ARTICLE TYPE

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

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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
10 **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
15 various fullerene materials as the electron acceptor material.[1,2] 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
20 (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
25 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.[3,4] Therefore, to
30 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.

35 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.[5] In comparison with the well-known benzo[1,2-b:4,5-b']dithiophene (BDT),[6] quantum-
40 chemical calculations (B3LYP/6-31G*) predict the BTT unit to be of similar donor strength.[‡] 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-
45 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.[5b,7] We present here a highly soluble high molecular
50 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 C8C8
55 alkyl chain for solubility was prepared as previously described.[5b] 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
60 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.[§]

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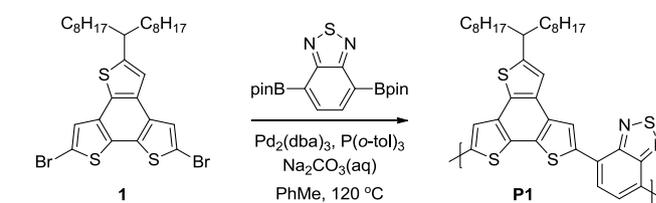
Scheme 1 Synthesis of benzotrithiophene-based polymer **P1**.

Optical absorption spectroscopy of **P1** in ODCB solution reveals an absorption band with a maximum at a wavelength λ = 373 nm from the π-π* transition and a much stronger ICT
70 absorption band with a maximum at λ = 577 nm, confirming the D-A nature of the copolymer (Figure 1). A maximum molar extinction coefficient (per repeat unit) of 17×10^3 M^{-1} cm^{-1} (corresponding to approximately 28 L g^{-1} cm^{-1}) was determined from a series of dilute ODCB solutions, while a maximum
75 absorption coefficient of approximately 1×10^5 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 λ = 585 nm and a small shoulder around 650 nm. The optical band gap as determined from the onset of absorption
80 in the solid state is found to be approximately 1.75 eV. As can be seen in Figure 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.
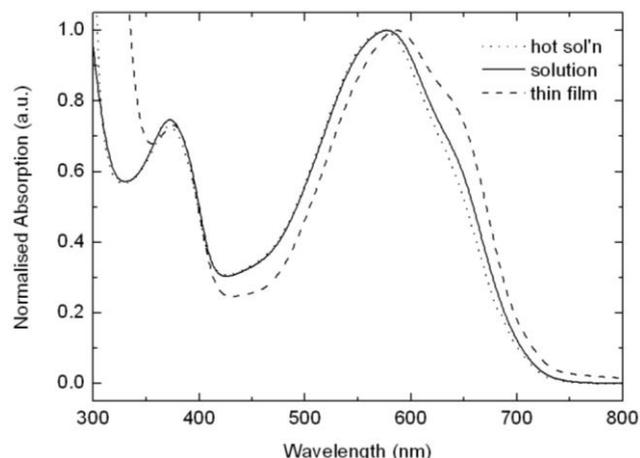

Fig. 1 Optical absorption spectra of **P1** in ODCB solution and as a spin-cast film from ODCB.

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).[8] 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 Figure 2, 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.
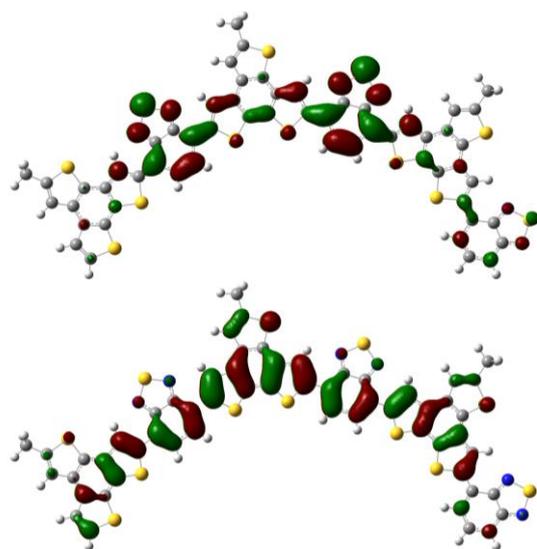

Fig. 2 HOMO (bottom) and LUMO (top) distributions for the minimum-energy conformation of a methyl-substituted BTT-BT trimer optimized with Gaussian at the B3LYP/6-31G* level.

