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# Tuning optical and electronic properties of star-shaped conjugated molecules with enlarged $\pi$ -delocalization for organic solar cell application<sup>†</sup>

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Three structurally related conjugated molecules (BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2) in star shape have been designed and synthesized as donor materials for small molecule based bulk heterojunction (BHJ) solar cells. The structural features of these molecules include a planarized benzo[1,2-b:3,4-b':5,6-b"]trithiophene (BTT) with a  $C_{3h}$  symmetry as the central core and three conjugated arms incorporating electron deficient benzo[2,1,3]thiadiazole (BTD) units, with arms being linked to the core via different number of thiophene connecting units (e.g., 0, 1, 2 corresponding to BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2, respectively). Comparative analyses of optical and electronic properties indicate that the molecules bearing more thiophene units between the BTT core and the BTD arms possess higher-lying HOMO levels while their LUMO levels remain almost unchanged. The improvement of BHJ device performance, with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the acceptor, is observed with increasing number of thiophene units between the BTT core and BTD arms, from BTT-BTD-0 to BTT-BTD-1 and BTT-BTD-2. The BTT-BTD-2:PC<sub>61</sub>BM based BHJ devices show the highest power conversion efficiency (PCE) of 0.74%, with an open-circuit voltage ( $V_{oc}$ ) of 0.69 V, a short-circuit current density ( $I_{sc}$ ) of 2.93 mA cm<sup>-2</sup>, and a fill factor (FF) of 0.37 under 1 sun (100 mW cm<sup>-2</sup>) AM 1.5G simulated solar illumination. The PV performance of **BTT-BTD-2** is further improved when [6,6]-phenyl- $C_{71}$ -butyric acid methyl ester (PC<sub>71</sub>BM) is used as the electron acceptor, yielding the best device performance with  $J_{sc}$  of 4.13 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.72 V, FF at 0.46 and PCE of 1.36%. The effect of the different number of thiophenes linking the BTT core and the conjugated BTD arms has been clearly demonstrated on regulating optical and electrochemical properties of the three molecules and their BHJ device performances.

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## Introduction

Research efforts on polymer-based solar cells have been mainly focused on polymers as the electron-donating material and fullerene derivatives as the electron-accepting material, both of which are typically blended in a bulk heterojunction (BHJ) configuration to achieve the photovoltaic effect.<sup>1</sup> The power conversion efficiency of such polymer–fullerene based BHJ cells has been progressively improved to 7–9% for single junction cells,<sup>2-13</sup> while over 10% has been reported for the multi-junction design (tandem cells).<sup>14</sup> Impressive as these efficiency values are, these semiconducting polymers pose outstanding issues such as structural polydispersity, end-group contamination and trace impurities originating from their syntheses.<sup>15-17</sup> All these catalyzed the emergence of solution processed small molecule-based BHJ cells, since small molecules can have welldefined structures, extremely high purity (*e.g.*, defect-free), and superior batch-to-batch reproducibility. For these reasons, solution processed small molecule-based BHJ solar cells have recently gained significant momentum, with efficiency numbers rivalling those achieved by polymer-based ones.<sup>18-24</sup>

However, active research on small molecules for solution processed BHJ cells poses different challenges, as well as opportunities. For example, it appears that very subtle changes on the molecular structure can have significant influence on the performance of related solar cells, while the photovoltaic properties of polymers are quite insensitive or much more tolerant to these minor structural changes. One such example is

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given by Bazan et al. recently,24 where they showed that the relative orientation of two flanking [1,2,5]thiadiazolo[3,4-c]pyridines had significant impact on the efficiencies of devices based on these molecules (from 3% to 7%). In contrast, when these [1,2,5]thiadiazolo[3,4-c]pyridines were employed in a related polymer - presumably in a random fashion,25 You et al. demonstrated an efficiency of 6.3% in an earlier study, without observing such an "orientation" effect (likely non-existing). Furthermore, the early studied molecular species largely emerged from the design of polymers for BHJ solar cells. However, recently a variety of molecular structures - quite specific to small molecules - have appeared, including dendritic, star-shaped, in addition to more traditional, linear conjugated molecules, with reported device efficiencies ranging from 1-7%.<sup>23,26-40</sup> In particular, star-shaped conjugated materials are a very intriguing class of organic materials. The high structural symmetry and planarity of star-shaped conjugated molecules may promote the  $\pi$ - $\pi$  stacking of conjugated arms due to a broad  $\pi$ -delocalization of armed molecules. On the other hand, the increased steric hindrance associated with these armed molecules may also prevent the formation of an ordered, long-range and coplanar  $\pi$ - $\pi$  stacking, which could be beneficial to charge transport across the thin film based devices. Such interesting effects for star-shaped conjugated materials, stemming from both their molecular structures and morphology at the solid state, contribute to their interesting optical and electronic properties. All these properties, together with the morphological features in the solid state, will determine the device performance of these materials when applied in organic electronics and photonics.41

In the spirit of further exploring the structure–property relationship of these star-shaped molecules for organic solar cells, we investigated a family of three star-shaped conjugated molecules of different degree of conjugation, **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2** as shown in Fig. 1, and their application as electron donors in combination with fullerene acceptors in typical BHJ devices. We chose planarized benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (BTT) with  $C_{3h}$  symmetry as the central core. Three



Fig. 1 Molecular structures of BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2.

conjugated arms were constructed with a "donor-acceptor" motif of one electron deficient benzo[2,1,3]thiadiazole (BTD) and one electron rich α-alkylated thiophene. All three conjugated arms were then connected to the central core via un-substituted thiophenes (0, 1, or 2). We envisioned that such star-shaped chemical construction could provide tunable  $\pi$ -conjugation regulated by the number of thiophene units used as the linkage between the BTT core and BTD arms. Furthermore, the "donor-acceptor" or "push-pull" molecular framework on the arms can reduce the band-gap through the partial intramolecular charge transfer between the electron rich unit and the electron deficient one on the arms. Finally, these aliphatic side chains at  $\alpha$ -positions of these terminal thiophenes would offer the solubility of resultant molecules, facilitating material characterization and BHJ device fabrication. Through a combination of synthesis, calculation and characterization, we found that the number of un-substituted thiophenes, *i.e.*, the connecting units, significantly impacts the observed efficiency of BHJ devices. The highest efficiency of 1.4% was obtained from BTT-BTD-2 that contains the greatest number of "connecting" thiophenes in this studied series of molecules.

