71</sub>BM and PDTSDTTSe:PC<sub>71</sub>BM both show high  $V_{\text{oc}}$  ( $0.78$ – $0.89$  V), due to the low-lying HOMO levels of the polymers. However, the high bandgap ( $\sim 2.3$  eV) and moderate light absorption of the polymers lead to very poor  $J_{\text{sc}}$ , although the  $J_{\text{sc}}$  of PDTSDTTSe is slightly better than that of PBDDTTSe because of better light absorption of PDTSDTTSe. The LUMO levels ( $\sim -3.2$  eV) of both polymers are much higher than that of PC<sub>71</sub>BM, which will cause unexpected energy loss in the process of free charge carrier generation. The thicknesses of the active layers for the devices were optimized. 55–60 nm thick active layers gave the highest PCE of 0.14 and 0.20% for PBDDTTSe and PDTSDTTSe devices, respectively.



**Figure 2** Absorption spectra of the copolymers (a) in solution and (b) in film. A full color version of this figure is available at *Polymer Journal* online.



**Figure 3** Cyclic voltammograms of the polymer films measured in CH<sub>3</sub>CN containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. A full color version of this figure is available at *Polymer Journal* online.

**Table 1** Photovoltaic properties of the solar cells based on PBDDTTSe and PDTSDTTSe under the illumination of AM1.5G 86 mW cm<sup>-2</sup>

Active layer	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>a</sup>
PBDDTTSe:PC <sub>71</sub> BM	0.89	0.56	22.7	0.14
PDTSDTTSe:PC <sub>71</sub> BM	0.78	0.80	22.9	0.20

Abbreviations: FF, fill factor; J<sub>sc</sub>, short-circuit current density; PCE, power conversion efficiency; V<sub>oc</sub>, open-circuit voltage.  
<sup>a</sup>Values in the parentheses are averages of 6–9 devices.

**Table 2** Optical and electrochemical properties of the polymers

Polymers	UV-vis absorption spectra			Cyclic voltammetry					
	λ <sub>max</sub> (nm)		λ <sub>onset</sub> (nm)	E <sub>g</sub> <sup>opt</sup> (eV) <sup>c</sup>	E <sub>onset</sub> <sup>ox</sup> (V)	E <sub>onset</sub> <sup>red</sup> (V)	HOMO (eV)	LUMO (eV)	E <sub>g</sub> <sup>ec</sup> (eV) <sup>d</sup>
	Solution <sup>a</sup>	Film <sup>b</sup>							
PBDDTTSe	402, 473	409, 487	609	2.04	0.71	-1.62	-5.51	-3.18	2.33
PDTSDTTSe	499	495	620	2.00	0.70	-1.51	-5.50	-3.29	2.21

Abbreviations: HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

<sup>a</sup>Measured in chloroform solution.

<sup>b</sup>Cast from chloroform solution.

<sup>c</sup>Calculated from the absorption onset of the films, E<sub>g</sub><sup>opt</sup> = 1240/λ<sub>onset</sub>.

<sup>d</sup>Calculated from E<sub>g</sub><sup>ec</sup> = e(E<sub>onset</sub><sup>red</sup> - E<sub>onset</sub><sup>ox</sup>).

## SUMMARY

We have successfully synthesized the thioselenadiazole unit through the condensation reaction between thiophene diamine and SeO<sub>2</sub> and applied the thioselenadiazole unit for D–A-conjugated polymers. The thioselenadiazole-based polymers, PBDDTTSe and PDTSDTTSe, exhibit good solubility in common organic solvents, good thermal stability and deep HOMO levels. The solar cells based on thioselenadiazole-containing polymers gave high V<sub>oc</sub>. Further improving of the light-absorption properties of the thioselenadiazole-containing polymers to achieve high J<sub>sc</sub> and high PCEs is currently underway.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)