

# High-Performance Solar Cells using a Solution-Processed Small Molecule Containing Benzodithiophene Unit

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Bulk heterojunction (BHJ) organic solar cells (OSCs) based on intimate blends of electron donor and electron acceptor materials have become one of the most promising low-cost solar energy technologies.<sup>[1–3]</sup> In the past few years, tremendous progress has been made using the BHJ architecture, and the power conversion efficiencies (PCEs) have reached to 7 to 8% via designing novel low bandgap polymer donors,<sup>[4–8]</sup> which have wide absorption spectra, matched energy level positions, and good miscibility with the fullerene derivative acceptor. Recently, solution-processed small molecule OSCs have also advanced significantly with efficiencies in the 2–5% range.<sup>[9–15]</sup> Although solution-processed small molecule OSCs have not met the high expectations of their polymeric counterparts, they possess numerous advantages including relatively simple synthesis and purification, monodispersity and well-defined structures, no end group contaminants, high charge carrier mobility, and better batch-to-batch reproducibility. To date, the highest published PCE (5.08%) for solution-processed small molecule based BHJ OSCs has been achieved by our group using a oligothiophene derivative DCAO7T (Scheme 1).<sup>[10]</sup>

In most cases, small molecule devices using solution process seem always have low fill factor ( $FF < 50\%$ ) due to the poorer film quality and unbalanced charge transport compared to their polymeric counterparts in BHJ solar cells,<sup>[16]</sup> and this has become a bottleneck of solution-processed small molecule based device. It is thus expected that better power conversion efficiency could be achieved by designing new small molecules with balanced consideration for band structure and morphology. The benzo[1,2-b:4,5-b']dithiophene (BDT) unit has been emerging recently as an attractive donor building block for conjugated polymers used in high performance OSCs due to its large and rigid planar conjugated structure, which can enhance the electron delocalization and promote cofacial  $\pi$ - $\pi$  stacking in the solid state, thus benefiting charge transport in

the devices.<sup>[5–8,17–21]</sup> To date, conjugated polymers containing a BDT unit with optimized electronic and optical properties have led to PCEs higher than 7%.<sup>[5–8]</sup> Such small molecules using BDT as the building block for OSCs, to the best of our knowledge, have not been reported.

Based on the notable  $FF$  and high efficiency of our recent work on DCAO7T, we think replacing the central thiophene unit with a more electron-rich and better planar structure such as BDT may maintain the high  $FF$  and enhance the overall OPV performance of this class of small molecules due to the increased overall planarity, mobility, and solar absorption. The results should also help us understand better the relationship between the OPV performance and recent proposal using donor–acceptor structure. In this work, we designed and synthesized a new small molecule, DCAO3T(BDT)3T (Scheme 1), with BDT as the central unit and electron-withdrawing alkyl cyanoacetate groups as the end-capped group. Using the simple solution spin-coating fabrication process, the highest PCE of 5.44% was obtained by using a blend of DCAO3T(BDT)3T and PC<sub>61</sub>BM ([6,6]-phenyl-C61-butyric acid methyl ester) at a weight ratio of 1:0.5 as the active layer, combined with a high open circuit voltage ( $V_{oc}$ ) of 0.93 V, a short circuit current density ( $J_{sc}$ ) of 9.77 mA cm<sup>-2</sup>, and a notable  $FF$  of 59.9%. This high efficiency, coupled with the high  $V_{oc}$  and notable  $FF$  demonstrate that linear donor–acceptor systems containing BDT units could become a strategic choice for solution-processed small molecule based highly efficient OSCs.