#### Experimental

General information of reagents, instrumentations and conditions on optical spectroscopy and electrochemistry testing and quantum chemical calculations can be found in the ESI.† Benzo-[1,2-*b*:3,4-*b*':5,6-*b*"]trithiophene was synthesized according to the procedure reported in the literature.<sup>42</sup>

#### Synthesis

[5-(2-Hexyldecyl)-thiophen-2-yl]-tributyl-stannane. To a mixture of thiophene (7 mL, 110 mmol) and 50 mL of anhydrous THF under nitrogen was added dropwise 2.5 M n-BuLi in hexane (40 mL, 100 mmol) under stirring at 0 °C. The mixture was allowed to warm to room temperature after 1 hour and 1-bromo-2-hexyldecane (27.5 g, 90 mmol) was added before being heated to reflux overnight. After cooling down to room temperature, the mixture was poured into 200 mL of cold water and extracted with petroleum ether (3  $\times$  50 mL). The combined organics was dried over anhydrous magnesium sulfate and concentrated under vacuum. The crude product was purified by silica gel column chromatography eluted with petroleum ether to afford 17.7 g of pure 2-(2-hexyldecyl)thiophene (compound 1, 64%). <sup>1</sup>H-NMR (400 MHz,  $CDCl_3$ , ppm): 7.11 (dd, J = 5.1; 1.2 Hz, 1H), 6.91 (dd, J = 5.1; 3.4 Hz, 1H), 6.78-6.70 (dd, J = 3.3; 1.2 Hz, 1H),2.75 (d, J = 6.6 Hz, 2H), 1.60 (m, 1H), 1.27–1.25 (m, 24H), 0.90– 0.86 (m, 6H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 144.26, 126.48, 124.93, 122.87, 39.99, 34.17, 33.11, 31.91, 29.96, 29.66, 29.65, 29.37, 26.55, 22.72, 14.20. EI-MS for C<sub>20</sub>H<sub>36</sub>S: calcd, 308.25; found, 308 (M<sup>+</sup>). To a mixture of 2-(2-hexyldecyl)thiophene (6.16 g, 20.0 mmol) and 40 mL of anhydrous THF was added dropwise 2.5 M n-BuLi in hexane (8.2 mL, 20.5 mmol) under stirring at room temperature under N2. Bu3SnCl (7.5 g, 22.0 mmol) was then added 30 minutes later. After stirring for another 1 hour, the mixture was poured into 100 mL of water and extracted with petroleum ether (3  $\times$  20 mL). The combined organics was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give the crude product as yellow oil. <sup>1</sup>H-NMR spectrum of the crude oil indicated that the conversion efficiency of the reaction was almost quantitative and the crude product was then used directly for the next step without further purification.

4-Bromo-7-((5-(2-hexyldecyl))-thiophen-2-yl) benzo[2,1,3]thiadiazole (2). To a flame-dried flask containing 4,7-dibromo-benzo [2,1,3]thidiazole (6.4 g, 22.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (115 mg, 0.1 mmol, 0.5% equiv.) under N2 was transferred a solution of compound 1 (20.0 mmol) in 50 mL of anhydrous THF through a cannula. The mixture was then heated to reflux overnight. After removal of the solvent under reduced pressure, the mixture was redissolved in 40 mL of petroleum ether and filtered to remove unconsumed 4,7-dibromo-benzo[2,1,3]thidiazole. The filtrate was concentrated by rotoevaporation and was purified by silica gel column chromatography eluted by gradient petroleum etherdichloromethane (from 6/1 to 1/1, v/v) to afford 3.8 g of the target compound (yield, 37%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.95 (d, J = 3.7 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 6.85 (d, J = 3.7 Hz, 1H), 2.80 (d, J = 6.7 Hz, 2H), 1.70 (m, 1H), 1.32–1.26 (m, 24H), 0.89–0.85 (m, 6H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 153.59, 151.52, 146.95, 135.95, 132.10, 128.07, 127.19, 126.40, 124.77, 111.30, 39.95, 34.58, 33.11, 31.87, 31.56, 29.93, 29.60, 29.32, 26.53, 22.66, 14.10. EI-MS for C<sub>26</sub>H<sub>37</sub>BrN<sub>2</sub>S<sub>2</sub>: calcd, 520.16; found,  $520/522 (1:1, M^+).$ 

Compound 3. To a flame-dried 100 mL two-necked flask was sequentially added compound 2 (5.53 g, 10.6 mmol), 2-(tributylstannyl)thiophene (3.68 g, 11.6 mmol), Ph(PPh<sub>3</sub>)<sub>4</sub> (61 mg, 0.053 mmol, 0.5% equiv.) and 40 mL of anhydrous toluene under N2. The resulted mixture was then stirred and heated to reflux for 7 hours. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography eluted by petroleum ether-dichloromethane (3/1, v/v) to afford 5.0 g of the target compound (yield, 90%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 8.09 (d, *J* = 3.0 Hz, 1H), 7.97 (d, J = 3.6 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 4.6 Hz, 1H), 7.20 (dd, J = 3.8; 5.0 Hz, 1H), 6.85 (d, J = 3.6 Hz, 1H), 2.82 (d, J = 6.7 Hz, 2H), 1.71 (m, 1H), 1.33-1.27 (m, 24H), 0.90-0.85 (m, 6H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 152.50, 152.37, 146.45, 139.41, 136.87, 127.84, 127.50, 127.13, 126.39, 126.27, 126.17, 125.68, 125.09, 124.75, 40.01, 34.65, 33.18, 31.89, 29.96, 29.62, 29.33, 26.57, 22.67, 14.12. EI-MS for  $C_{30}H_{40}N_2S_3$ : calcd, 524.24; found, 524 (M<sup>+</sup>).

**Compound 4.** To a mixture of compound 3 (2.62 g, 5.0 mmol) and 80 mL of chloroform–acetic acid (1/1, v/v) was added NBS (0.89 mg, 5.0 mmol) in several parts under stirring at room temperature. When the reaction completed, the mixture was washed with water, solution of 10% sodium hydroxide and saturated brine consecutively. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated under vacuum to afford 2.72 g of pure product (yield, 90%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.95 (d, J = 3.7 Hz, 1H), 7.74 (d, J = 4.0 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.12 (d, J = 4.0 Hz, 1H), 6.84 (d, J = 3.7 Hz, 1H), 2.81 (d, J = 6.7 Hz, 2H), 1.71 (m, 1H), 1.40–1.18 (m, 24H), 0.92–0.81 (m, 6H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 151.95, 151.86, 146.54, 140.60, 136.62, 130.35, 127.65, 126.49, 126.28, 126.20,

124.70, 124.29, 123.74, 114.02, 39.96, 34.58, 33.15, 31.89, 29.98, 29.67, 29.63, 29.35, 26.54, 22.68, 14.14. EI-TOF MS for  $C_{30}H_{39}BrN_2S_3$ : calcd, 602.15; found, 602/604 (1 : 1, M<sup>+</sup>).

**Compound 5.** Compound 5 was prepared from compound 4 (2.72 g, 4.5 mmol) and 2-(tributylstannyl)thiophene (2.02 g, 5.4 mmol) according to the same procedure for compound 3. The crude product from the reaction was purified by silica gel column chromatography eluted by petroleum ether–dichloromethane (6/1, v/v) to afford 1.84 g of the target compound (yield, 68%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.99 (d, J = 3.8 Hz, 2H), 7.83 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.19 (d, J = 3.9 Hz, 1H), 7.04 (d, J = 3.8 Hz, 1H), 7.02 (d, J = 3.8 Hz, 1H), 6.87 (d, J = 3.6 Hz, 1H), 2.81 (d, J = 6.7 Hz, 2H), 1.71 (m, 1H), 1.33–1.20 (m, 24H), 0.90–0.85 (m, 6H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 152.50, 146.68, 138.47, 138.19, 137.31, 136.94, 127.94, 127.60, 126.38, 126.27, 125.31, 124.89, 124.71, 124.49, 123.95, 40.05, 34.72, 33.21, 31.70, 29.97, 29.63, 29.33, 26.60, 22.68, 14.12. MALDI-TOF MS for C<sub>34</sub>H<sub>42</sub>N<sub>2</sub>S<sub>4</sub>: calcd, 606.22; found, 606.97 (M<sup>+</sup>).

