New small molecules with thiazolothiazole and benzothiadiazole acceptors for solution-processed organic solar cells

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A new thiazolothiazole based small molecule (DTTz-DTBTT) has been designed and synthesized. The small molecule exhibited good thermal stability and excellent solubility. The optical gap of DTTz-DTBTT was estimated to be 1.65 eV. The solution-processed photovoltaic device based on DTTz-DTBTT and PC61BM exhibited a power conversion efficiency of 1.64%.

Introduction

Organic solar cells (OSCs) have been extensively investigated due to their unique features, such as low energy consumption, mechanical flexibility, large area coverage and low-cost manufacturing.1–4 In the past decade, intensive interdisciplinary efforts have been dedicated to improving the power conversion efficiencies (PCEs) of solar cells.4,5 Solution-processed solar cells based on π-conjugated polymers and fullerene derivatives have reached over 9% PCEs,6 and the perovskite-sensitized solar cells have shown exciting 15% PCEs.7 At this point, the small molecular OSCs over polymeric counterparts is their facile characterization and purification.13 The purification of semiconducting materials has recently been proven to be crucial to achieve high PCEs in solution-processed OSCs.16–20 Furthermore, the PCEs have been rapidly increasing in solution-processed small molecule OSCs.10–12 One main advantage of small molecule OSCs over polymeric counterparts is their facile characterization and purification.13 The purification of semiconducting materials has recently been proven to be crucial to achieve high PCEs in solution-processed organic small molecules exhibited a wide absorption spectrum and suitable energy levels which could contribute to the open circuit voltage (VOC) and efficient exciton dissociation in solar cell devices.16,17 The PCEs of solution-processed OSCs based on D–A low band-gap small molecules as donors have exceeded 8%, as reported by groups of Y. S. Chen and G. C. Bazan, respectively.18,19 In order to obtain a broad absorption spectrum and lower energy levels of small molecules, the introduction of two different acceptors into the conjugated small molecule backbone may be a good choice. However, there were very few small molecule OSC donor materials, based on two different acceptors units, exhibiting remarkable success.20 Recently, the small molecule donor materials with two acceptor units have achieved PCEs of 3.07–5.5%, which are promising donor materials for solution-processed OSCs.16–20 A further study on this type of solution-processed small molecule OSCs is underway.

Thiazolothiazole (Tz) has a rigid and coplanar fused ring, thereby ensuring a highly extended π-electron system and strong π–π stacking. As a result, conjugated small molecules and polymers based on Tz units exhibited high charge carrier mobilities.21,22 Recently, several thiazolothiazole-based copolymers and small molecules have been successfully applied in organic solar cells.23 Among the variety of developed acceptor units, benzothiadiazole (BT) has attracted much attention because of its special properties of controlling the energy levels in D–A conjugated molecules.24–26 High performance OSCs were achieved by blending BT-based copolymers and fullerene derivatives, such as benzo[1,2-b:4,5-b’]dithiophene-BT,27 diketopyrrolopyrrole-BT,28 and carbazole-BT.29 Thus, Tz and BT units could be employed in the design of...
semiconductive small molecules for solution-processed OSC applications.

In this work, we reported a new conjugated small molecule, DTTz-DTBTT, using the Tz unit as the central core, thiophene as the π-bridge, and BT as the acceptor unit (Scheme 1). The targeted molecule has good solubility in common organic solvents, such as dichloromethane (CH₂Cl₂), chloroform (CHCl₃) and tetrahydrofuran (THF). The optical gap of DTTz-DTBTT estimated from the absorption onset of thin film was 1.65 eV with a highest occupied molecular orbital (HOMO) level of around -5.05 eV. The solution-processed OSCs based on DTTz-DTBTT were investigated in typical BHJ devices using PC₆₀BM as an acceptor.

