Post-Polymerization Ketalisation for Improved Organic Photovoltaic Materials

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ABSTRACT: Poor organic photovoltaic device performance of a ketone-functionalized benzotrithiophene polymer with desirable frontier energy levels and a broad absorption in the visible region is successfully addressed through a new post-polymerisation ketalization approach. Hereby, the initial ketone-functionalized polymer is converted to two different ketal derivatives, which show superior processability leading to significantly enhanced photovoltaic device performance.

Introduction

The development of new materials for organic photovoltaic (OPV) devices has progressed rapidly over recent years and the performance of bulk heterojunction (BHJ) solar cells with fullerene acceptors has now surpassed the 10% mark.¹⁻³ Much attention has been paid to the

development of new polymeric donor materials and the ability to precisely control the frontier energy levels in order to harvest as much of the solar energy as possible while at the same time maintaining a sufficient energetic driving force for charge separation. Significant research efforts have concurrently been devoted to the control and optimisation of the bulk heterojunction blend morphology, either through chemical modifications of the polymeric donor material (or the fullerene acceptor) or with processing stimuli such as additives, thermal annealing and solvent annealing.⁴ Controlling the blend morphology through chemical modifications of the donor polymer is typically pursued by means of alkyl side chain variations or subtle modifications to the conjugated backbone.⁵⁻⁷ While these approaches often have proven successful, very laborious synthetic efforts – typically involving a repeat of most of the synthetic protocol – are required since the solubilising side chains generally are introduced early in the synthetic route for practical purposes.

Here, we report a new and very versatile approach to structurally modifying the solubilising side chains of polymeric donor materials as the very last step in the synthetic route, post-polymerisation, in order to quickly and efficiently assess the photovoltaic properties of a polymeric donor candidate as a function of various side chain motifs. Another important advantage of this post-polymerisation approach is the fact that the degree of polymerisation remains constant across the series of polymer derivatives that are being tested and compared. This is very rarely the case in pre-polymerisation approaches to side chain studies and variations in the degree of polymerisation can consequently mask – or falsely accentuate – the observed trend in a series of polymer derivatives.

With a benzotrithiophene-based polymer, we have previously shown how the thermal cleavage of a side chain ketal functionality – to restore the original ketone functionality – results in a

dramatic decrease in solubility and concurrently a significant increase in structural order and charge transport properties.^{8,9} Benzotrithiophene (BTT) has also shown promise as a building block in OPV donor materials,^{10,11} and here we show how the inverse functional group conversion – from ketone to ketal – can be used to efficiently improve the OPV device performance of a BTT-based polymer.

Experimental Section

Materials and Methods. All chemicals were purchased from commercial suppliers unless otherwise specified. Microwave experiments were performed in a Biotage initiator V 2.3. ¹H NMR spectra were recorded on a BRUKER DRX400 spectrometer in 1,1,2,2-tetrachloroethane-d₂ solution at 373 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent Technologies 1200 series GPC in chlorobenzene at 80°C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA) using a TA Instruments Q50 under a continuous nitrogen purge of 60 mL/min. The samples were heated from room temperature to 600°C with a uniform heating rate of 10°C/min. UV-Vis absorption spectra were recorded on a UV-1601 Shimadzu UV-Vis spectrometer. Infrared spectra were obtained using a Perkin Elmer FTIR Spectrometer 100. Atomic force microscopy (AFM) was carried out using an Agilent 5500 in close-contact (tapping) mode. Photoelectron spectroscopy in air (PESA) was carried out with a Riken Keiki Model AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5.

Polymer Synthesis.

BTT-DTBT-CO. A degassed solution of 2,8-bis(5-bromo-3-hexyl-2-thienyl)-5-hexadecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (273.9 mg, 0.2809 mmol), 4,7-bis(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (109.0 mg, 0.2809 mmol) tris(dibenzylideneacetone) dipalladium (5.5 mg, 0.006 mmol), tri(o-tolyl) phosphine (7.7 mg, 0.025 mmol), and Aliquat 336 (one drop) in toluene (5 ml) was mixed with a degassed sodium carbonate solution (1.0 M, 1 ml). The biphasic mixture was heated at 120 °C for 72 hours. The crude polymer was subsequently precipitated into methanol and further purified by Soxhlet extractions with acetone, cyclohexane and dichloromethane before the polymer was extracted with chloroform (as a fine suspension) and precipitated into methanol to afford **BTT-DTBT-CO** (143 mg, 0.1505 mmol, 54 %) as a black solid.

