

Cite this: *J. Mater. Chem.*, 2011, **21**, 17642

www.rsc.org/materials

## COMMUNICATION

## A benzotrithiophene-based low band gap polymer for polymer solar cells with high open-circuit voltage†

Christian B. Nielsen,<sup>\*a</sup> Bob C. Schroeder,<sup>a</sup> Afshin Hadipour,<sup>b</sup> Barry P. Rand,<sup>b</sup> Scott E. Watkins<sup>c</sup> and Iain McCulloch<sup>a</sup>

Received 18th July 2011, Accepted 14th September 2011

DOI: 10.1039/c1jm13393d

A new benzotrithiophene-containing donor–acceptor type copolymer for polymer solar cells is reported. The promise of benzotrithiophene as a weak donor material is reflected in a polymer band gap of 1.75 eV affording a high  $V_{oc}$  of 0.81 V and a moderate PCE of 2.2% in a polymer solar cell.

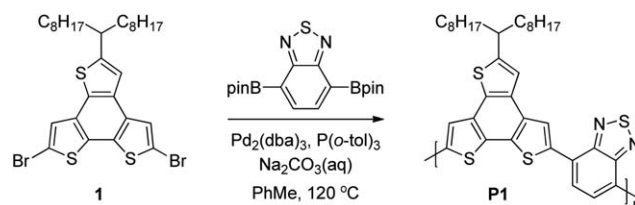
Extensive research has recently focused on the development of novel polymeric electron donor materials for use in bulk heterojunction (BHJ) organic photovoltaic (OPV) devices with various fullerene materials as the electron acceptor material.<sup>1,2</sup> To optimise optical absorption for efficient exciton generation in the donor material and simultaneously allow for efficient electron transfer to the acceptor material, precise adjustment of the frontier energy levels is needed. Most commonly, donor–acceptor (D–A) copolymers are used as the electron donor material due to their low band gap as a result of a strong intramolecular charge transfer (ICT). The broad absorption of narrow band gap polymers ensures a good match with the solar spectrum and hence efficient light absorption. On the down-side, lowering of the lowest unoccupied molecular orbital (LUMO) of the polymer can be detrimental to the electron transfer to the fullerene material and raising of the highest occupied molecular orbital (HOMO) of the polymer will reduce the open-circuit voltage ( $V_{oc}$ ) and hence the efficiency of the OPV device.<sup>3,4</sup> Therefore, to balance the fine interplay between efficient light harvesting and high  $V_{oc}$ , a slight weakening of the ICT in D–A copolymers to afford a relatively low band gap and yet a low-lying HOMO is an obvious successful compromise in the design of high-performing polymer solar cells.

We have recently reported on the design and synthesis of a novel electron-rich fused aromatic unit, namely benzo[1,2-b:3,4-b':5,6-d'']trithiophene (BTT), which holds promise as a building block for semiconductor materials.<sup>5</sup> In comparison with the well-known benzo[1,2-b:4,5-b']dithiophene (BDT),<sup>6</sup> quantum-chemical calculations

(B3LYP/6-31G\*) predict the BTT unit to be of similar donor strength.<sup>‡</sup> Thus, with R being alkyl chains, BTT is predicted to act as a weak donor and form suitable D–A copolymers with moderate band gaps and low HOMO values when copolymerised with strong acceptors such as 2,1,3-benzothiadiazole (BT). The larger BTT unit is expected to be advantageous for promoting favourable intermolecular  $\pi$ -stacking interactions, just as the backbone curvature introduced with the slightly bent BTT unit aids polymer solubility and flexibility.<sup>5b,7</sup> We present here a highly soluble high molecular weight BTT-based copolymer with a band gap of approximately 1.75 eV that performs well in a BHJ solar cell with PCBM, affording a power conversion efficiency (PCE) of 2.2% with  $V_{oc}$  = 0.81 V.