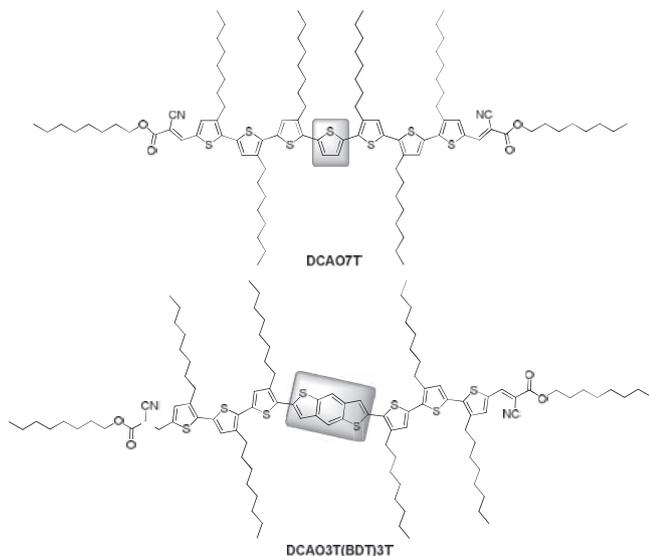
The synthesis of DCAO3T(BDT)3T is outlined in Scheme 2. Compound 5''-bromo-3,4',4''-trioctyl-2,2':5',2''-trithiophene-5-carbaldehyde (**6**) was synthesized through a five-step reaction from 2-bromo-3-octylthiophene using Vilsmeier–Haack, Stille coupling, and bromination reactions. BDT containing dicarbaldehyde compound **8** was synthesized from Stille coupling between **6** with 5,5'-bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene **7** in refluxing toluene under Ar in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst for 48 h. The targeted molecule, DCAO3T(BDT)3T, was obtained using a Knoevenagel condensation. This molecule has good solubility in common organic solvents, such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, tetrahydrofuran (THF), and toluene, and shows a rather good stability up to 364 °C with a melting point at 181 °C (Figure S1, Supporting Information.).

As shown in Figure 1a, DCAO3T(BDT)3T has an absorption maxima at 478 nm in CHCl<sub>3</sub> with an absorption coefficient of  $3.1 \times 10^4$  m<sup>-1</sup> cm<sup>-1</sup>, which is similar to that of DCAO7T. Its film absorption spectrum shows an obvious broadening and bathochromic shift (85 nm) compared to its solution spectrum. The absorption maxima was observed at 563 nm with a sub-shoulder peak structure at longer wavelength, suggesting a

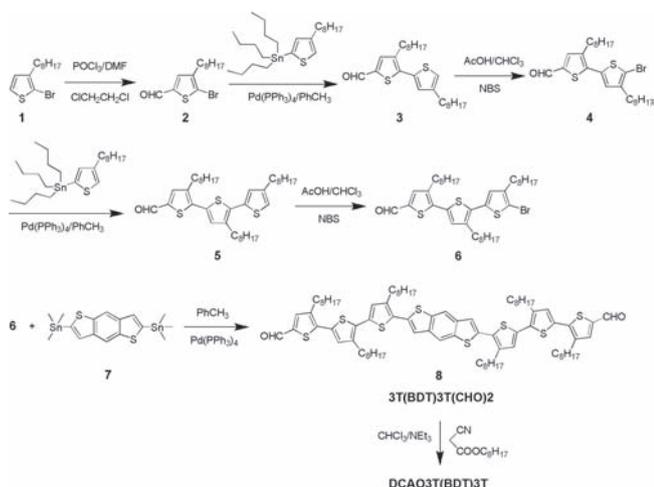
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DOI: 10.1002/adma.201102790



Scheme 1. Structures of DCAO7T and DCAO3T(BDT)3T.



Scheme 2. Synthesis route to DCAO3T(BDT)3T.