BTT-DTBT-Me. A solution of **BTT-DTBT-CO** (88.6 mg, 0.0933 mmol), 2,2-dimethyl-1,3-propanediol (3.32 g, 31.9 mmol) and p-toluenesulfonic acid monohydrate (100 mg, 0.526 mmol) in toluene (200 ml) was heated to reflux with a Dean-Stark trap for 48 hours. The reaction mixture was washed with aqueous sodium acetate and water. After removal of the toluene, the polymer was precipitated from hot chlorobenzene into methanol to afford **BTT-DTBT-Me** (89 mg, 0.0859 mmol, 92 %) as a black solid.

BTT-DTBT-Bu. A solution of **BTT-DTBT-Me** (68 mg, 0.0657 mmol), 2,2-dibutyl-1,3-propanediol (2.00 g, 10.6 mmol) and p-toluenesulfonic acid monohydrate (100 mg, 0.526 mmol) in toluene (70 ml) was heated to reflux with a Dean-Stark trap for 72 hours. The reaction mixture was washed with aqueous sodium acetate and water. After removal of the toluene, the polymer was precipitated from hot chlorobenzene into methanol to afford **BTT-DTBT-Bu** (67 mg, 0.0598 mmol, 91 %) as a black solid.

Results and Discussion

As depicted in Scheme 1, **BTT-DTBT-CO** was synthesised from the dibrominated dithieno-BTT unit and the diboronate of 2,1,3-benzothiadiazole (BT) using a microwave-assisted Pd-catalysed Suzuki-coupling methodology. Subsequent conversion of **BTT-DTBT-CO** to the 2,2-dimethyltrimethylene ketal (**BTT-DTBT-Me**) and then to the 2,2-dibutyltrimethylene ketal (**BTT-DTBT-Bu**) was carried out with a catalytic amount of acid and a large excess of the corresponding glycol in refluxing toluene with a Dean-Stark trap to ensure complete conversion. Size exclusion chromatography was employed to obtain a polystyrene-equivalent number-average molecular weight (M_n) of 16.7 kDa, a weight-average molecular weight (M_w) of 64.5 kDa and a polydispersity index (PDI) of 3.87 for **BTT-DTBT-Bu**; the measured value of M_n corresponds to an average degree of polymerisation of 15.¹² Thermal gravimetric analysis (TGA) was performed on the three polymers as illustrated by the TGA traces in Figure 1. **BTT-DTBT-CO** showed a high degree of thermal stability with 5% weight loss observed at 448°C, whereas distinct weight losses – corresponding to the loss of the ketal moiety – were observed for both **BTT-DTBT-Me** (8.3% weight loss) and **BTT-DTBT-Bu** (15.2% weight loss) around 425°C indicating that the post-polymerisation ketalisation reaction proceeds with a high degree of conversion.

Scheme 1. Linear Synthetic Approach towards the three **BTT-DTBT** Polymers

Figure 1. TGA traces recorded at 10°C/min under nitrogen of **BTT-DTBT-CO** (black line), **BTT-DTBT-Me** (red line) and **BTT-DTBT-Bu** (blue line) with dashed lines indicating the theoretical weight loss upon ketal cleavage for **BTT-DTBT-Me** (red) and **BTT-DTBT-Bu** (blue).