The dibrominated BTT monomer **1** with a branched C<sub>8</sub>C<sub>8</sub> alkyl chain for solubility was prepared as previously described.<sup>5b</sup> Polymer **P1** was synthesised by a Suzuki–polycondensation with the pinacol ester of 2,1,3-benzothiadiazole-4,7-diboronic acid as depicted in Scheme 1. **P1** was obtained as a deep purple solid with good solubility in chlorinated solvents such as chlorobenzene (CB) and *o*-dichlorobenzene (ODCB); a number-average molecular weight ( $M_n$ ) of 41,000 and a polydispersity index of 6.2 was measured by gel permeation chromatography (GPC) in CB at 80 °C.<sup>‡</sup>

Optical absorption spectroscopy of **P1** in ODCB solution reveals an absorption band with a maximum at a wavelength  $\lambda$  = 373 nm from the  $\pi$ – $\pi^*$  transition and a much stronger ICT absorption band with a maximum at  $\lambda$  = 577 nm, confirming the D–A nature of the copolymer (Fig. 1). A maximum molar extinction coefficient (per repeat unit) of  $17 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  (corresponding to approximately 28 L g<sup>−1</sup> cm<sup>−1</sup>) was determined from a series of dilute ODCB solutions, while a maximum absorption coefficient of approximately  $1 \times 10^5 \text{ cm}^{-1}$  was obtained from a series of thin films. In the solid state (spin-cast from ODCB), the ICT absorption band is slightly red-shifted with a maximum at  $\lambda$  = 585 nm and a small shoulder around

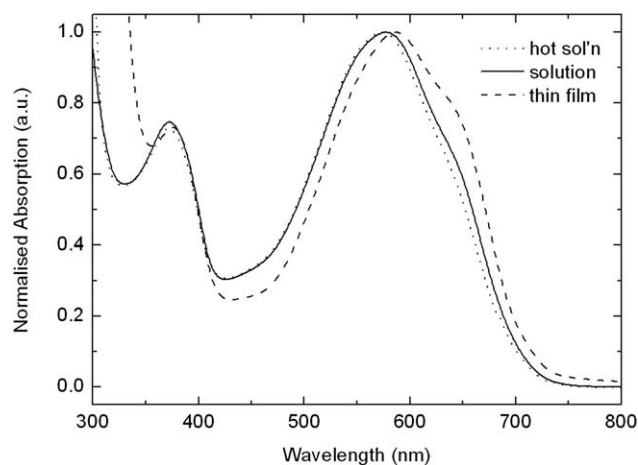
Scheme 1 Synthesis of benzotrithiophene-based polymer **P1**.

<sup>a</sup>Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, SW7 2AZ, UK. E-mail: c.nielsen@imperial.ac.uk

<sup>b</sup>IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>c</sup>CSIRO Materials Science and Engineering, VIC 3169, Australia

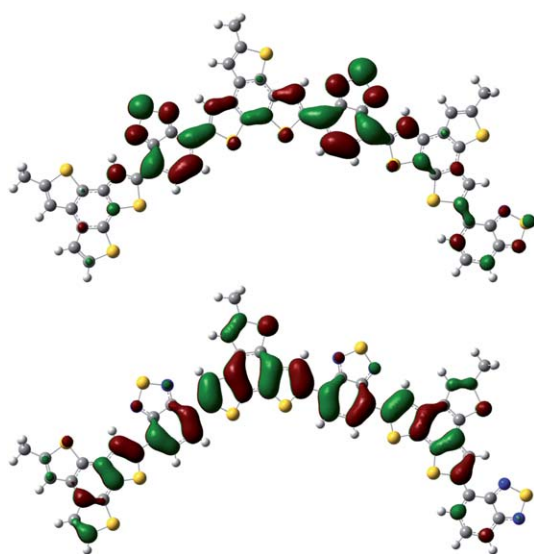
† Electronic supplementary information (ESI) available: Experimental details for the synthesis of **P1**, PESA spectra and additional *J*–*V* curves and AFM images. See DOI: 10.1039/c1jm13393d



**Fig. 1** Optical absorption spectra of **P1** in ODCB solution and as a spin-cast film from ODCB.

650 nm. The optical band gap as determined from the onset of absorption in the solid state is found to be approximately 1.75 eV. As can be seen in Fig. 1, a hot ODCB solution displays almost identical absorption features to the solution at room temperature apart from a minimal decrease in the high wavelength shoulder. This indicates that the relatively small red-shift observed when comparing the solid state to the solution UV-vis is more likely due to a lack of molecular order in the solid state as opposed to strong aggregation in solution.