**Experimental**

**General**

All starting reagents were purchased commercially as analytical reagents and used directly without any purification. N,N-Dimethylformamide (DMF) was purified by vacuum distillation. Toluene was dried over sodium benzophenone as an indicator. The sample was dried at 40 °C under vacuum. Compounds 4,7-dibromo-benzo[1,2,5]thiadiazole (1) and 2,5-bis(trimethyltin-4-(2-ethylhexyl)thiophen-2-yl)-thiazolo[5,4-d]thiazole (6) were prepared according to the literature.

NMR spectroscopy was carried out on a Bruker Advance III 600 spectrometer using tetramethylsilane as an internal standard. High resolution mass spectra were recorded on a Bruker Maxis UHR 600 spectrometer using tetramethylsilane as an internal standard.

**Synthesis**

**Synthesis of DTBT (2).** 4,7-Dibromo-benzo[1,2,5]thiadiazole (1) (2.94 g, 10 mmol), tributyl-[4-octyl-thiophen-2-yl]-stannane (1.5 g, 3.3 mmol) and Pd[PPh₃]₄ (35 mg, 0.03 mmol) were dissolved in 30 ml of anhydrous degassed toluene. The reaction mixture was heated up to 110 °C and stirred overnight under argon. Then the cooled mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure. The dark solid was purified by column chromatography over silica gel with CH₂Cl₂-petroleum ether as an eluent and compound (2) was obtained as a dark red solid (2.25 g, 85%).

**Synthesis of DTBT-Br (3).** Compound (2) (1.81 g, 3 mmol), tributyl-[5-hexyl-thiophen-2-yl]-stannane (1.5 g, 3.3 mmol) and Pd[PPh₃]₄ (35 mg, 0.03 mmol) were dissolved in 30 ml of anhydrous degassed toluene. The reaction mixture was heated up to 110 °C and stirred overnight under argon. Then the cooled mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.

**Synthesis of DTBT-Tr (4).** Compound (3) (1.81 g, 3 mmol), tributyl-[5-hexyl-thiophen-2-yl]-stannane (1.5 g, 3.3 mmol) and Pd[PPh₃]₄ (35 mg, 0.03 mmol) were dissolved in 30 ml of anhydrous degassed toluene. The reaction mixture was heated up to 110 °C and stirred overnight under argon. Then the cooled mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.

**Synthesis of DTBT-Tr (5).** Compound (4) (1.38 g, 2 mmol) was dissolved in 40 ml of DMF at room temperature, and N-bromosuccinimide (NBS) (1.42 g, 8 mmol) was added slowly. After stirring under the light protection overnight, the reaction mixture was poured into ice water and extracted with chloroform. The organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure. The dark solid was purified by column chromatography over silica gel with CH₂Cl₂-petroleum ether as an eluent and a red solid (3) (1.92 g, 40%) was obtained.

**Synthesis of DTBT-Tr (6).** Compound (5) (1.81 g, 3 mmol), tributyl-[5-hexyl-thiophen-2-yl]-stannane (1.5 g, 3.3 mmol) and Pd[PPh₃]₄ (35 mg, 0.03 mmol) were dissolved in 30 ml of anhydrous degassed toluene. The reaction mixture was heated up to 110 °C and stirred overnight under argon. Then the cooled mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.

**Synthesis of DTBT-Tr (7).** Compound (6) (1.38 g, 2 mmol) was dissolved in 40 ml of DMF at room temperature, and N-bromosuccinimide (NBS) (1.42 g, 8 mmol) was added slowly. After stirring under the light protection overnight, the reaction mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.

**Synthesis of DTBT-Tr (8).** Compound (7) (1.81 g, 3 mmol), tributyl-[5-hexyl-thiophen-2-yl]-stannane (1.5 g, 3.3 mmol) and Pd[PPh₃]₄ (35 mg, 0.03 mmol) were dissolved in 30 ml of anhydrous degassed toluene. The reaction mixture was heated up to 110 °C and stirred overnight under argon. Then the cooled mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.