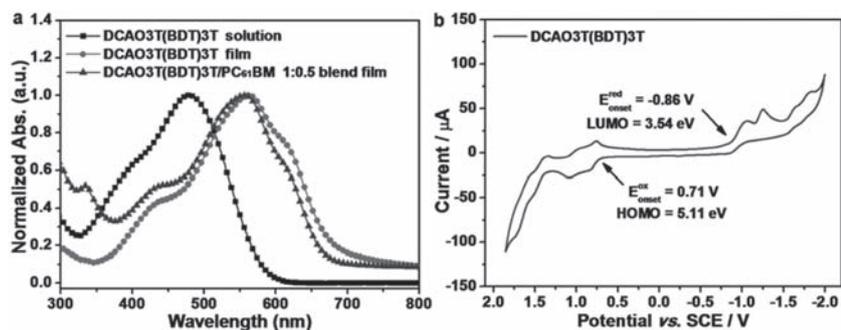


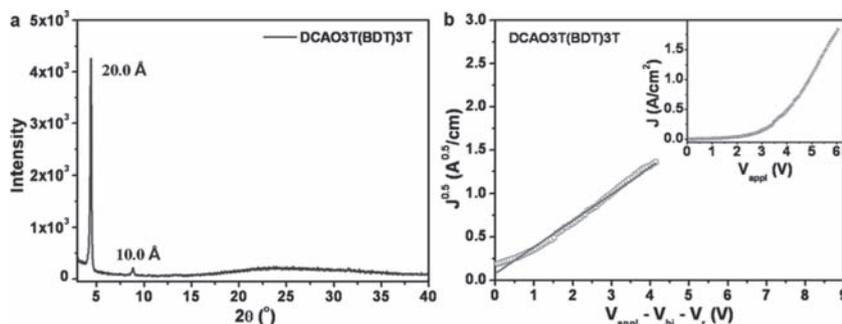
Figure 1. a) UV absorption spectra of DCAO3T(BDT)3T in a CHCl<sub>3</sub> solution, as a film and DCAO3T(BDT)3T/PC<sub>61</sub>BM (1:0.5, w:w) blend film on a quartz substrate. b) Cyclic voltammogram of DCAO3T(BDT)3T in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte and a scan speed of 50 mV s<sup>-1</sup>.

vibronic progression due to a rigid coplanarization of the conjugated systems enforced by the molecular packing.<sup>[22,23]</sup> The optical bandgap of DCAO3T(BDT)3T film was estimated from the onset of the absorption spectra to be 1.83 eV, which is a slightly higher than that (1.74 eV) of a DCAO7T film. Compared with the pristine donor films, the absorption maxima of DCAO3T(BDT)3T/PC<sub>61</sub>BM (1:0.5, w:w) blend film is observed at 556 nm and blue-shifted to shorter wavelengths. The blue shift, which is also observed in DCAO7T based blend films, can be attributed to the good miscibility of PC<sub>61</sub>BM molecules with our donor materials.<sup>[24]</sup> Cyclic voltammograms (Figure 1b) show two reversible oxidation waves and two irreversible reduction waves. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which are -5.11 and -3.54 eV for DCAO3T(BDT)3T, were calculated from the onset oxidation potential and the onset reduction potential.<sup>[25,26]</sup>

To investigate the structural ordering of DCAO3T(BDT)3T at solid state, we performed X-ray diffraction (XRD) analysis for its thin-film spin-coated from CHCl<sub>3</sub> solution onto glass substrate. As shown in Figure 2a, the  $\pi$ -conjugated molecules exhibited strong (100) reflection peak at  $2\theta = 4.4^\circ$ , corresponding to a  $d_{100}$ -spacing values of 20.0 Å. The  $d_{100}$ -spacing value is the distance between the planes of the main conjugation chains of DCAO3T(BDT)3T separated by alkyl side chains, which is almost the same as that observed for P3OT (poly(3-octylthiophene)) (20.1 Å).<sup>[27]</sup> The second-order diffraction peak (200) at  $2\theta = 8.8^\circ$ , corresponding to a  $d_{200}$ -spacing values of 10.0 Å, was also clearly observed, implying a highly organized assembly of this  $\pi$ -conjugated molecules in the solid state.

The hole mobility of the pristine DCAO3T(BDT)3T was measured using the space charge limited current (SCLC) method,<sup>[17,18]</sup> as plotted in Figure 2b. The calculated mobility value of this material is  $4.50 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is higher than that of the recent reported donor material DCAO7T ( $3.26 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). This high mobility is probably due to its strong intermolecular orbital overlap after introducing the large and rigid planar conjugated BDT unit, and thus it forms good packing and/or crystalline structures as observed in the XRD data. The hole mobility of this material is comparable to that of the very promising BDT containing donor polymers PTB4 ( $7.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )<sup>[18]</sup> and PBDTTT-C ( $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )<sup>[17]</sup> measured using the same SCLC method.

BHJ solar cells were fabricated using DCAO3T(BDT)3T as the electron donor material and PC<sub>61</sub>BM as the electron acceptor material with a general device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/donor:PC<sub>61</sub>BM/LiF/Al using the conventional solution spin-coating process. The optimized results are summarized in Table 1. It is important to note that the performances of this molecule with different ratios of the electron acceptor PC<sub>61</sub>BM are all among the best of small molecules reported so far, with the best result comes from the donor:acceptor weight ratio of 1:0.5 from chloroform solution. The current density versus voltage ( $J$ - $V$ ) curves of



**Figure 2.** a) XRD patterns of DCAO3T(BDT)3T films spin-coated from  $\text{CHCl}_3$ . b)  $J^{0.5}$ - $V$  plots for the DCAO3T(BDT)3T based device. The solid lines are fits of the data points. The inset depicts the  $J$ - $V_{\text{app}}$  plot of the devices from these materials before correction for the applied voltage.