**Compound 6.** Compound **6** was prepared from compound **5** (1.76 g, 2.91 mmol) and NBS (0.52 g, 2.91 mmol) by the same procedure for compound **4**. The resulted crude mixture was loaded onto a silica gel column eluted by petroleum ether-dichloromethane (8/1, v/v) to present 1.62 g of pure product (yield, 81%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.95 (d, J = 3.7 Hz, 1H), 7.74 (d, J = 4.0 Hz, 1H), 7.71 (s, 1H), 7.70 (s, 1H), 7.12 (d, J = 4.0 Hz, 1H), 6.84 (d, J = 3.7 Hz, 1H), 2.82 (d, J = 6.7 Hz, 2H), 1.71 (m, 1H), 1.45–1.15 (m, 24H), 0.92–0.85 (m, 6H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 152.41, 146.75, 138.79, 138.59, 137.26, 136.66, 130.73, 127.76, 127.69, 126.40, 125.34, 125.33, 124.74, 124.58, 123.87, 111.27, 40.05, 34.71, 33.22, 31.90, 29.97, 29.63, 29.34, 26.59, 22.68, 14.12. MALDI-TOF MS for  $C_{34}H_{41}BrN_2S_4$ : calcd, 685.87; found, 686.1 (M<sup>+</sup>).

1,3,5-Tri(trimethylstannyl) benzo[1,2-b:3,4-b':5,6-b"]trithiophene (7). To a solution of benzo[1,2-b:3,4-b':5,6-b"]trithiophene (0.246 g, 1.0 mmol) in 50 mL of anhydrous THF was added dropwise 2.5 M n-BuLi in hexane (2.4 mL, 6 mmol) at 0 °C under N2. The resulting mixture was then warmed up to room temperature and stirred for 1 hour. 1 M trimethyltin chloride in anhydrous THF (7.0 mL, 7 mmol) was then added to the mixture. After stirring for another 1 hour, the mixture was diluted with 50 mL of ethyl ether and washed with saturated ammonium chloride and water consequently. The organic layer was dried over anhydrous MgSO4 and concentrated by rotoevaporation. The crude solid was washed with a small amount of methanol and then dried under vacuum to give 0.6 g of pure product (yield, 82%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.70 (s, 3H), 0.48 (s, 27H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 137.94, 135.78, 132.70, 130.40, -8.15. MALDI-TOF MS for  $C_{21}H_{30}S_3Sn_3$ : calcd, 734.79; found, 734.1 (M<sup>+</sup>).

**BTT-BTD-0.** To a flame-dried two-necked round bottom flask containing 1,3,5-tri(trimethylstannyl) benzo[1,2-*b*:3,4-*b*':5,6-*b*'']-trithiophene (0.367 g, 0.5 mmol) and Ph(PPh<sub>3</sub>)<sub>4</sub> (18.0 mg, 0.015 mmol) under nitrogen was transferred a solution of compound 2 (0.94 g, 1.8 mmol) in 40 mL of anhydrous toluene *via* a cannula. The resulting mixture was then stirred and heated to reflux overnight. After removal of the solvent under reduced pressure, the crude product was washed with 50 mL of methanol and dried. The solid was then further purified by silica gel

column chromatography eluted by petroleum ether–dichloromethane (2/1, v/v) to give 0.35 g of the target molecule (yield, 44%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.62 (s, 3H), 7.38 (d, J =2.4 Hz, 3H), 6.94 (d, J = 7.0 Hz, 3H), 6.84 (d, J = 7.0 Hz, 3H), 6.48 (s, 3H), 2.69 (d, J = 5.7 Hz, 6H), 1.69 (m, 3H), 1.36 (m, 66H), 1.02–0.87 (m, 18H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 151.02, 145.03, 136.93, 136.40, 130.98, 130.40, 127.62, 125.95, 124.92, 124.23, 123.40, 122.90, 121.44, 77.32, 77.00, 76.68, 39.90, 34.58, 33.16, 32.04, 30.19, 30.18, 29.84, 29.81, 29.50, 26.61, 26.57, 22.81, 14.26. MALDI-TOF MS for C<sub>90</sub>H<sub>114</sub>N<sub>6</sub>S<sub>9</sub>: calcd, 1566.66; found, 1568.0 (M + H<sup>+</sup>). Elemental analysis for C<sub>90</sub>H<sub>114</sub>N<sub>6</sub>S<sub>9</sub>: calcd C, 68.92; H, 7.33; N, 5.36; S, 18.40. Found: C, 68.40; H, 7.20; N, 5.35; S, 19.05%.

Compound BTT-BTD-1. The compound was synthesized by the same method for BTT-BTD-0 through the reaction of compound 4 with 1,3,5-tri(trimethylstannyl) benzo[1,2-b:3,4b':5,6-b'']trithiophene (0.35 mmol). After the reaction finished as indicated by TLC, the mixture was added dropwise into 250 mL of acetone and precipitated. The precipitate was extracted using acetone and hexane sequentially on a Soxhlet extractor. The extraction from hexane was concentrated and further purified by silica gel column chromatography by petroleum ether-dichloromethane (1/1, v/v) to give 0.35 g of pure product (yield, 54%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.10 (s, 3H), 6.95 (s, 3H), 6.64-5.87 (m, 15H), 2.58 (s, 6H), 1.56 (m, 3H), 1.50-1.11 (m, 66H), 1.07–0.78 (m, 18H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>, ppm): 150.75, 150.54, 144.66, 137.76, 136.50, 135.17, 127.11, 125.81, 123.94, 123.87, 123.48, 123.07, 115.77, 39.78, 34.50, 33.17, 31.95, 30.08, 29.71, 29.40, 26.54, 22.72, 14.14. MALDI-TOF MS for C<sub>102</sub>H<sub>120</sub>N<sub>6</sub>S<sub>12</sub>: calcd, 1812.62; found, 1813.0 (M<sup>+</sup>). Elemental analysis for C<sub>102</sub>H<sub>120</sub>N<sub>6</sub>S<sub>12</sub>: calcd C, 67.50; H, 6.66; N, 4.63; S, 22.20. Found: C, 66.50; H, 6.44; N, 4.37; S, 22.69%.

BTT-BTD-2. The compound was synthesized by the same method for BTT-BTD-0 through the reaction of compound 6 with 1,3,5-tri(trimethylstannyl) benzo[1,2-b:3,4-b':5,6-b"]trithiophene (0.35 mmol). When the reaction finished, the mixture was added dropwise into 100 mL of acetone and precipitated. The precipitate was loaded onto a Soxhlet extractor and extracted using acetone, hexane and methylene dichloride consequently. The extraction from methylene dichloride was concentrated under reduced pressure and the resulted solid was then dried under vacuum to give 503 mg of pure product (yield, 70%). With conventional liquid phase NMR spectroscopy aromatic protons of BTT-BTD-2 could not be efficiently detected, presumably because of strong shielding effects of aromatic ring current caused by enlarged  $\pi$ -conjugation in **BTT-BTD-2**. As a result, isotope-resolved MS with mild ionization methods (e.g., MALDI-TOF) and elemental analysis were the only applicable techniques for its structure characterization. MALDI-TOF MS for  $C_{114}H_{126}N_6S_{15}$ : calcd, 2058.59; found, 2060.2 (M + H<sup>+</sup>). Elemental analysis for C<sub>114</sub>H<sub>126</sub>N<sub>6</sub>S<sub>15</sub>: calcd C, 66.43; H, 6.16; N, 4.08; S, 23.33. Found: C, 66.20; H, 6.20; N, 4.06; S, 23.54%.

