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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# Low Band Gap Benzothiophene-Thienothiophene Copolymers with Conjugated Alkylthiothieryl and Alkoxy carbonyl Cyanovinyl Side Chains for Photovoltaic Applications

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX  
DOI: 10.1039/b000000x

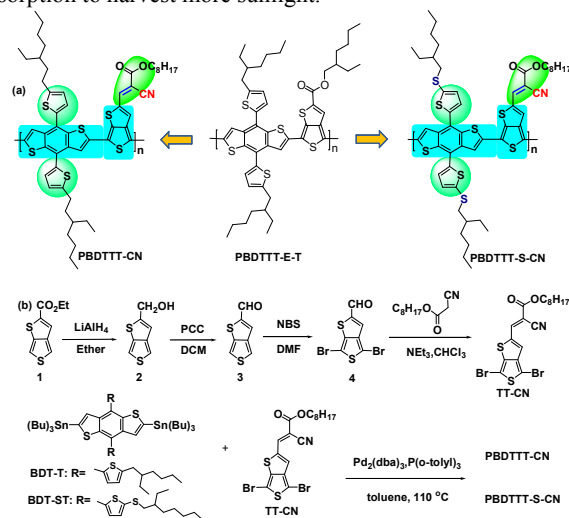
Alkylthiothieryl substituted benzothiophene (BDT) and alkoxy carbonyl cyanovinyl modified thienothiophene (TT) were copolymerized to obtain a new two dimensional low band gap polymer of PBDTTT-S-CN, which exhibited a promising efficiency of 7.0% in organic solar cells.

In recent years, polymer solar cells (PSCs) have attracted a lot of scientific researchers because of their low cost, light weight, easy solution process, flexibility and transparency.<sup>1</sup> To achieve a high PCE, significant efforts have been devoted to increase the parameters of open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), and fill factor (FF) by designing polymers structures and optimizing device fabrication technologies.<sup>2</sup> Bulk-heterojunction (BHJ) device has been found to be the most successful device architecture, which consists of a blend film based on a conjugated polymer donor and a fullerene acceptor.<sup>3</sup> In most of the high performance polymer donors in BHJ PSCs, their conjugated backbones often contain an electron-donating (D) block and an electron-accepting (A) block, which is named as low band gap (LBG) polymers.<sup>4</sup> The push-pull effect of the donor and the acceptor segments in this system will result in an intra- and/or intermolecular charge transfer (ICT), giving rise to a lower energy absorption band and a better photo response.<sup>5</sup>

For building efficient LBG polymers, thieno[3,4-b]thiophene (TT) has been received a wide attention due to its stabilization of the quinoidal structures and narrowness of energy gap the resulting polymers. In 2009, Yu *et al.* reported a new LBG D-A conjugated polymers (PTB1), which exhibited a high PCE of 5.6%, with a  $J_{sc}$  of 15.1 mA cm<sup>-2</sup> and FF of 0.65.<sup>6</sup> Subsequently, they introduced a fluorine atom onto the TT skeleton, and reported another polymer (PTB7) with a higher PCE over 7%.<sup>7</sup> In order to obtain the lower-lying HOMO energy levels, Yang *et al.* used the ketone group in place of the ester group and synthesized a new polymer (PBDTTT-C) with a PCE of 6.58%.<sup>8</sup> Two dimensional (2D) BDT-based polymer (PBDTTT-C-T) was first reported by Hou *et al.* in 2011.<sup>9</sup> In that polymer, alkoxy groups were replaced with alkylthienyl groups to red-shift the absorption edge, lower the HOMO energy level and improve the hole mobility. The PCE of PBDTTT-C-T was then greatly increased to 7.59%.<sup>9</sup> Recently, Li *et al.* introduced an alkylthio group on the thiophene side chains and reported a new polymer of PBDTTT-S-TT with a high PCE of 8.42%.<sup>10</sup> The elevation of efficiency was

attributed to the improved hole mobility and lowered HOMO level by this alkylthio substitution. Beside the groups of ketone, ester and fluorine atom, sulfonyl was also introduced on TT skeleton to build another D-A polymer of PBDTTT-S.<sup>11</sup> The PCE of PBDTTT-S device reached 6.22% with an improved  $V_{oc}$  of 0.76 V. Since the HOMO level and any other properties can be finely modulated by introducing electron-withdrawing groups on the TT core, different electron-withdrawing side moieties are still necessary to be tried to achieve highly efficient poly(BDT-TT)s.