**Table 1.** Effect of donor/acceptor blend ratios on the organic photovoltaic (OPV) performance of DCAO3T(BDT)3T/PC<sub>61</sub>BM devices.

Blend ratio	$J_{\text{sc}}$ [mA cm <sup>-2</sup> ]	$V_{\text{oc}}$ [V]	$FF$ [%]	PCE [%]
1:0.3	5.90	0.94	59.3	3.29
1:0.5	9.77	0.93	59.9	5.44
1:0.8	8.25	0.92	64.2	4.87

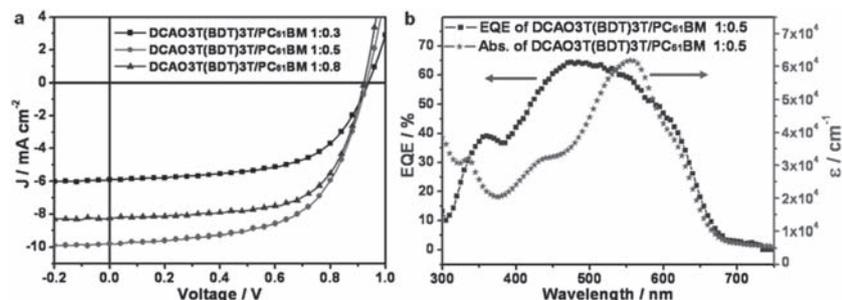
DCAO3T(BDT)3T/PC<sub>61</sub>BM with different weight blend ratio are shown in **Figure 3a**. The devices for a 1:0.3 blend ratio exhibits a  $J_{\text{sc}}$  of 5.90 mA cm<sup>-2</sup>, a  $V_{\text{oc}}$  of 0.94 V, and a  $FF$  of 59.3%, which yields a PCE of 3.29%. With increasing the donor:acceptor blend ratios from 1:0.3 to 1:0.8, the  $J_{\text{sc}}$  first increased and then decreased, but the  $FF$  increased to 64.2%. The optimized device based on DCAO3T(BDT)3T/PC<sub>61</sub>BM with blend ratio of 1:0.5 (molar blend ratio ca. 1:1) give the highest PCE of 5.44%, with a  $J_{\text{sc}}$  of 9.77 mA cm<sup>-2</sup>, a  $V_{\text{oc}}$  of 0.93 V, and a  $FF$  of 59.9%. Further increase the content of PC<sub>61</sub>BM, the  $J_{\text{sc}}$  decreased to 8.25 mA cm<sup>-2</sup> for device with a 1:0.5 to 1:0.8 blend ratios. Combined with a  $V_{\text{oc}}$  of 0.92 V and a PCE of 4.87%, the device using the 1:0.8 ratio yields a very notable  $FF$  of 64.2%, which is the highest  $FF$  of solution-processed small molecule based BHJ devices.<sup>[16]</sup> The lower  $J_{\text{sc}}$  of the DCAO3T(BDT)3T-based device compared with DCAO7T-based device (10.74 mA cm<sup>-2</sup>) is probably due to the narrow absorption band and higher optical bandgap (1.83 vs. 1.74 eV). We suspect that more comparable size and matched

mobility of DCAO3T(BDT)3T (molar mass of 1771 g mol<sup>-1</sup>,  $4.50 \times 10^{-4}$  cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup>) with that of PC<sub>61</sub>BM (molar mass of 911 g mol<sup>-1</sup>,  $2 \times 10^{-3}$  cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup>) could make this conjugated molecule have a better miscibility with PC<sub>61</sub>BM and balanced charge transport. Overall, the extended  $\pi$ -conjugation system due to the introduction of BDT unit to conjugated backbone afford strong inter-molecular orbital overlap and give a higher mobility, which, coupled with an optimized morphology as discussed below from atomic force microscopy (AFM) data, result in a higher  $FF$ . With the notable  $FF$  and high  $V_{\text{oc}}$ , the DCAO3T(BDT)3T-based device has a high PCE of 5.44%, which is higher than our published record for power conversion efficiency (PCE) of 5.08% based on DCAO7T, thus it becomes the highest efficiency so far for solution-processed small molecule based BHJ OSCs. We note that the device performance is generally lower when other solvents, such as dichlorobenzene or chlorobenzene, are used and poorer film quality was observed. The PCE was not improved either by using PC<sub>71</sub>BM ([6,6]-phenyl-C71-butyric acid methyl ester) as acceptor or thermal annealing.