#### BHJ device fabrication and characterization

BHJ solar cells were fabricated with a general device configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)

poly(styrenesulfonate) (PEDOT:PSS)/donor-PCBM/Ca (20 nm)/Al (80 nm). Glass substrates with patterned ITO were sonicated for 10 minutes consecutively in DI water, acetone and isopropyl alcohol, followed by drying under a stream of N2. The substrates were then treated over UV-ozone for 10 minutes. A layer (45 nm) of PEDOT:PSS film was then spin-coated onto the substrates at 3000 RPM for 60 s and baked at 150 °C for 30 minutes. The substrates were then transferred into a glove box under N<sub>2</sub>. Subsequently, the active layer was spin-cast from a different blend ratio (weight-to-weight, w/w) of donor (10 mg mL<sup>-1</sup>) and PC<sub>61</sub>BM in 1,2-dichlorobenzene (o-DCB) onto the ITO/ PEDOT:PSS substrate and dried naturally in the glove box. Finally, Ca (20 nm) and Al (80 nm) were sequentially deposited on the top of the active layer as cathode at a pressure of  ${\sim}2 \times 10^{-6}$ mbar through a shadow mask that defines 8 devices with each active area of 18 mm<sup>2</sup>. The thicknesses of active layers were recorded by a DEKTAK XT profilometer.

Current-voltage measurements were carried out in a nitrogen-filled glove box under AM 1.5G irradiation with the intensity of 100 mW cm<sup>-2</sup> (from a 450 W solar simulator, Newport 94023A-U) calibrated by a NREL certified standard silicon cell. Current *versus* potential (*J–V*) curves were recorded with a Keithley 2420 digital source meter. For external quantum efficiency (EQE) tests, devices were transferred by a self-made testing box under the protection of nitrogen atmosphere into the sample chamber of a 7-SCSpec Spectral Performance Solar Cell Test System consisting of a 500 watt SCS028-7ILX500 xenon light source, a 7ISW301 vertical grating spectrometer, a 7IFW6 filter wheel, a SR540 chopper and a SR810 lock-in amplifier. The calibration of the incident monochromatic light was carried out with a Hamamatsu S1337-1010 BQ Silicon photo detector.

Morphology of films was characterized through traditional Tapping Mode on an Agilent 5500 AFM (Agilent Technologies, Santa Clara, CA) under ambient conditions. Si<sub>3</sub>N<sub>4</sub>-coated silicon AFM tips (NSC19/Si<sub>3</sub>N<sub>4</sub>, Mikromasch, Estonia) with a spring constant of 0.6 N m<sup>-1</sup> and a resonance frequency of 80 kHz were used in imaging. Powder X-ray diffraction (XRD) and BHJ thin film grazing incident X-ray diffraction (GIXRD) data were recorded in reflection mode with a D8 ADVANCE X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.540598$  Å) at room temperature. BHJ thin films of **BTT-BTD-x** (x = 0, 1, 2 respectively)/PC<sub>61</sub>BM were spun-coated on a silicon substrate covered by a layer of PEDOT:PSS before the measurements.

Hole mobilities of donor-PC<sub>61</sub>BM (w/w, 1 : 1) blended films were measured in configuration of ITO/PEDOT:PSS (45 nm)/ donor-PC<sub>61</sub>BM (w/w at optimized ratio)/Pd (40 nm) by taking dark current-voltage in the range of 0–15 V and fitting the results to a space charge limited form.<sup>43</sup>

#### **Results and discussion**

#### 1 Synthesis

The detailed synthetic route to the series of **BTT-BTD-0**, **BTT-BTD-1**, **BTT-1**, **BTT-1**, **BTT-BTD-2** molecules is depicted in Scheme 1. As the key building block of the conjugated arms, asymmetric 4-bromo-7-[5-(2-hexyldecyl)-thiophen-2-yl]-benzo[2,1,3]thiadiazole (compound 2) was prepared from a Stille coupling reaction between



Scheme 1 Synthetic route to BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2.

4,7-dibromo-benzo[2,1,3]thiadiazole and [5-(2-hexyldecyl)-thiophen-2-yl]-tributyl-stannane as an orange liquid. Iterative Stille coupling reactions of compound **2** with stannylated thiophene and subsequent bromination with NBS were then executed to afford the other two building blocks of conjugated arms as compounds **4** and **6**, respectively. Compound **2**, **4** or **6** was then reacted with 2,5,8-tris(trimethylstannyl)benzo[1,2-*b*:3,4-*b*':5,6*b''*]trithiophene (compound 7) *via* the Stille coupling reaction condition to afford the target material of **BTT-BTD-0**, **BTT-BTD-1**, or **BTT-BTD-2**, respectively. These star-shaped materials showed good solubility in common organic solvents, such as chloroform, toluene and chlorinated benzene.

#### 2 Thermal stability

Thermal properties of the three molecules were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The decomposition temperatures ( $T_d$ , referring to 5% weight loss) were all above 400 °C (Fig. S1a in the ESI†), indicating good thermal stability of all three molecules. A good thermal stability would minimize any possible morphological deformation and degradation of the active layer in BHJ devices. DSC data also indicate that increasing the number of thiophene spacer leads the melting point dropping from 194 °C for **BTT-BTD-0** to 158 °C for **BTT-BTD-2** (ESI, Fig. S1b†), while no obvious phase transition was detected from the DSC curve of **BTT-BTD-1**. The higher melting point of **BTT-BTD-0** indicates stronger intermolecular interactions in the solid state.<sup>39</sup>

#### 3 Spectroscopic properties

Steady-state UV-Vis absorption spectroscopy was carried out to gain insight into the electronic structure of these star-shaped molecules. The normalized UV-Vis absorption spectra both in solution and thin film are plotted in Fig. 2. The absorption maxima of **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2** solution in dichloromethane are located at 497, 510 and 523 nm,



Fig. 2 Normalized UV-Vis absorption spectra of BTT-BTD-0 (gray solid), BTT-BTD-1 (black solid) and BTT-BTD-2 (gray dash) in (a) dichloromethane solution and (b) thin films.

respectively. For thin films cast from the chlorobenzene solution, BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2 exhibited absorption maxima at 528, 545 and 547 nm, red-shifted by 31, 35 and 24 nm, respectively, when compared with those of corresponding solutions. This absorption red-shift suggests the presence of weak intermolecular interactions from BTT-BTD-0 and BTT-BTD-1 to BTT-BTD-2 in films. It is worth noting that the absorption maxima of these molecules in solution exhibit a bathochromic shift  $(\Delta \lambda)$  of 13 nm for every added thiophene connecting unit, confirming the effect of spectral tuning by these inserted thiophene units between the BTT core and the BTD arms. This progressing red shift of  $\lambda_{max}$ can be attributed to a more extended  $\pi$ -conjugation as the number of thiophene connecting units increases. For absorption maxima in films, a bathochromic shift of 17 nm was also observed from BTT-BTD-0 to BTT-BTD-1. However, adding one more thiophene unit - converting BTT-BTD-1 to BTT-BTD-2 - only leads to negligible red-shift in the absorption maximum. It appears that the band gap of BTT-BTD based materials would reach its lower limit with just two of thiophene connecting units between the BTT core and the BTD arms, implying additional thiophenes would not be necessary if only for the purpose of narrowing the band gap.