The effective post-polymerization approach was confirmed by Fourier transform infrared (FTIR) spectroscopy as depicted in Figure 2. A strong band at 1660 cm^{-1} arising from the carbonyl C=O stretch was observed for **BTT-DTBT-CO**, while this band was significantly reduced for **BTT-DTBT-Me** and even more so for **BTT-DTBT-Bu**. We furthermore ascribe the new band appearing for **BTT-DTBT-Me** and **BTT-DTBT-Bu** around 1020 cm^{-1} to ketal formation (C-O stretch). From the FTIR data, it appears that the ketal formation is somewhat closer to completion for **BTT-DTBT-Bu** than for **BTT-DTBT-Me**, which is most likely related to the solubility of the three polymers. While the very poor solubility of **BTT-DTBT-CO** and the limited solubility of **BTT-DTBT-Me** can impair the degree of conversion from ketone to 2,2-dimethyltrimethylene ketal, it is conceivable that the improved solubility of **BTT-DTBT-Bu** will aid the formation of the 2,2-dibutyltrimethylene ketal substantially.

Figure 2. Attenuated total reflectance FTIR spectra of powders of **BTT-DTBT-CO** (black line), **BTT-DTBT-Me** (red line) and **BTT-DTBT-Bu** (blue line).

UV-vis spectroscopy clearly confirms that the solubility in *o*-dichlorobenzene (ODCB) increases when going from **BTT-DTBT-CO** to **BTT-DTBT-Me** to **BTT-DTBT-Bu** as expected. At room temperature, all three polymers show comprehensive signs of aggregation in dilute ODCB solution (Figure 3a) with strong absorption bands around 680-700 nm. Upon heating the solutions to 85°C, it is evident from Figure 3b that **BTT-DTBT-CO** remains in a highly aggregated state, while the spectral contribution from aggregated species is diminished for **BTT-DTBT-Me** and even more so for **BTT-DTBT-Bu**, thus confirming the improved solubility when introducing the ketal. More detailed temperature-dependant UV-vis studies (see Supporting Information) reveals that, for **BTT-DTBT-CO** the aggregated species have an absorption maximum at 709 nm, while the fully dissolved species have an absorption maximum at 520 nm; for both **BTT-DTBT-Me** and **BTT-DTBT-Bu**, the corresponding values are 693 nm and 518 nm. UV-vis spectroscopy of thin films of the three polymers (Figure 3c) shows absorption maxima around 440 nm for the π - π^* transition and around 630 nm for the intramolecular charge-transfer (ICT) band (Table 1). The slight blue-shift of the ICT band when

going from **BTT-DTBT-CO** (630 nm) to **BTT-DTBT-Me** (627 nm) and **BTT-DTBT-Bu** (624 nm) is indicative of a slight disruption to the molecular packing upon introducing the bulkier ketal moieties as compared to the ketone functionality. The poor solubility and film-forming properties of **BTT-DTBT-CO** is reflected in the clear evidence of scattering effects in the UV-vis spectrum and therefore an ill-defined onset of absorption (ca. 1.58 eV), while the improved solubility of **BTT-DTBT-Me** and **BTT-DTBT-Bu** resulted in homogeneous films with well-defined optical band gaps of 1.65 eV and 1.66 eV, respectively.

Table 1. Optical Properties and Experimental and Calculated Energy Levels of the **BTT-DTBT** Polymers

	λ_{max} (nm) soln. ^a	λ_{max} (nm) film ^b	E_g (eV) exp. ^c /calc. ^d	HOMO (eV) exp. ^e /calc. ^d
BTT-DTBT-CO	429, 580	439, 630	1.58/1.64	-5.23/-4.91
BTT-DTBT-Me	419, 568	441, 627	1.65/1.59	-5.06/-4.67
BTT-DTBT-Bu	409, 558	441, 624	1.66/1.59	-5.03/-4.67

^a Measured in dilute *o*-dichlorobenzene solution at 85°C. ^b Spin-coated from *o*-dichlorobenzene solution. ^c Estimated from the optical absorption onset. ^d Calculated with Gaussian using the B3LYP/6-31G* model. ^e Measured by UV-PESA (photoelectron spectroscopy in air).