The HOMO energy level of **P1** was measured by photoelectron spectroscopy in air and found to be  $-5.09$  eV. For comparison, the HOMO value of P3HT is  $-4.65$  eV under identical conditions (Figure S2†).<sup>8</sup> From the HOMO value and the optical band gap, the LUMO value can be estimated to  $-3.34$  eV. These frontier molecular orbital energy levels indicate both excellent ambient stability and high potential for good OPV performance including efficient charge transfer and a high open-circuit voltage. As illustrated in Fig. 2,



**Fig. 2** HOMO (bottom) and LUMO (top) distributions for the minimum-energy conformation of a methyl-substituted BTT-BT trimer optimized with Gaussian at the B3LYP/6-31G\* level.

quantum-chemical calculations (B3LYP/6-31G\*) predict the HOMO to be widely distributed along the polymer backbone, whereas the LUMO is predominantly localised around the BT acceptor units.

Bulk heterojunction solar cells were fabricated with a conventional device configuration consisting of ITO/PEDOT:PSS/**P1**:PCBM/Ca/Ag and tested under simulated  $100 \text{ mW cm}^{-2}$  AM1.5G illumination. Initial device optimization was carried out with PC<sub>61</sub>BM investigating polymer:fullerene blend ratios from 1 : 1 to 1 : 4 and thicknesses from 45 nm to 100 nm; all devices were processed from chloroform:ODCB (4 : 1). The best device with PC<sub>61</sub>BM was achieved with a blend ratio of 1 : 2 (**P1**:PC<sub>61</sub>BM) and a film thickness of 55 nm affording a modest PCE of 1.64% and a high  $V_{oc}$  of 0.80 V; device performance was limited by a low short-circuit current density ( $J_{sc}$ ) and a poor fill factor (FF) (Figure S3† and Table 1). To increase the photocurrent, the more absorptive fullerene, PC<sub>71</sub>BM,<sup>9</sup> was tested as the acceptor material and a slightly improved PCE of 2.12% was extracted from the  $J$ - $V$  curve depicted in Fig. 3 (55 nm device). The better performance was due to an improved  $J_{sc}$  as well as a higher fill factor (Table 1). For the devices with PC<sub>71</sub>BM, a thickness of 45 nm was found to be optimum for the photoactive layer increasing the PCE to 2.18% due to a slightly increased fill factor compared to the 55 nm device. Although initial attempts to improve the device performance by the addition of 1,8-octanedithiol did not afford better photovoltaic properties (Figure S5†), we believe that there is ample room for improvement through further optimisation of the blend morphology for this system.<sup>10</sup>

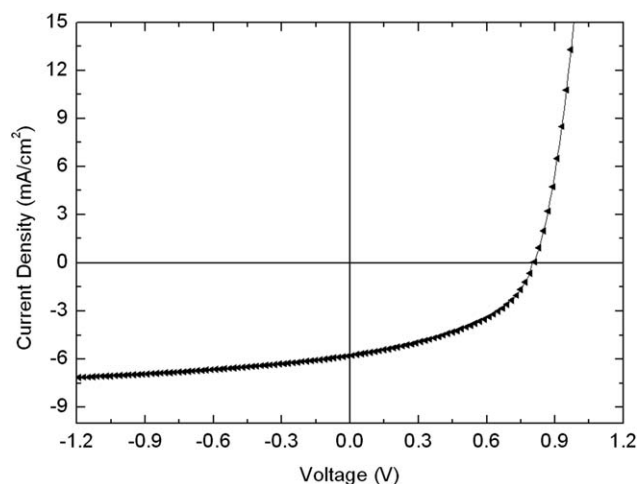
The external quantum efficiency (EQE) of the best device is shown in Fig. 4. The device exhibited a fairly broad response with efficiencies in the range of 35–41% from  $\lambda = 350$  to 580 nm, and a peak EQE of 41.4% at  $\lambda = 475$  nm. Upon integration of the EQE spectrum with the AM1.5G solar spectrum, a  $J_{sc} = 6.55 \text{ mA cm}^{-2}$  is expected, higher than but in good agreement with the measured value. The absorption spectra of the polymer:fullerene blends are also included in Fig. 4 and a very good correlation between the EQE spectrum and the optical absorption of the **P1**:PC<sub>71</sub>BM blend is evident. We furthermore note the anticipated increase in absorption when comparing the PC<sub>71</sub>BM blend to the PC<sub>61</sub>BM blend. This correlates nicely with the increased  $J_{sc}$  (Table 1) as discussed above.