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 mW cm^{-2} AM1.5G illumination. Initial device optimization was carried out with PC$_{61}$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$_{61}$BM was achieved with a blend ratio of 1:2 (**P1**:PC$_{61}$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) (see Supporting Information (SI), Figure S3 and Table 1). To increase the photocurrent, the more absorptive fullerene, PC$_{71}$BM,[9] was tested as the acceptor material and a slightly improved PCE of 2.12% was extracted from the *J-V* curve depicted in Figure 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$_{71}$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 (Figures S5), we believe that there is ample room for improvement through further optimisation of the blend morphology for this system.[10]

Table 1 Photovoltaic properties of polymer solar cells from **P1**

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

*^{a} All devices made from chloroform:ODCB with a 1:2 ratio of **P1**:PCBM*
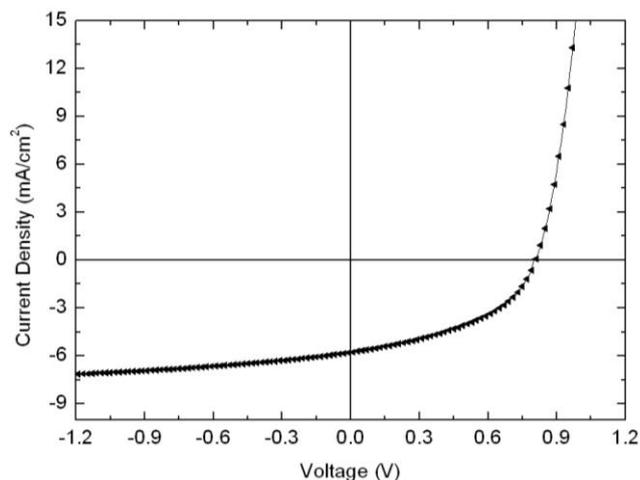

Fig. 3 *J-V* characteristics of the **P1**:PC$_{71}$BM device with a 55 nm thick photoactive layer under 100 mW/cm^2 AM1.5G simulated solar illumination.

The external quantum efficiency (EQE) of the best device is shown in Figure 4. The device exhibited a fairly broad response with efficiencies in the range of 35-41% from λ = 350 to 580 nm, and a peak EQE of 41.4% at λ = 475 nm. Upon integration of the EQE spectrum with the AM1.5G solar spectrum, a J_{sc} = 6.55 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 Figure 4 and a very good correlation between the EQE spectrum and the optical absorption of the **P1**:PC$_{71}$BM blend is evident. We furthermore note the anticipated increase in absorption when comparing the PC$_{71}$BM blend to the PC$_{61}$BM blend. This correlates nicely with the increased J_{sc} (Table 1) as discussed above.
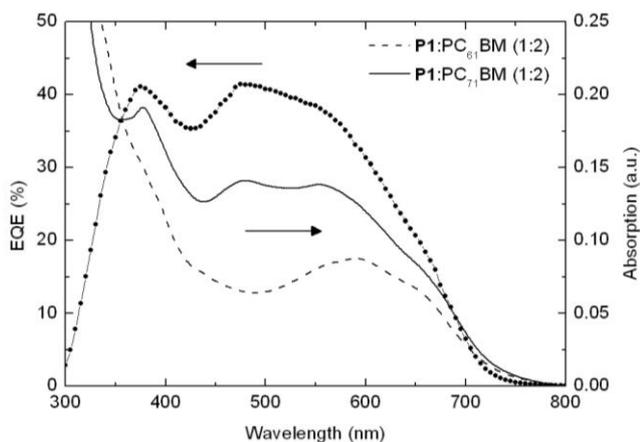

Fig. 4 The external quantum efficiency (EQE) spectrum for the **P1**:PC$_{71}$BM solar cell (1:2 blend , 55 nm thickness) and the UV-vis spectra of the **P1**:PC$_{61}$BM (1:2) and **P1**:PC$_{71}$BM (1:2) blends in the solid state.

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.[6a] 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 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 same group, it appears that the third thiophene unit of BTT is preferable to a benzene unit.[11] Again, the main difference is manifested in the J_{sc} (2.90 mA/cm^2 for NDT-BT), while the open-circuit voltages are similar (0.83 V for NDT-BT).
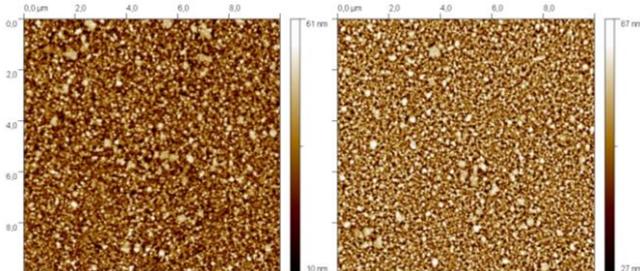

Fig. 5 AFM images (tapping-mode, 10 × 10 μm) of **P1**:PC$_{61}$BM (left) and **P1**:PC$_{71}$BM (right) blends; both samples are 55 nm thick 1:2 **P1**:fullerene blends.

The surface morphology of the polymer:fullerene blends was examined with atomic force microscopy (AFM) and the resulting micrographs are depicted in Figure 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$_{61}$BM and PC$_{71}$BM is in good agreement with the OPV device data, where the larger J_{sc} obtained with PC$_{71}$BM can be ascribed to the increased photocurrent. A slightly larger root mean square surface roughness was observed for the blend with PC$_{71}$BM (11.8 nm) than for the blend with the smaller and more spherical PC$_{61}$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 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

Notes and references

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† 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/b000000x/
‡ 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 (5mg/mL) required for the measurement.

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