Semi-empirical calculations (Gaussian, Table 1 and Supporting Information) estimated the band gap of **BTT-DTBT-Me** and **BTT-DTBT-Bu** to be slightly narrower than that of **BTT-DTBT-CO**. This can be rationalized by the electron-donating character of the ketal group and thus a slightly stronger donor-acceptor interaction between the electron-rich dithieno-BTT unit and the electron-deficient BT unit. The UV-vis data, on the other hand, indicate a narrower optical band gap for **BTT-DTBT-CO** than for the two ketal polymers (as well as a red-shifted

absorption band for the aggregated species), which is most likely related to stronger intermolecular interactions and improved backbone coplanarity in the case of the less sterically demanding ketone functionality as also mentioned above. The semi-empirical calculations additionally predict – independent of the functionalisation of the ketone-functionality – the highest occupied molecular orbitals (HOMOs) to be distributed in a delocalised fashion along the polymer backbone, while the lowest unoccupied molecular orbitals (LUMOs) are localised on the electron-deficient BT units. This is a commonly observed feature of donor-acceptor type copolymers.⁵

Photoelectron spectroscopy in air was used to determine the highest occupied molecular orbital (HOMO) levels of the polymer thin films (Table 1). The electron-rich ketal group is responsible for a relatively high HOMO level around -5.05 eV for **BTT-DTBT-Me** and **BTT-DTBT-Bu**, while the electron-withdrawing keto-group accounts for the lower HOMO level of -5.23 eV for **BTT-DTBT-CO**. These values are corroborated by the semi-empirical calculations, which also predict a shift of around 0.2 eV when converting the ketone to the ketal. The LUMO levels of the polymers can be estimated from the experimental HOMO energies and the optical band gaps. Using that estimation, a LUMO level of -3.65 eV is found for **BTT-DTBT-CO**, while **BTT-DTBT-Me** and **BTT-DTBT-Bu** both have LUMO levels around -3.40 eV. We note that the measured frontier energy levels of the studied polymers are ideally positioned for highly efficient OPV devices as predicted in theoretical work by both Scharber and Kirkpatrick.^{13,14}

Figure 3. UV-vis spectroscopy for dilute ODCB solutions (3.3×10^{-5} M) recorded at 15°C (A) and 85°C (B) and for thin films spin-cast from ODCB solution (5 mg/mL) (C) of **BTT-DTBT-CO** (black line), **BTT-DTBT-Me** (red line) and **BTT-DTBT-Bu** (blue line).

Having established the fundamental properties of these three new BTT-polymers, attention was turned to BHJ OPV devices with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the acceptor material using a conventional device configuration and a 1:2 polymer:PC₇₁BM blend ratio as this was previously established to be the best blend ratio for these systems.¹¹ The limited solubility of **BTT-DTBT-CO** meant that no working OPV devices could be obtained with this material. **BTT-DTBT-Me** and **BTT-DTBT-Bu**, on the other hand, both gave decent power conversion efficiencies (PCEs) around 1.6% emphasizing the drastic improvement upon post-polymerisation ketalization (Table 2). The current-voltage (J-V) curves of two devices with **BTT-DTBT-Me** and **BTT-DTBT-Bu** are depicted in Figure 4A and they illustrate that while **BTT-DTBT-Me** affords a slightly higher fill factor (FF) than **BTT-DTBT-Bu**, the device with **BTT-DTBT-Bu** is compensated by a slightly higher short-circuit current (J_{sc}). Following the recent report from Lan and co-workers,¹⁵ where optimal OPV device performance of a series of BTT-polymers were obtained with a 1:1.5 polymer:PC₇₁BM blend cast from ODCB and annealed at 150°C, these conditions were also tested for the polymers studied herein. Before annealing, the device performance was virtually unaffected by the change in device fabrication conditions (a PCE of 1.61% was observed for **BTT-DTBT-Bu**), while thermal annealing at 150°C afforded a slightly improved PCE of 1.97% for **BTT-DTBT-Bu** (Figure 4B, Table 2). The external quantum efficiency (EQE) spectra are depicted in Figure 4C; a broad spectral response extending to 750 nm is observed, which is in good agreement with the absorption profile of the polymers. The higher J_{sc} of **BTT-DTBT-Bu**, in particular upon annealing, is clearly reflected in the significantly higher EQE values as compared to those of **BTT-DTBT-Me**. Again, it is important to stress that these three polymers all have the same degree of

polymerisation, which means that the observed differences in device performance is directly related to the variations of the solubilising side chain.