The previously mentioned benzo[1,2-b:4,5-b']dithiophene (BDT) has been copolymerised with BT by You and co-workers for photovoltaic studies.<sup>6a</sup> Compared to **P1**, The BDT-BT copolymer displays a similar  $V_{oc}$  (0.77 V) confirming the similar HOMO levels for the two systems reflecting the comparable donor strengths of BDT and BTT. The PCE (0.94%) for BDT-BT, on the other hand, is strongly limited by a low  $J_{sc}$  ( $3.02 \text{ mA cm}^{-2}$ ), which supports our hypothesis that the larger BTT unit has a favourable influence on the charge transport in an OPV device. Furthermore, when compared to a naphtho[2,1-b:3,4-b']dithiophene (NDT) system reported by the

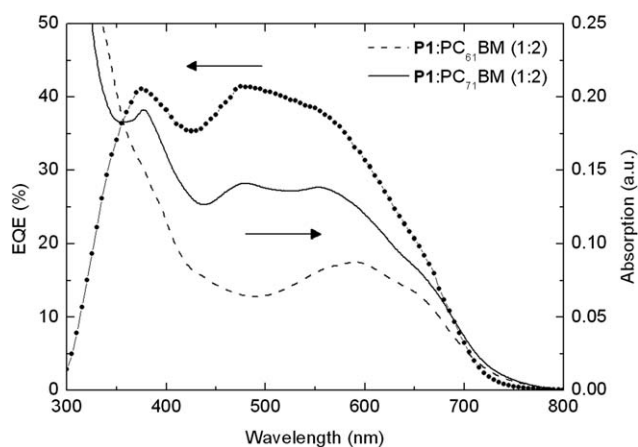
**Table 1** Photovoltaic properties of polymer solar cells from **P1**<sup>a</sup>

PCBM	Thickness (nm)	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)
C <sub>60</sub>	55	0.80	5.09	0.40	1.64
C <sub>70</sub>	45	0.81	6.07	0.44	2.18
C <sub>70</sub>	55	0.81	6.36	0.41	2.12

<sup>a</sup> All devices made from chloroform:ODCB with a 1 : 2 ratio of **P1**:PCBM.



**Fig. 3**  $J$ - $V$  characteristics of the **P1**:**PC**<sub>71</sub>**BM** device with a 55 nm thick photoactive layer under 100 mW cm<sup>-2</sup> AM1.5G simulated solar illumination.

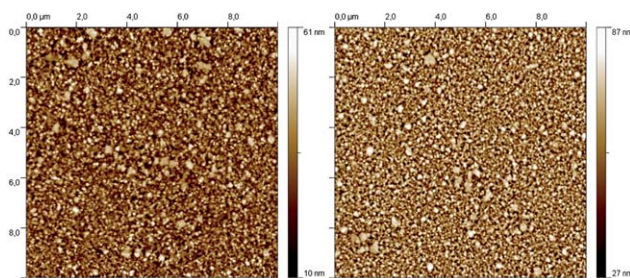


**Fig. 4** The external quantum efficiency (EQE) spectrum for the **P1**:**PC**<sub>71</sub>**BM** solar cell (1 : 2 blend, 55 nm thickness) and the UV-vis spectra of the **P1**:**PC**<sub>61</sub>**BM** (1 : 2) and **P1**:**PC**<sub>71</sub>**BM** (1 : 2) blends in the solid state.

same group, it appears that the third thiophene unit of BTT is preferable to a benzene unit.<sup>11</sup> Again, the main difference is manifested in the  $J_{sc}$  (2.90 mA cm<sup>-2</sup> for NDT-BT), while the open-circuit voltages are similar (0.83 V for NDT-BT).