**Synthesis of DTBT-Tr (9).** Compound (8) (1.38 g, 2 mmol) was dissolved in 40 ml of DMF at room temperature, and N-bromosuccinimide (NBS) (1.42 g, 8 mmol) was added slowly. After stirring under the light protection overnight, the reaction mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.

**Synthesis of DTBT-Tr (10).** Compound (9) (1.81 g, 3 mmol), tributyl-[5-hexyl-thiophen-2-yl]-stannane (1.5 g, 3.3 mmol) and Pd[PPh₃]₄ (35 mg, 0.03 mmol) were dissolved in 30 ml of anhydrous degassed toluene. The reaction mixture was heated up to 110 °C and stirred overnight under argon. Then the cooled mixture was poured into ice water and extracted with CH₂Cl₂. The combined organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure.
The dark solid was purified by column chromatography with CHCl₃:petroleum ether as an eluent and a dark red solid (5) (1.38 g, 90%) was obtained.

¹H NMR (600 MHz, CDCl₃, δ): 7.96 (s, 1H), 7.77 (d, 1H), 7.75 (s, 1H), 7.73 (d, 1H), 7.03 (d, 1H), 6.75 (d, 1H), 2.83 (m, 4H), 2.63 (t, 2H), 1.72 (m, 6H), 1.44–1.28 (m, 26H), 0.91–0.87 (m, 9H).

¹³C NMR (150 MHz, CDCl₃, δ): 152.44, 152.36, 146.61, 143.01, 139.91, 138.71, 136.16, 133.36, 133.24, 130.83, 127.83, 125.88, 125.76, 124.99, 124.94, 124.81, 124.51, 111.34, 31.91, 31.90, 30.69, 30.19, 29.79, 29.69, 29.63, 29.49, 29.45, 29.42, 29.31, 29.28, 28.84, 22.70, 22.69, 22.60, 14.14, 14.13, 14.10.

Synthesis of DTTz-DTBTT. Compound (5) (385 mg, 0.5 mmol), 2,5-bis(trimethyltin-4-(2-ethylhexyl)thiophen-2-yl)-thiazolo[5,4-d]thiazole (6) (171 mg, 0.2 mmol) and Pd(PPh₃)₄ (23 mg, 0.02 mmol) were dissolved in 20 ml of anhydrous toluene. The reaction mixture was heated up to 110 °C and stirred at this temperature for 48 h under argon. Then the cooled mixture was poured into water and extracted with diethyl ether. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography over silica gel with petroleum ether: CH₂Cl₂ (2:1) as the eluent and compound DTTz-DTBTT (7) (110 mg, 31%) was obtained as a dark purple solid.

¹H NMR (600 MHz, CDCl₃, δ): 7.96 (s, 4H), 7.77 (m, 4H), 7.05 (m, 2H), 6.75 (d, 2H), 2.91 (m, 8H), 2.83 (t, 4H), 2.80 (t, 4H), 1.84 (m, 2H), 1.78 (m, 4H), 1.72 (m, 8H), 1.51–1.29 (m, 8H), 0.97–0.88 (m, 30H).

¹³C NMR (150 MHz, CDCl₃, δ): 160.83, 152.47, 150.04, 146.48, 142.45, 141.31, 139.80, 137.48, 137.45, 136.21, 133.37, 133.15, 131.87, 131.82, 130.66, 130.62, 129.60, 125.67, 125.63, 125.47, 125.27, 124.88, 124.83, 124.47, 39.61, 39.60, 34.77, 32.63, 31.96, 31.94, 31.61, 31.59, 30.61, 30.37, 30.19, 29.95, 29.78, 29.74, 29.72, 29.69, 29.61, 29.58, 29.53, 29.48, 29.38, 29.25, 28.87, 28.69, 14.22, 14.17, 14.15, 14.13, 14.11, 10.73.