Figure 4. J–V characteristics (A, B) and EQE spectra (C) of the polymer:PC₇₁BM devices under 100 mW/cm² AM1.5G simulated solar illumination; **BTT-DTBT-Me** (red line) and **BTT-DTBT-Bu** (blue line). The photoactive layers were prepared either with a blend ratio of 1:2 (polymer:PC₇₁BM) by spin-coating from a 4:1 solvent mixture of chloroform:ODCB (4A, left), or with a blend ratio of 1:1.5 (polymer:PC₇₁BM) from neat ODCB (4B, right) and annealed at 150°C for 20 minutes.

Table 2. Photovoltaic Properties of the **BTT-DTBT** Polymers

	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
BTT-DTBT-CO	– ^a	– ^a	– ^a	– ^a
BTT-DTBT-Me^b	0.71	4.76	0.48	1.63
BTT-DTBT-Bu^b	0.71	5.48	0.43	1.67
BTT-DTBT-Bu^c	0.77	5.52	0.38	1.61
BTT-DTBT-Bu^{c,d}	0.77	6.91	0.37	1.97

^aNo working device could be obtained with **BTT-DTBT-CO**. The device configuration was ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Ag. ^bThe photoactive layer was prepared with a blend ratio of 1:2 (polymer:PC₇₁BM) by spin-coating from a 4:1 solvent mixture of chloroform:ODCB. ^cThe photoactive layer was prepared with a blend ratio of 1:1.5 (polymer:PC₇₁BM) by spin-coating from ODCB. ^dAnnealed at 150°C for 20 minutes.

Figure 5. AFM phase (left) and height (right) images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the photoactive blend for **BTT-DTBT-Me** (top) and **BTT-DTBT-Bu** (bottom).

The surface morphology of the photoactive blends was investigated with atomic force microscopy (AFM) and the resulting micrographs are depicted in Figure 5. While local areas with a beneficial mixing of polymer and fullerene can be observed for both **BTT-DTBT-Me** and **BTT-DTBT-Bu** as evident from Figure 5, it is also evident from larger area AFM scans as well as optical micrographs (see Supporting Information) that large agglomerates are formed upon spin-coating. This non-homogeneity on a macroscopic level is most likely responsible for the moderate device performance.

In conclusion, we have developed an efficient post-polymerization ketalisation approach that can be applied as a versatile tool to further modify pi-conjugated polymers with a ketone (or aldehyde) functionality. The ketal moiety introduces an additional avenue for altering the alkyl chain density and thus the polymer solubility, which is of course of paramount importance for the solution processing of organic semiconducting materials. Moreover, focusing on OPV applications, the easily accessible ketal functionality provides an additional means to influence and control the blend morphology with the acceptor material and thus improve the photovoltaic device performance of BHJ solar cells without having to repeat laborious polymer syntheses. Importantly, as this structural modification is carried out after the polymerization step, the resulting ketal derivatives can be directly compared to each other and their ketone precursors unambiguously without interfering effects from variations in the degree of polymerization.

Herein, we have illustrated the significance of this novel approach by investigating the **BTT-DTBT-CO** polymer. Despite desirable characteristics including a broad optical absorption from 400 nm to 800 nm and ideally-positioned frontier energy levels,¹⁴ the polymer's poor solubility prevents the formation of a photoactive bulk heterojunction with PC₇₁BM. We have resolved this by converting the **BTT-DTBT-CO** polymer first to the 2,2-dimethyltrimethylene ketal **BTT-DTBT-Me** and subsequently to the 2,2-dibutyl analogue **BTT-DTBT-Bu**. With both these ketal derivatives, the successful preparation of OPV devices with efficiencies approaching 2% clearly highlights the potential of this novel approach for the optimization of organic photovoltaic materials.

ASSOCIATED CONTENT

Supporting Information. Images of Gaussian-predicted frontier orbital distributions, temperature-dependant UV-vis spectra, NMR spectra, optical micrographs and AFM images of blend films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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