The optical gaps ( $E_{g,opt}$ ) of **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2**, calculated from the absorption onset of thin films, are ~2.02, 1.90 and 1.85 eV, respectively (Table 1). In comparison with the film absorption of a related star-shaped molecule with only bithiophene in the three arms linked to the BTT core,<sup>44</sup> these three molecules show significant red-shift of absorption maxima by 108 nm, 125 nm and 127 nm from **BTT-BTD-0** to **BTT-BTD-2**, respectively. This clearly demonstrates the benefit of incorporating the electron deficient BTD unit into arms: BTD can lead to strong charge transfer characteristics, resulting in broad optical absorption spectra extending to 700 nm.

#### 4 Electrochemical characteristics

The electrochemical properties of the three molecules in thin films were investigated by cyclic voltammetry (CV) to determine their frontier orbital energy levels and the potentials were calibrated to Fc/Fc<sup>+</sup> (Fig. S2 in the ESI<sup>†</sup>). All three molecules showed irreversible anodic oxidation processes and no cathodic reduction processes were recorded. Therefore the first onset oxidation potential was used to calculate the energy level of the highest occupied molecular orbital (HOMO) (*i.e.*, HOMO =  $-(E_{\text{ox}} + 4.8)$  eV (ref. 43)), while the energy level of the lowest molecular orbital (LUMO) was estimated by adding the optical band gap ( $E_{\text{g,opt}}$ ) to the HOMO energy level. For example, the HOMO level of **BTT-BTD-0** was found to be -5.41 eV, and the LUMO level was estimated to be -3.39 eV after considering the band gap of **BTT-BTD-0** is 2.02 eV. All data are summarized in Table 1.

Table 1 clearly shows that both of the HOMO energy levels of BTT-BTD-1 and BTT-BTD-2 are almost identical, and higher than the HOMO level of BTT-BTD-0. This not only indicates that the extension of the conjugation length in arms through adding thiophene units makes BTT-BTD-1 and BTT-BTD-2 easier to oxidize, but also implies that just one thiophene unit is sufficient to raise the HOMO level for this series of materials. In contrast, the LUMO levels of all three molecules remain almost unaffected by increasing the conjugation length of arms through additional thiophene units from BTT-BTD-0 to BTT-BTD-2, i.e., the LUMO level is "pinned" around -3.4 eV. This observation, i.e., a "tunable" HOMO level and a LUMO level with negligible variation for structurally related organic materials, is consistent with other similarly constructed "donor-acceptor" polymers.43,45 This is because the LUMO level is typically localized on the "acceptor", which would determine the LUMO level of the entire molecule, whereas the HOMO level is more delocalized along the entire molecular system and significantly impacted by the electronic nature of the "donor".<sup>1,46</sup> Further

#### 5 Quantum chemical calculations

The frontier molecular orbitals of the three molecules were calculated by density functional theory (DFT) at the B3LYP/6-31G (d) level to gain better insights into their electronic structures (Fig. 3). The optimized geometry of arms tends to take a planarized structure, which promotes the  $\pi$ -electrons delocalization. As indicated in Fig. 3, while the electron density of the HOMO of BTT-BTD-0 is delocalized on the whole molecule, such a delocalization across the entire molecule is much less for BTT-BTD-1 and BTT-BTD-2. On the other hand, the electron density of the LUMO of BTT-BTD-0 is mainly localized on the BTD moieties, whereas it is slightly more delocalized on the entire molecules for BTT-BTD-1 and BTT-BTD-2. These results help to explain the negligible change of the LUMO levels for all three molecules and a slight rise (0.15 eV) of the HOMO levels of BTT-BTD-1 and BTT-BTD-2 in comparison with that of BTT-BTD-0 (Table 1).

#### 6 Solar cell characteristics

To probe the photovoltaic properties of this series of star-shaped molecules, we first prepared the solution for the BHJ device fabrication by blending **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2** as the electron donor with PC<sub>61</sub>BM as the electron acceptor in 1,2-dicholorobenzene (*o*-DCB). Then we spun-coated a thin film from such a blended solution in a typical device configuration of ITO/PEDOT:PSS (45 nm)/**BTT-BTD-x** (x = 0, 1, 2):PC<sub>61</sub>BM/Ca



Fig. 3 The frontier molecular orbitals of BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2 based on optimized geometries (calculated with DFT at the B3LYP/6-31G level).

Table 1	Optical and electrochemical	property of BTT-BTD-0	BTT-BTD-1 and BTT-BTD-2
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Compound	$\lambda_{ m max, solution} \ ({ m nm})$	λ <sub>max,film</sub> (nm)	$\lambda_{ m onset, film}$ (nm)	$E_{ m g,opt}$ (eV)	$E_{\rm ox,onset}$ (V)	HOMO (eV)	LUMO (eV)
BTT-BTD-0	497	528	614	2.02	0.61	-5.41	-3.39
BTT-BTD-1	510	545	657	1.90	0.46	-5.26	-3.36
BTT-BTD-2	523	547	670	1.85	0.46	-5.26	-3.43

(20 nm)/Al (80 nm). Different weight ratios of BTT-BTD*x*:PC<sub>61</sub>BM were attempted, but the concentrations of BTT-BTD-*x* in all solutions were fixed at 10 mg mL $^{-1}$  in *o*-DCB. We found that PV performance of BTT-BTD-0 based devices did not vary much in regard to the weight ratios of BTT-BTD-0:PC<sub>61</sub>BM, with the observed  $V_{\rm oc}$  around 0.55  $\pm$  0.05 V. Such a ratio-insensitivity was also observed for the PV performance of BTT-BTD-1 based devices, with  $V_{\rm oc}$  around 0.60  $\pm$  0.05 V. However, in the case of BTT-BTD-2, the ones fabricated from the 1:1 weight ratio in the blend showed the best PV properties with V<sub>oc</sub> approaching 0.7 V (all these data are tabulated in the ESI, Table S1<sup>†</sup>). Therefore, we decided to use the weight ratio of 1 : 1 of BTT-BTD-x:PC<sub>61</sub>BM to compare the PV performance for all three molecules. Representative current density-voltage (J-V) characteristics of the three molecules blended with PC<sub>61</sub>BM at a weight ratio of 1:1 are shown in Fig. 6a, and the related data are tabulated in Table 2.