**Result and discussion**

**Synthesis and thermal stability**

The synthetic route for preparation of small molecules, DTTz-DTBTT, is outlined in Scheme 1. Compound (5) was synthesized through a four-step reaction of compound 4,7-dibromo-benzothiadiazole (1) using Stille coupling and bromination reactions. The targeted molecule was synthesized by Stille coupling between compound (5) and 2,5-bis(trimethyltin-4-(2-ethylhexyl)thiophen-2-yl)-thiazolo[5,4-d]thiazole (6). All the synthesis process and the purification procedure were all well repeated with moderate and high yields. The purity of the targeted compound for the device fabrication was guaranteed by repeated column purification. The small molecule was soluble in common organic solvents, which was a prerequisite for solution-processed small molecule OSCs. The thermal properties of DTTz-DTBTT were investigated by thermogravimetric analysis (TGA) using a differential scanning calorimeter (DSC). This molecule exhibited good thermal stability with a decomposition temperature (5% weight loss) of 419 °C and a DSC melting point at 170 °C in nitrogen (Fig. 1). The high thermal stability of the small molecule decreases the possibility of molecule degradation and morphology degradation in solar cells.

**Optical properties**

Fig. 2 showed the normalized UV-vis absorption of DTTz-DTBTT in dilute CHCl₃ solution and in thin solid film. The UV-vis optical spectrum of DTTz-DTBTT in chloroform presented an absorption peak at 535 nm. The thin film of DTTz-DTBTT showed intense absorption throughout the visible region (300–700 nm). The film exhibited an obvious red-shifted λmax = 587 nm absorption.

Fig. 1  TGA and DSC plots of DTTz-DTBTT at the heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.
Compared to that in solution, the absorption spectrum of the film as well as its red-shift (52 nm) suggested that strong intermolecular interaction and aggregation existed in the film. The optical gap of DTTz-DTBTT was estimated to be 1.65 eV from the absorption onset (752 nm) in the thin film.

**Electrochemical properties**

The electrochemical properties of DTTz-DTBTT were investigated by cyclic voltammetry (CV) as film on a glassy carbon working electrode in 0.1 M \([\text{[n-But}_{4}\text{N}]^{+}\text{[PF}_6^{-}\text{]}\] / C\(_2\)H\(_3\)CN solution (\(n\)-butyl) at a potential scan rate of 100 mV s\(^{-1}\). As shown in Fig. 3, DTTz-DTBTT exhibited a couple of reversible reduction wave and quasi-reversible oxidation wave. The redox potential of the Fc/Fc\(^+\) internal reference was 0.38 V vs. SCE.

The HOMO and lowest unoccupied molecular orbital (LUMO) energy levels of the molecule were determined by the empirical formula of \(E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8 - E_{1/2,(\text{Fc/Fc}^+)} \) \), \(E_{\text{LUMO}} = -e(E_{\text{red}} + 4.8 - E_{1/2,(\text{Fc/Fc}^+)} \). The onset oxidation and reduction potentials of DTTz-DTBTT were 0.63 V and \(-1.35\) V, thus the corresponding HOMO and LUMO energy levels were \(-5.05\) eV and \(-3.07\) eV, respectively.

**Photovoltaic properties**

BHJ OSCs were fabricated with a device structure of glass/ITO/PEDOT:PSS/DTTz-DTBTT:PC\(_{61}\)BM/Ca/Al, and tested under a simulated AM 1.5G illumination at 100 mW cm\(^{-2}\). The blends of the DTTz-DTBTT and PC\(_{61}\)BM at different weight ratios of 1:2, 1:1, and 2:1 were used to optimize the device performances and their current density versus voltage (\(J-V\)) curves were shown in Fig. 4, and for all the optimized conditions, we had averaged the performance over 5 devices and the data were given in Table 1. Finally, the PCE of 1.64% for DTTz-DTBTT was obtained with an open-circuit voltage (\(V_{\text{OC}}\)) of 0.66 V, a short circuit current density (\(J_{\text{SC}}\)) of 5.11 mA cm\(^{-2}\), and a fill factor (FF) of 48%, when the device was made at a donor–acceptor weight ratio of 1:1 in chloroform with a concentration of 10 mg ml\(^{-1}\), spun cast at 1500 rpm. The devices fabricated with DTTz-DTBTT exhibited moderate performance that could be caused by a low \(V_{\text{OC}}\) of 0.66 V. The \(V_{\text{OC}}\) was governed by the gap between the HOMO level of DTTz-DTBTT and the LUMO of PCBM (\(-3.9\) eV to \(-4.2\) eV). Thus, the high HOMO level (\(-5.05\) eV) of DTTz-DTBTT caused lower \(V_{\text{OC}}\) in this case.