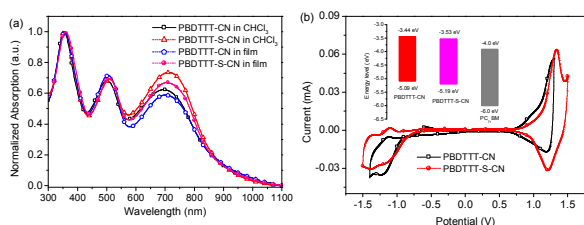
In this communication, we presented two new copolymers of alkylthiothieryl modified BDT and alkoxy carbonyl cyanovinyl modified TT. These two polymers are named as PBDTTT-CN and PBDTTT-S-CN, respectively (Scheme 1). Cyano group was introduced onto the skeleton because of its strong electron-withdrawing ability, which was expected to lower the HOMO levels of the resulting copolymers. On the other hand, conjugated vinyl bridge was also introduced between the ester side chain and TT core to extend the conjugation of TT skeleton. Both the introduction of cyano moiety and vinyl bridge would red-shift the absorption to harvest more sunlight.



Scheme 1 Molecular structures (a) and synthesis routes (b) of the copolymers.

The molecular structures and synthesis of monomers and copolymers are shown in Scheme 1. The alternating copolymers of PBDTTT-CN and PBDTTT-S-CN were synthesized by Stille

coupling polymerization with good yields using  $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tolyl})_3$  as catalysts. Detailed procedures of synthesis of copolymers are described in the ESI.† Both polymers have good solubility in common organic solvents, such as chloroform, toluene, chlorobenzene, dichlorobenzene, *etc.* The number-average molecular weights ( $M_n$ ) of PBDTTT-CN and PBDTTT-S-CN were estimated by gel permeation chromatography to be 14.4 kDa and 18.7 kDa, with the polydispersities (PDI) of 1.75 and 1.72, respectively. No glass transition behaviours were observed in both cases by differential scanning calorimetry analysis (Fig. S1, ESI†). PBDTTT-CN and PBDTTT-S-CN showed the decomposition temperatures (5% weight loss) of 322 °C and 309 °C, respectively, which indicated that alkylthio hybrid electron-donating side chains decreased the thermal stability of the related polymers.<sup>10,12</sup> However, the thermal stability is adequately suitable for PSC applications.



**Fig. 1** (a) Normalized absorption spectra of the copolymers in chloroform solutions and as thin solid films. (b) Cyclic voltammograms of the copolymer films. (Insert: HOMO and LUMO levels of the copolymers and PC<sub>71</sub>BM.)

The UV-vis absorption spectra of PBDTTT-CN and PBDTTT-S-CN in dilute  $\text{CHCl}_3$  solutions and in thin films are shown in Fig. 1a and Fig. S2. Both polymers show the strong absorption ability in solution and as thin solid films with a range starting from 300 nm to 1100 nm. The low-energy peak of PBDTTT-CN and PBDTTT-S-CN were located at about 695 nm and 711 nm in  $\text{CHCl}_3$ , respectively. PBDTTT-S-CN showed a little red-shift of 6 nm as compared to PBDTTT-CN, which should be attributed to electron-donating ability of introduced alkylthio moieties. Going from solution to the solid state, this type of peaks were red-shifted to about 704 and 712 nm. PBDTTT-S-CN film peaked at almost the same location, signifying easy aggregation of this alkylthio modified polymer backbones even in dilute solution. The optical band gaps of PBDTTT-CN and PBDTTT-S-CN were determined from the absorption onsets of the corresponding polymer films to be 1.32 eV and 1.30 eV, respectively. It is clearly that both polymers possess wide absorption shapes and smaller band gaps than those of PBDTTT-E-T,<sup>9</sup> which are expected to harvest more sun light to increase the  $J_{\text{sc}}$  in their PSCs. The reason can be attributed to the stronger electron-withdrawing ability of cyano group and longer extended  $\pi$ -conjugation of the vinyl bridge between the ester side chain and TT skeleton.