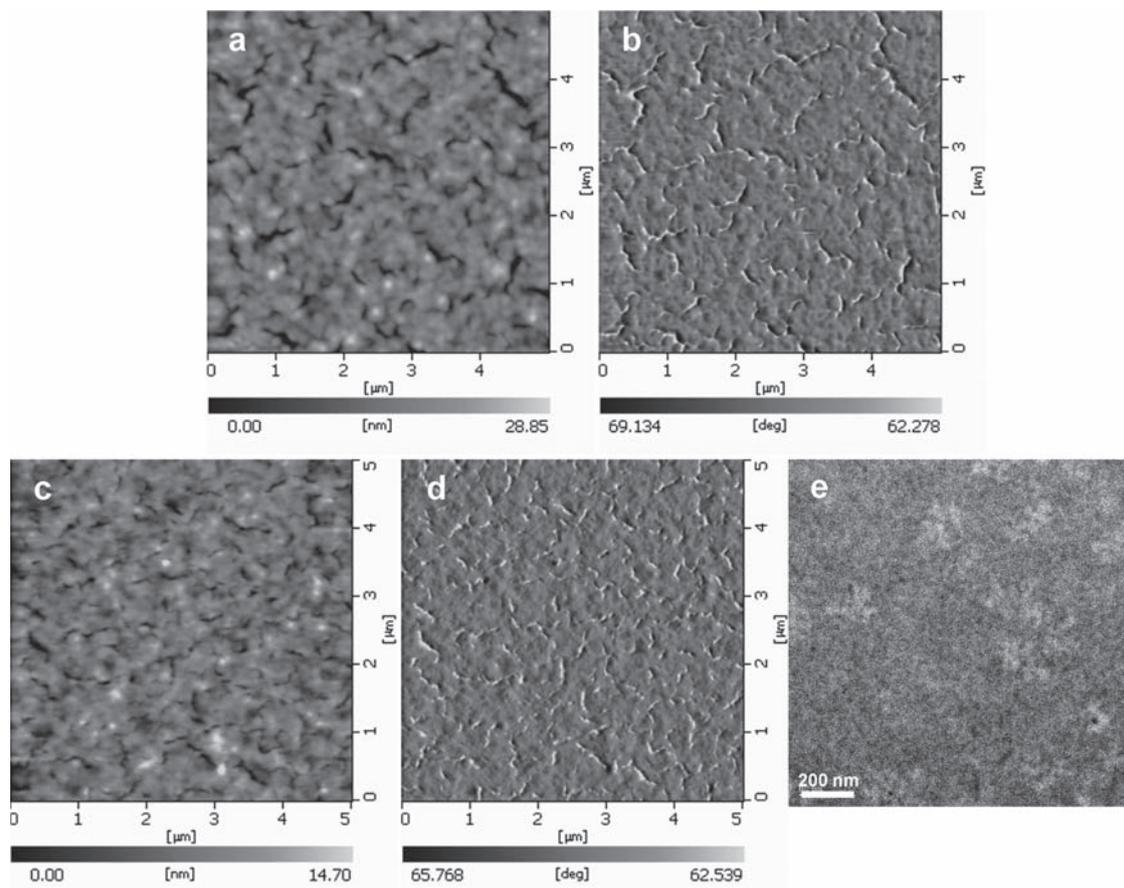
The external quantum efficiencies (EQEs) curve of the optimized BHJ device based on DCAO3T(BDT)3T/PC<sub>61</sub>BM (w:w, 1:0.5) under monochromatic light is shown in **Figure 3b**. The EQE curve exhibits monochromatic EQE maximum of 64% at 485 nm and a broad response covering 300–650 nm, consistent with the optical absorption profile (**Figure 3b**). This EQE value indicates that the photoresponse is very efficient for this small molecule based BHJ device. The  $J_{\text{sc}}$  calculated from the integral of EQE curve based on DCAO3T(BDT)3T with an AM1.5G reference spectrum were 9.0 mA cm<sup>-2</sup>, consistent with the  $J_{\text{sc}}$  value obtained from the  $J$ - $V$  measurement (within 9% error).