The external quantum efficiency (EQE) curve of the optimized BHJ device based on DTTz-DTBTT/PC\(_{61}\)BM (w:w, 1:1) is shown in Fig. 5. The EQE curve exhibits a monochromatic EQE maximum of 28% at 442 nm and a broad response covering at 350–750 nm, consistent with the absorption spectrum. This EQE value indicates that the photoresponse is moderate for this small molecule based BHJ device. The \(J_{\text{SC}}\) calculated from the integral of EQE curve based on DTTz-DTBTT with an AM 1.5G reference spectrum is 5.02 mA cm\(^{-2}\), which is consistent with the \(J_{\text{SC}}\) value obtained from the \(J-V\) measurement (5.11 mA cm\(^{-2}\)).

**Table 1** Solar cells performance of DTTz-DTBTT:PC\(_{61}\)BM with different blend ratios

<table>
<thead>
<tr>
<th>Small molecule</th>
<th>Ratio</th>
<th>(V_{\text{OC}}) (V)</th>
<th>(J_{\text{SC}}) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE(<em>{\text{max}})/ PCE(</em>{\text{ave}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTTz-DTBTT:PC(_{61})BM</td>
<td>1:2</td>
<td>0.62</td>
<td>1.35</td>
<td>46.2</td>
<td>0.39/0.35 ± 0.03</td>
</tr>
<tr>
<td>DTTz-DTBTT:PC(_{61})BM</td>
<td>1:1</td>
<td>0.66</td>
<td>5.11</td>
<td>48.3</td>
<td>1.64/1.58 ± 0.03</td>
</tr>
<tr>
<td>DTTz-DTBTT:PC(_{61})BM</td>
<td>2:1</td>
<td>0.66</td>
<td>3.73</td>
<td>51.1</td>
<td>1.25/1.23 ± 0.02</td>
</tr>
</tbody>
</table>
The morphology of the film is important for the performance of small molecule/PCBM BHJ solar cells. In order to investigate the relationship between solar cell performance and morphology, the atomic force microscopy (AFM) of the DTTz-DTBTT/PC61BM (w:w, 1:1) blend film was performed. The active layer was spin coated from CHCl3 solution onto the glass/ITO/PEDOT:PSS substrate for 1 : 1) blend film was performed. The active layer was spin coated from CHCl3 solution onto the glass/ITO/PEDOT:PSS substrate for 1 : 1) blend film was performed. The active layer was spin coated from CHCl3 solution onto the glass/ITO/PEDOT:PSS substrate for 1 : 1) blend film was performed.

### Conclusions

A solution-processed small molecule DTTz-DTBTT, using a thiazolo-thiazole (Tz) unit as the core, has been synthesized through the Stille reaction and employed as an electron donor for small molecule organic solar cells. The small molecule exhibited good thermal stability, excellent solubility and film forming properties. The optical gap of DTTz-DTBTT was estimated to be 1.65 eV. The photovoltaic properties of DTTz-DTBTT were investigated in typical BHJ devices using PC61BM as an acceptor. A PCE of 1.64% was obtained with an open-circuit voltage ($V_{oc}$) of 0.66 V, a short circuit current density ($J_{sc}$) of 5.11 mA cm$^{-2}$, and a fill factor (FF) of 48%. The results indicate that the molecule based on two different acceptors is an effective strategy for the design of small molecule donor materials.

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