The cyclic voltammetry was employed to measure the HOMO and LUMO levels of the polymers. As shown in Fig. 1b, the onset oxidation potentials of PBDTTT-CN and PBDTTT-S-CN were located at -0.90 V and -0.81 V, leading to the corresponding HOMO levels to be -5.09 eV and -5.19 eV, respectively. Also from the onset reduction potentials, the LUMO levels of PBDTTT-CN and PBDTTT-S-CN were determined to be -3.44

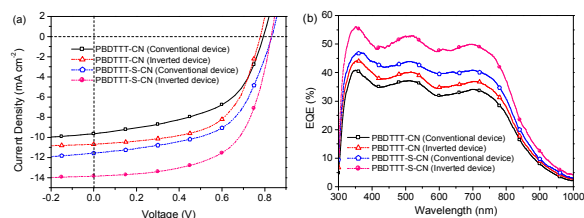
eV and -3.53 eV. Thus, the band gaps of PBDTTT-CN and PBDTTT-S-CN were calculated to be about 1.67 and 1.66 eV. PBDTTT-S-CN showed the deeper HOMO and LUMO levels than those of PBDTTT-CN, which indicated that alkylthio substitution would significantly influence the electronic properties of the BDT-TT copolymers keeping the similar band gap. The lower-lying HOMO level would make the PBDTTT-S-CN devices exhibit a higher  $V_{\text{oc}}$ . The electronic energy level diagrams of the copolymers and PC<sub>71</sub>BM are described in the inserted graph of Fig. 1b. The LUMO gaps of 0.47-0.56 eV and HOMO gaps of 0.81-0.91 eV between the copolymers and PC<sub>71</sub>BM guarantee a sufficient driving force for efficient exciton dissociation at the D-A interface, ensuring energetically favorable electron transfer.<sup>13</sup> Molecular simulations (Fig. S3, ESI†) on PBDTTT-CN and PBDTTT-S-CN confirmed this trend of variation for molecular orbital energy levels. The localization of HOMO distributed in the middle part of the conjugated backbone, but mainly focused on the donor skeletons. From a HOMO-LUMO transition, the electron clouds of LUMO localized almost on the part of the TT fragment, implying an efficient charge-transfer process giving rise to the strong low-energy absorption band observed in Fig. 1a.

The crystallinity and film organization of the polymers were investigated by X-ray diffraction measurements (Fig. S4, ESI†). The PBDTTT-CN and PBDTTT-S-CN film showed clear (100) peaks at  $2\theta = 22.84^\circ$  and  $23.96^\circ$ , which corresponds to a  $d$ -spacing of  $\pi$ - $\pi$  stacking distances ( $d_\pi$ ) between coplanar conjugated polymers were 3.88 Å and 3.71 Å, respectively. Another peaks (010) appeared at  $2\theta$  of  $3.58^\circ$  and  $3.37^\circ$  for PBDTTT-CN and PBDTTT-S-CN, corresponding to the lamellar packing with a  $d$ -spacing ( $d_l$ ) of 24.65 Å and 28.01 Å. The  $d_l$  values are very close due to the similar alkyl side chains on the polymer backbones. But the alkylthio substitution can efficiently improve  $\pi$ - $\pi$  stacking property of the resulting copolymer, which can be attributed to the more planar structure. As shown in Fig. S3, the dihedral angle of BDT and TT is the same (*ca.*  $16^\circ$ ). However, the dihedral angle of alkylthiophene and BDT in PBDTTT-S-CN ( $54^\circ$ ) is smaller than that of alkylthiophene and BDT in PBDTTT-CN ( $57^\circ$ ). This slight structural transform would afford PBDTTT-S-CN with the higher carrier mobility. This was further verified by the mobility measurements using the space charge limited current (SCLC) method (Fig. S5, ESI†). The hole mobilities were measured to be  $2.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for PBDTTT-CN and  $5.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for PBDTTT-S-CN. As expected, PBDTTT-S-CN film exhibited higher hole mobility, which is about two times of that of PBDTTT-CN film. The results are agreed well with those obtained from XRD measurements.

Conventional PSCs were firstly fabricated to investigate the photovoltaic properties of the resulting copolymers with a structure of ITO/PEDOT:PSS/copolymer:PC<sub>71</sub>BM/Ba/Al. The performances were optimized by varying the weight ratios of blend, changing the thickness of the active layer, choosing the different solvent and processing additives. The optimized weight ratio between the copolymer and PC<sub>71</sub>BM is 1:1.5 (w/w). 1,8-Diiodooctane (DIO) was used as an additive to optimize the morphology of the active blends. All the active layers were finally added with 2% (v/v) DIO in *o*-dichlorobenzene.