Charge carrier mobilities in blend films have a crucial effect on the performance of OSCs. To gain insight into the high performance of DCAO3T(BDT)3T/PC<sub>61</sub>BM (w:w, 1:0.5) based device, hole and electron mobilities of the blend film were measured using the charge-only SCLC method.<sup>[28]</sup> The hole mobility of the blend film is  $1.51 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and it is the same order of magnitude as the hole mobility of the pure donor film. Similarly, the electron mobility is  $1.65 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This indicates that indeed a better balanced electron and hole mobilities in the blends exist, which could help to explain the high performance of this solution-processed small molecule based device.<sup>[29]</sup>

The surface morphology of pristine film and blend film (w:w, 1:0.5) of DCAO3T(BDT)3T/PC<sub>61</sub>BM spin-coated from chloroform solutions were studied by tapping-mode AFM, and the topography and phase images are shown in **Figure 4**. The pristine donor films have root mean square ( $r_{\text{ms}}$ ) roughness of 4.39 nm. As shown in **Figure 4**, the blend film morphology is quite different from that of pristine donor films. The  $r_{\text{ms}}$  roughness of blend films is 2.16 nm for DCAO3T(BDT)3T/PC<sub>61</sub>BM with the blend ratio of 1:0.5. The lower  $r_{\text{ms}}$



**Figure 3.** a)  $J$ - $V$  curves of BHJ solar cells prepared from DCAO3T(BDT)3T/PC<sub>61</sub>BM with different weight blend ratios. b) EQE and film absorption curve of a DCAO3T(BDT)3T/PC<sub>61</sub>BM-based device with a weight blend ratio of 1:0.5.



**Figure 4.** Tapping-mode AFM height (left) and (right) phase images ( $5 \mu\text{m} \times 5 \mu\text{m}$ ) of DCAO3T(BDT)3T (a,b) and DCAO3T(BDT)3T/PC<sub>61</sub>BM (w:w: 1:0.5) blend films (c,d) spin-coated from chloroform solutions on glass/ITO/PEDOT:PSS substrates. e) TEM image of DCAO3T(BDT)3T/PC<sub>61</sub>BM (w:w, 1:0.5) blend film from CHCl<sub>3</sub>.

roughness after blending with PC<sub>61</sub>BM indicates that this donor material has a good miscibility with PC<sub>61</sub>BM molecules in the blend films, and an optimized donor/acceptor (D/A) interpenetrating network (IPN) has formed. As shown in Figure 4, the interpenetrating network of the blend films can be seen from the phase images, which reveal two distinct feature types and indicate that efficient percolation channels are formed. To have a deeper insight into active layer morphology, we recorded transmission electron microscopy (TEM) image of the blend film (Figure 4e). The dark regions in the TEM image can be attributed to PC<sub>61</sub>BM domains due to its relatively high electron scattering density ( $\approx 1.5 \text{ g cm}^{-3}$ ),<sup>[30]</sup> and the bright regions can be attributed to DCAO3T(BDT)3T domains. The blend film possesses uniform and fine features with well-connected DCAO3T(BDT)3T networks and IPN structures, suggesting nanoscale phase separation has formed. The well-defined IPN structure ensure large D/A interfaces and efficient percolation channels for charge transport, thus improving the exciton separation and carrier collection efficiency and leading to a high  $J_{sc}$  and  $FF$ .

In conclusion, we have designed and synthesized a new solution-processable small molecule containing BDT unit for application in BHJ OSCs. This small molecule shows high PCEs for solution-processed BHJ solar cells with different blend ratios and a PCE of 5.44% with a high  $V_{oc}$  of 0.93 V and a notable  $FF$  of

59.9% was achieved based on DCAO3T(BDT)3T/PC<sub>61</sub>BM (w:w, 1:0.5) without any special treatment. This is the highest efficiency to date for solution-processed small molecule based BHJ solar cells. Our results show a great potential for the BDT and oligothiophene building blocks in creating donor-acceptor conjugated small molecules for high performance BHJ solar cells. The development of this kind of small molecules based high performance OSCs materials will accelerate their commercial application.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors gratefully acknowledge financial support from the MOST (Grants 2012CB933401 and 2011DFB50300), NSFC (Grants 50933003, 50902073 and 50903044) and NSF of Tianjin City (Grant 10ZCGHHZ00600).

Received: July 20, 2011

Revised: September 10, 2011

Published online: October 21, 2011

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