Typically, the V<sub>oc</sub> of BHJ devices roughly linearly depends on the interface energy difference between the HOMO level of the electron donor and the LUMO of the electron acceptor.15,47 Therefore, if PC<sub>61</sub>BM is used as the common electron acceptor for all the devices (e.g., in our study), the  $V_{oc}$  would increase as the HOMO levels decrease. With the energy level alignment presented in Fig. 4, one would project the highest  $V_{oc}$  should appear for BTT-BTD-0 based devices. Interestingly, despite the lower-lying HOMO of BTT-BTD-0 at -5.41 eV and similarly higher HOMO level at -5.26 eV for BTT-BTD-1 and BTT-BTD-2, devices based on BTT-BTD-2 deliver a higher Voc of around 0.70  $\pm$  0.05 V while BTT-BTD-0 and BTT-BTD-1 provide lower values around 0.55  $\pm$  0.05 V and 0.60  $\pm$  0.05 V, respectively. This is because the energetics is just one factor (though dominating) that decides the Voc. Others, including charge recombination at the donor-acceptor interface, resistance related to the thickness of the active layer, degree of phase-separation between the components and intermolecular interactions of active materials in the blend, have also been demonstrated to significantly modify the energetically predicted  $V_{\rm oc}$  value.<sup>48-50</sup> For example, donor materials that show evidence for strong aggregation by their thin-film absorption spectra and polycrystallinity by their thin film X-ray diffraction result in a lower  $V_{\rm oc}$  than the simple estimated value (*i.e.*,  $V_{oc} \sim E_{LUMO(acceptor)} - E_{HOMO(donor)}$ ).<sup>49</sup> It was believed that such a strong aggregation/polycrystallinity indicates strong intermolecular interactions between active components, leading to the observed high saturation dark current density and thereby reducing the  $V_{\rm oc}$  according to the Shockley equation. Similarly, an increased electronic coupling between the donor polymers and the fullerene acceptors would



Fig. 4 Determined energy diagram with HOMO/LUMO levels of BTT-BTD-0, BTT-BTD-1, BTT-BTD-2 and PCBM in relation to the work functions of the electrode materials ITO/PEDOT:PSS and Ca in a BHJ OSC device.

increase the dark saturation current and result in a lower  $V_{\rm oc}.^{48,50}$ 

Based on the current understanding of the origin of the  $V_{\rm oc}$ in organic solar cells, we next attempt to offer an explanation of the seemingly unusual trend of  $V_{\rm oc}$  for the studied series of molecules. The high structural symmetry and planarity of these star-shaped conjugated molecules may promote the  $\pi$ - $\pi$ stacking of conjugated arms due to a broad  $\pi$ -delocalization of armed molecules. On the other hand, the increased steric hindrance associated with these armed molecules may also prevent the formation of an ordered, long-range and coplanar  $\pi$ - $\pi$  stacking. All these would have a significant impact on the intermolecular interaction between the donor molecule and the fullerene at the donor-acceptor (D-A) interface, thereby affecting the  $V_{\rm oc}$ . However, the intermolecular interaction between the donor molecule and PCBM at the D-A interface is very difficult to probe directly in a BHJ blend. Fortunately, the easily accessible intermolecular interaction among the donor molecules can be investigated instead, on the assumption that greater intermolecular interactions between donor molecules would give rise to stronger interactions between the donor molecules and PCBM at the D-A interface. To this end, X-ray diffraction (XRD) characterizations of donor molecules and the BHJ blend can provide insights into qualitative understanding and comparison of these intermolecular interactions. Similar approaches have been employed in previous reports.48

We thus conducted powder XRD experiments on these three molecules without being blended with  $PC_{61}BM$ , and grazing incident X-ray diffraction (GIXRD) measurements of both BHJ films of these three molecules to gain insight into the solid state structures of the three molecules. The data from powder XRD indicate that there are indeed different intermolecular

Table 2 Average photovoltaic parameters of BTT-BTE-0, BTT-BTD-1 and BTT-BTD-2 blended with PC<sub>61</sub>BM at the optimized weight ratios (1 : 1) and BTT-BTD-2 with PC71BM at the weight ratio of 1 : 2

Active lover	Patio	Thickness (nm)	V (V)	$I (m \Lambda cm^{-2})$	FF	<b>DCE</b> (%)	$u (cm^2 V^{-1} c^{-1})$
Active layer	Katio	fillekiless (iiiii)	$V_{\rm oc}(\mathbf{V})$	$J_{\rm sc}$ (mA cm )	ΓΓ	FCE (70)	$\mu_{\rm h}$ (cm v s )
BTT-BTD-0:PC <sub>61</sub> BM	1:1	90	0.54	0.95	0.31	0.16	$2.2 imes 10^{-6}$
BTT-BTD-1:PC61BM	1:1	65	0.55	1.59	0.31	0.27	$2.2 imes 10^{-6}$
BTT-BTD-2:PC <sub>61</sub> BM	1:1	75	0.69	2.93	0.37	0.74	$3.0 imes10^{-6}$
BTT-BTD-2:PC71BM	1:2	55	0.72	4.13	0.46	1.36	_

interactions for these three molecules (Fig. 5a). BTT-BTD-0, **BTT-BTD-1** and **BTT-BTD-2** show a diffraction peak at  $2\theta$  about 25.7°, 25.4° and 24.7°, corresponding to a distance of 3.45 Å, 3.50 Å and 3.60 Å from the Bragg equation, respectively. The reflections are a typical  $\pi$ -stacking spacing of conjugated backbones. BTT-BTD-0 shows the strongest intermolecular interaction through  $\pi$ - $\pi$  stacking and the shortest  $\pi$ -stacking distance, as indicated in Fig. 5a, whereas BTT-BTD-2 shows the weakest  $\pi$ - $\pi$  stacking interactions (e.g., lowest intensity of the diffraction peak and longest  $\pi$ -stacking distance). It appears that inserting more connecting thiophene units between the BTT core and the BTD arms leads to a decrease of structural rigidity and less planarity of the entire molecule, which would explain the reduced  $\pi$ - $\pi$  intermolecular interaction from BTT-**BTD-0** to **BTT-BTD-2** in the solid state (please note that the  $\pi$ - $\pi$ intermolecular distance is commonly assigned to the (010) distance as shown in Fig. S3<sup>†</sup>). The reduced  $\pi$ - $\pi$  stacking interactions among donors from BTT-BTD-0 to BTT-BTD-1 imply a weaker interaction between donor molecules and PC<sub>61</sub>BM (acceptor) in the BHJ blend, which can (at least partly) account for the observed lower  $V_{oc}$  in **BTT-BTD-0** based devices.

GIXRD data offer further insights into the structural order (e.g., crystallinity) of these three molecules in their BHJ blends with PC<sub>61</sub>BM. Specifically, GIXRD spectra of these BHJ films indicate that BTT-BTD-0:PC61BM and BTT-BTD-1:PC61BM exhibit a reflection peak at  $2\theta$  around  $3.33^{\circ}$  and  $3.07^{\circ}$ , respectively (Fig. 5b), indicative of a spacing value of 26.40 Å and 28.72 Å. Such a difference of ~2.3 Å between BTT-BTD-0 and BTT-BTD-1 BHJ films is close to the size of a unit thiophene, which is around 2.7 Å calculated with the MM2 force field method. It is thus very likely that these spacing values correspond to the distance between conjugated backbones, which is determined by the length of conjugated arms and the terminal long alkyl chains in this set of molecules (e.g., (100) or (001) distance as proposed in Fig. S3<sup>†</sup>). It is worth noting that the intensity of the reflection peak of the BTT-BTD-0:PC61BM film is much stronger than that of BTT-BTD-1:PC61BM (Fig. 5b), indicating more polycrystalline domains in the BTT-BTD-0:PC61BM BHJ film than the BTT-BTD-1 based BHJ film. Furthermore, no reflection peaks were observed for the BHJ film of BTT-BTD-2:PC<sub>61</sub>BM, indicating little evidence of aggregation of BTT-BTD-2 in its BHJ film. The largest amount of polycrystalline domains in the BTT-BTD-0 based BHJ blend (among all blends) likely leads to strongest donor-PC61BM interactions, which is consistent with

the observation from powder XRD (*vide supra*). Again, the presumably stronger donor-acceptor interaction in the **BTT-BTD-0** based BHJ films would contribute to a larger saturation dark current density and thereby a lower  $V_{oc}$  value, based on the same reasoning as presented by Forrest and Thompson *et al.* in their study.<sup>49</sup>