As shown in Fig. 2a, the PBDTTT-CN device exhibited a

PCE of 4.06% under the optimized conditions, with a  $V_{oc}$  of 0.79 V, a  $J_{sc}$  of 9.65 mA cm<sup>-2</sup>, and an FF of 0.53. However, PBDTTT-S-CN devices showed a higher PCE of 5.45% with a  $V_{oc}$  of 0.83 V, a  $J_{sc}$  of 11.57 mA cm<sup>-2</sup>, and an FF of 0.57. Both devices had higher  $V_{oc}$  than that of PBDTTT-E-T,<sup>9</sup> which is the top value in BDT-TT molecular system. Apparently, the alkylthio and cyano substitutions played an important role on above elevation of  $V_{oc}$ . Since the  $V_{oc}$  is related to the HOMO<sub>donor</sub>-LUMO<sub>acceptor</sub> energy offset,<sup>14</sup> the higher  $V_{oc}$  of PBDTTT-S-CN device is caused by its lower-lying HOMO level of -5.19 eV as determined in CV experiments.<sup>14</sup> In order to elucidate the origin of  $J_{sc}$ , the dependence of the external quantum efficiencies (EQEs) of the PSCs on the wavelength of incident light was presented in Fig. 2b. As shown in Fig. 2b, both EQE spectra cover a broad wavelength range from 300 to 1000 nm. PBDTTT-S-CN device showed higher photo-conversion efficiency with a peak EQE value of about 47%, whereas PBDTTT-CN device had a peak EQE value of 41%. The integrated  $J_{sc}$  values from EQE curves were less than 5% error, which implied the accuracy of  $J_{sc}$  values obtained by J-V measurements. The EQE results also verified the increased  $J_{sc}$  of PBDTTT-S-CN device in comparison with that of PBDTTT-CN device. The morphology of the both blending film was checked by AFM (Fig. S6, ESI<sup>†</sup>), implying a uniform and bicontinuous network with a well-defined nanoscale feature. The PBDTTT-CN film was a little smooth. But the domain size of the PBDTTT-S-CN blend became larger, which would promote to enhance carrier drift length and increase photocurrent with strong electric field dependence, resulting in high FF of the relevant devices. The roughness was determined to be about 0.33 and 1.95 for PBDTTT-CN and PBDTTT-S-CN, respectively. Considering the elevation of  $V_{oc}$ ,  $J_{sc}$  and FF, the PBDTTT-S-CN devices showed two times of PCE compared to the PBDTTT-CN devices.



**Fig. 2** (a) J-V curves of copolymer/PC<sub>71</sub>BM (1:1.5) based polymer solar cells. (b) EQE curves of copolymer/PC<sub>71</sub>BM (1:1.5) based polymer solar cells.

The inverted device architecture should bring a higher efficiency and longer-term stability compared to a conventional devices.<sup>15</sup> Thus, inverted PSCs were fabricated with a configuration of ITO/ZnO/PNFB/copolymer:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag. ZnO and MoO<sub>3</sub> were chosen as electron-transport and hole-transport layers, respectively. To modulate energy barrier and mutual interaction at the top and bottom interfaces, a thin layer of PNFB was incorporated between ZnO and the blending active layer.<sup>16</sup> As shown in Fig. 2a, both inverted device exhibited a largely enhanced PCE of 4.94% and 7.00%. The improved efficiencies were attributed to the elevation of  $J_{sc}$  and FF simultaneously, although the  $V_{oc}$  was almost the same as compared to their conventional devices. The  $J_{sc}$  values were elevated from 9.65 and 11.57 mA cm<sup>-2</sup> to 10.68 and 13.85 mA cm<sup>-2</sup> for PBDTTT-CN and PBDTTT-S-CN, respectively. This

was also verified by the improved EQE response, as shown in Fig. 2b. The integrated  $J_{sc}$  values of these inverted devices were also agreed well with those from J-V measurements, implying that the results were reliable. Finally, the optimized PCE up to 7.00% was achieved from PBDTTT-S-CN device, which indicated its promising application in BHJ solar cells.

In conclusion, two new copolymers of PBDTTT-CN and PBDTTT-S-CN were synthesized with alkylthiothiethyl modified BDT and alkoxy carbonyl cyanovinyl modified TT blocks. The introduced alkylthio and cyano substitution showed positive effects on extending the absorption range and down-shifting the energy levels, in comparison to the corresponding copolymer with alkyl substitution on the conjugated thiophene side chains. As expected, the PBDTTT-S-CN device exhibited a better performance than that of PBDTTT-CN device. A high PCE of 7.00% was obtained from an inverted device based on PBDTTT-S-CN. The design strategy of alkylthio and cyanovinyl substitution toward both BDT and TT blocks in this work is an effective way to develop efficient LBG copolymers for future PSC applications.

This work was supported by the NSFC (21272164, 21432005), the YSTF of Sichuan Province (2013JQ0032), the Foundation of State Key Laboratory of Polymer Materials Engineering (sklpme2014-3-05), and the FRF for the Central Universities (2012SCU04B01, YJ2011025).

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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