The surface morphology of the polymer:fullerene blends was examined with atomic force microscopy (AFM) and the resulting micrographs are depicted in Fig. 5 (see Figures S6 and S7 for additional micrographs†). Very similar nanostructures with a high degree of phase separation were observed for the two fullerene acceptors. This indication of good miscibility between **P1** and both **PC**<sub>61</sub>**BM** and **PC**<sub>71</sub>**BM** is in good agreement with the OPV device data, where the larger  $J_{sc}$  obtained with **PC**<sub>71</sub>**BM** can be ascribed to the increased photocurrent. A slightly larger root mean square surface roughness was observed for the blend with **PC**<sub>71</sub>**BM** (11.8 nm) than for the blend with the smaller and more spherical **PC**<sub>61</sub>**BM** (9.1 nm).

In conclusion, we have developed a new benzotrithiophene-containing D-A type copolymer with a good compromise between a low band gap and a low-lying HOMO. The polymer shows promise for



**Fig. 5** AFM images (tapping-mode, 10 × 10 μm) of **P1**:**PC**<sub>61</sub>**BM** (left) and **P1**:**PC**<sub>71</sub>**BM** (right) blends; both samples are 55 nm thick 1 : 2 **P1**:fullerene blends.

use as donor material in BHJ solar cells as manifested in a high  $V_{oc}$  (0.81 V) and a moderate PCE (2.2%). The improvements highlighted herein relative to similar systems, especially in terms of  $J_{sc}$ , will hopefully aid in the further understanding of structure-property relationships, which is needed for continued improvement of D-A type polymer solar cells.

## Acknowledgements

The authors thank Zhenggang Huang and Raja Shahid Ashraf for assistance with solar cell fabrication. This work was in part carried out under the EPSRC Project EP/F056710/1, EC FP7 ONE-P 245 Project 212311 and DPI Grant 678, with support from the Centre for Plastic Electronics at Imperial College and the National Research Fund of Luxembourg.

## Notes and references

‡ Quantum-chemical calculations with Gaussian at the B3LYP/6-31G\* level for methyl-substituted BDT-BT and BTT-BT trimers predict similar HOMO levels (−5.00 eV and −4.99 eV, respectively) and similar LUMO levels (−3.21 eV and −3.25 eV, respectively).

§ The relatively high PDI observed for this polymer is partly attributed to aggregation in solution due to the high concentration (5 mg mL<sup>-1</sup>) required for the measurement.

- (a) A. Facchetti, *Chem. Mater.*, 2011, **23**, 733; (b) C. L. Chochos and S. A. Choulis, *Prog. Polym. Sci.*, 2011, **36**, 1326.
- (a) S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297; (b) 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; (c) Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135; (d) C. Piliago, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2010, **132**, 7595; (e) H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 2995; (f) 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.
- S. Shoaee, T. M. Clarke, C. Huang, S. Barlow, S. R. Marder, M. Heeney, I. McCulloch and J. R. Durrant, *J. Am. Chem. Soc.*, 2010, **132**, 12919.
- M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, a. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789.
- (a) C. B. Nielsen, J. M. Fraser, B. C. Schroeder, J. Du, A. J. P. White, W. Zhang and I. McCulloch, *Org. Lett.*, 2011, **13**, 2414; (b) B. C. Schroeder, C. B. Nielsen, Y. Kim, J. Smith, S. E. Watkins, K. Song, T. D. Anthopoulos and I. McCulloch, *Chem. Mater.*, 2011, **23**, 4025.

- 
- 6 (a) S. C. Price, A. C. Stuart and W. You, *Macromolecules*, 2010, **43**, 797;  
(b) S. C. Price, A. C. Stuart and W. You, *Macromolecules*, 2010, **43**, 4609.
- 7 R. Rieger, D. Beckmann, A. Mavrinskiy, M. Kastler and K. Müllen, *Chem. Mater.*, 2010, **22**, 5314.
- 8 R. J. Davis, M. T. Lloyd, S. R. Ferreira, M. J. Bruzek, S. E. Watkins, L. Lindell, P. Sehati, M. Fahlman, J. E. Anthony and J. W. P. Hsu, *J. Mater. Chem.*, 2011, **21**, 1721.
- 9 M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.*, 2003, **42**, 3371.
- 10 J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497.
- 11 H. Zhou, L. Yang, S. Stoneking and W. You, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1377.