 $J_{\rm sc}$ , on the other hand, is closely related to the morphology of the donor:acceptor blend.<sup>51</sup> A nanoscale phase separation in the active layer of BHJ devices has been proven to be essential to enable a large interface area for exciton dissociation and to provide a continuous percolating path for charge transport, both are crucial for achieving a high  $J_{sc}$ . In this work, tappingmode atomic force microscopy (AFM) studies were carried out to investigate the influence of film morphology of different active layers on their PV performances. These AFM topography images are shown in Fig. S4 of the ESI.† A very rough surface with broad and deep grooves (and even some pinholes with the depth of 10-20 nm) was observed for the blended film of BTT-BDT-0:PC<sub>61</sub>BM according to the AFM topography image. Showing a slightly better surface morphology, BTT-BDT-1:PC<sub>61</sub>BM blended film still has significant surface roughness. Furthermore, phase images of both BTT-BDT-0:PC61BM and BTT-BDT-1:PC<sub>61</sub>BM blended films do not indicate any desirable phase separation. On the other hand, the average roughness of the blend films of **BTT-BTD-2** with  $PC_{61}BM$  is  $\sim 5$  nm. We also observed clusters for the blend film based on BTT-BTD-2:PC<sub>61</sub>BM. Given the similar hole mobilities for these molecules in their BHJ blends (Table 2), the much improved morphology for the BTT-BTD-2:PC<sub>61</sub>BM based blend, in contrast to those of the other two molecules based BHJ blends, indicates a better solid state structure for exciton dissociation, resulting in noticeably higher  $J_{sc}$  for BTT-BTD-2:PC<sub>61</sub>BM based BHJ cells than those of the other two molecules based counterparts.

With the highest  $V_{oc}$  and  $J_{sc}$  (and FF), the **BTT-BTD-2** based BHJ device offers the highest observed efficiency of 0.74% in all studied three molecules when blended with PC<sub>61</sub>BM. We then chose to blend **BTT-BTD-2** with the electron acceptor PC<sub>71</sub>BM to further optimize its PV performance, since PC<sub>71</sub>BM has a broader absorption and a larger extinction coefficient than those of PC<sub>61</sub>BM. All results from different attempts (*e.g.*, varying the ratio of donor:acceptor) are listed in the ESI (Table S2),† and the typical *J–V* curves of champion devices are presented in Fig. 6b. AFM study on the film of



**Fig. 5** Powder XRD patterns of **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2** (a). GIXRD patterns of the BHJ films of **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2** with PC<sub>61</sub>BM (b).



**Fig. 6** Current–voltage (*J–V*) characteristics of BHJ solar cells. (a) Devices based on molecular donor:  $PC_{61}BM$  blended films at an optimized weight ratio (1 : 1) and (b) devices based on various weight ratios of **BTT-BTD-2**:PC<sub>71</sub>BM under illumination of 1 sun at AM1.5G (100 mW cm<sup>-2</sup>).



Fig. 7 (a) EQE of preliminarily optimized devices of BTT-BTD-0, BTT-BTD-1 and BTT-BTD-2 and (b) the active layer absorption spectra of devices in (a).

**BTT-BTD-2**:PC<sub>71</sub>BM indicates further intimate mixing and a smoother surface with an average roughness around 1 nm (ESI, Fig. S4†). It appears that **BTT-BTD-2** is more homogeneously distributed in the blend with PC<sub>71</sub>BM in comparison to the **BTT-BTD-2**:PC<sub>61</sub>BM blend. These morphological differences might account for the better photovoltaic performance of **BTT-BTD-2**:PC<sub>71</sub>BM than that of the **BTT-BTD-2**:PC<sub>61</sub>BM blend. For example, the PV performance was much enhanced for devices based on **BTT-BTD-2**:PC<sub>71</sub>BM at an optimized donor:acceptor weight ratio of 1 : 2, which showed relatively larger values of  $V_{oc}$  (0.72 V),  $J_{sc}$  (4.13 mA cm<sup>-2</sup>) and FF (46%), leading to an increased average PCE of 1.36%.

Fig. 7a presents the external quantum efficiency (EQE) as a function of wavelength for all the optimized BHJ devices, while the absorption features of the active layers are shown in Fig. 7b. The EQE curves of all devices match the optical absorption of active layers well. The calculated  $J_{sc}$  values obtained by integrating the EQE spectra with the standard AM 1.5G solar spectrum match those (within  $\sim 5\%$  error) obtained from the *I*-V measurement, indicating these measurements are quite accurate. When increasing the number of connecting thiophene units between the BTT core and these BTD arms, progressively increased EQE values were observed. Devices of the BTT-BTD-2:PC<sub>61</sub>BM blend show more efficient photo conversion efficiency in the range between 300 and 550 nm with EQE value around 16%, which was improved to 25% when using PC<sub>71</sub>BM as the electron acceptor. It is worth noting that there exists a broad plateau around the maximum in EQE curves between 400 and 550 nm for devices based on BTT-BTD-2 due to stronger and wider absorption of BTT-BTD-2 and PC71BM in that wavelength region. Stronger and broader absorption together with better film morphology of blended films explain the better PV performance of BTT-BTD-2 based BHJ devices over the other two molecules based ones.

#### Conclusion

In summary, we have investigated the synthesis and photovoltaic application of three structurally closely related molecules, **BTT-BTD-0**, **BTT-BTD-1** and **BTT-BTD-2**, with 0, 1, 2 indicating the number of thiophene connecting units in between the BTT core and the BTD arms. Increasing the number of thiophene connecting units elevates the HOMO energy level of the BTT-BTD based molecule, while the LUMO level remains almost unchanged because of the common "acceptor", BTD. As expected, incorporating the electron deficient BTD units into arms leads to intramolecular charge transfer characteristics, resulting in broad optical absorption spectra extending to 700 nm. Nevertheless, it appears that band gaps and HOMO levels of this system will not be significantly affected by incorporating more than two of these thiophene connecting units between the BTT core and the BTD arms. However, the more thiophene connecting units there are, the better the performance of related solar cells. With just PC61BM, BTT-BTD-2 based BHJ devices already show the highest  $V_{oc}$ ,  $J_{sc}$  and FF among all devices based on these molecules. Furthermore, with PC71BM as the electron acceptor, the PV performance of BTT-BTD-2 based devices can be further improved to 1.36%, with  $J_{sc}$  of 4.13 mA  $cm^{-2}$ ,  $V_{oc}$  at 0.72 V and FF of 0.46. This discovered structureproperty relationship provides important insights into the future design of conjugated molecules for photovoltaic applications.

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#### Notes and references

- 1 H. Zhou, L. Yang and W. You, Macromolecules, 2012, 45, 607.
- 2 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649.
- 3 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, 3, 297.
- 4 Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135.
- 5 C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So and J. R. Reynolds, *J. Am. Chem. Soc.*, 2011, **133**, 10062.
- 6 T.-Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.-R. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding and Y. Tao, *J. Am. Chem. Soc.*, 2011, 133, 4250.
- 7 Z. He, C. Zhong, X. Huang, W.-Y. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv. Mater.*, 2011, 23, 4636.
- 8 L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angew. Chem., Int. Ed.*, 2011, **50**, 9697.
- 9 S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625.
- 10 M.-S. Su, C.-Y. Kuo, M.-C. Yuan, U. S. Jeng, C.-J. Su and K.-H. Wei, *Adv. Mater.*, 2011, 23, 3315.
- 11 Y. Sun, C. J. Takacs, S. R. Cowan, J. H. Seo, X. Gong, A. Roy and A. J. Heeger, *Adv. Mater.*, 2011, 23, 2226.
- 12 H. Zhou, L. Yang, S. C. Price, K. J. Knight and W. You, *Angew. Chem., Int. Ed.*, 2010, **49**, 7992.

- 13 C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S.-W. Tsang, T.-H. Lai, J. R. Reynolds and F. So, *Nat. Photonics*, 2012, 6, 115.
- 14 J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li and Y. Yang, *Nat. Commun.*, 2013, 4, 1446.
- 15 B. C. Thompson and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58.
- 16 W. L. Leong, G. C. Welch, L. G. Kaake, C. J. Takacs, Y. Sun,
   G. C. Bazan and A. J. Heeger, *Chem. Sci.*, 2012, 3, 2103.
- 17 Z. B. Henson, K. Mullen and G. C. Bazan, *Nat. Chem.*, 2012, 4, 699.
- 18 J. Roncali, Acc. Chem. Res., 2009, 42, 1719.
- 19 Y. Li, Q. Guo, Z. Li, J. Pei and W. Tian, *Energy Environ. Sci.*, 2010, 3, 1427.
- 20 B. Walker, C. Kim and T.-Q. Nguyen, *Chem. Mater.*, 2011, 23, 470.
- 21 Y. Lin, Y. Li and X. Zhan, Chem. Soc. Rev., 2012, 41, 4245.
- 22 A. Mishra and P. Bäuerle, Angew. Chem., Int. Ed., 2012, 51, 2020.
- 23 Y. M. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2012, **11**, 44.
- 24 C. J. Takacs, Y. Sun, G. C. Welch, L. A. Perez, X. Liu, W. Wen, G. C. Bazan and A. J. Heeger, *J. Am. Chem. Soc.*, 2012, 134, 16597.
- 25 H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, Angew. Chem., Int. Ed., 2011, **50**, 2995.
- 26 W. Zhang, G. M. Ng, H. L. Tam, M. S. Wong and F. Zhu, J. Polym. Sci., Part A: Polym. Chem., 2011, 49, 1865.
- 27 H. X. Shang, H. J. Fan, Y. Liu, W. P. Hu, Y. F. Li and X. W. Zhan, Adv. Mater., 2011, 23, 1554.
- 28 F. Lincker, N. Delbosc, S. Bailly, R. De Bettignies, M. Billon, A. Pron and R. Demadrille, *Adv. Funct. Mater.*, 2008, 18, 3444.
- 29 U. Mayerhöffer, K. Deing, K. Gruß, H. Braunschweig,
  K. Meerholz and F. Würthner, *Angew. Chem., Int. Ed.*, 2009,
  48, 8776.
- 30 B. Walker, A. B. Tamayo, X.-D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat and T.-Q. Nguyen, *Adv. Funct. Mater.*, 2009, **19**, 3063.
- 31 Y. Liu, X. Wan, B. Yin, J. Zhou, G. Long, S. Yin and Y. Chen, J. Mater. Chem., 2010, 20, 2464.
- 32 H. M. Ko, H. Choi, S. Paek, K. Kim, K. Song, J. K. Lee and J. Ko, *J. Mater. Chem.*, 2011, **21**, 7248.

- 33 Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian and Y. Chen, *Adv. Mater.*, 2011, **23**, 5387.
- 34 S. Loser, C. J. Bruns, H. Miyauchi, R. o. P. Ortiz, A. Facchetti, S. I. Stupp and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 8142.
- 35 G. C. Welch, L. A. Perez, C. V. Hoven, Y. Zhang, X.-D. Dang, A. Sharenko, M. F. Toney, E. J. Kramer, T.-Q. Nguyen and G. C. Bazan, *J. Mater. Chem.*, 2011, 21, 12700.
- 36 D. Bagnis, L. Beverina, H. Huang, F. Silvestri, Y. Yao, H. Yan, G. A. Pagani, T. J. Marks and A. Facchetti, *J. Am. Chem. Soc.*, 2010, **132**, 4074.
- 37 T. Rousseau, A. Cravino, T. Bura, G. Ulrich, R. Ziessel and J. Roncali, *Chem. Commun.*, 2009, 1673.
- 38 Y.-H. Chen, L.-Y. Lin, C.-W. Lu, F. Lin, Z.-Y. Huang, H.-W. Lin, P.-H. Wang, Y.-H. Liu, K.-T. Wong, J. Wen, D. J. Miller and S. B. Darling, *J. Am. Chem. Soc.*, 2012, **134**, 13616.
- 39 R. Fitzner, E. Mena-Osteritz, A. Mishra, G. Schulz,
  E. Reinold, M. Weil, C. Körner, H. Ziehlke, C. Elschner,
  K. Leo, M. Riede, M. Pfeiffer, C. Uhrich and P. Bäuerle,
  J. Am. Chem. Soc., 2012, 134, 11064.
- 40 J. Zhou, X. Wan, Y. Liu, Y. Zuo, Z. Li, G. He, G. Long, W. Ni, C. Li, X. Su and Y. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 16345.
- 41 A. L. Kanibolotsky, I. F. Perepichka and P. J. Skabara, *Chem. Soc. Rev.*, 2010, **39**, 2695.
- 42 Y. Nicolas, P. Blanchard, E. Levillain, M. Allain, N. Mercier and J. Roncali, *Org. Lett.*, 2004, **6**, 273.
- 43 S. Xiao, H. Zhou and W. You, Macromolecules, 2008, 41, 5688.
- 44 R. de Bettignies, Y. Nicolas, P. Blanchard, E. Levillain, J. M. Nunzi and J. Roncali, *Adv. Mater.*, 2003, 15, 1939.
- 45 H. Zhou, L. Yang, S. Stoneking and W. You, ACS Appl. Mater. Interfaces, 2010, 2, 1377.
- 46 J.-L. Brédas, J. E. Norton, J. Cornil and V. Coropceanu, *Acc. Chem. Res.*, 2009, **42**, 1691.
- 47 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk,C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, 18, 789.
- 48 L. Yang, H. Zhou and W. You, J. Phys. Chem. C, 2010, 114, 16793.
- 49 M. D. Perez, C. Borek, S. R. Forrest and M. E. Thompson, J. Am. Chem. Soc., 2009, 131, 9281.
- 50 K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganas and J. V. Manca, *Nat. Mater.*, 2009, **8**, 904.
- 51 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, 4, 864.