ORGANIC
LETTERS

2011
Vol. 13, No. 9
2414–2417

Benzotrithiophene - A Planar, Electron-Rich Building Block for Organic Semiconductors

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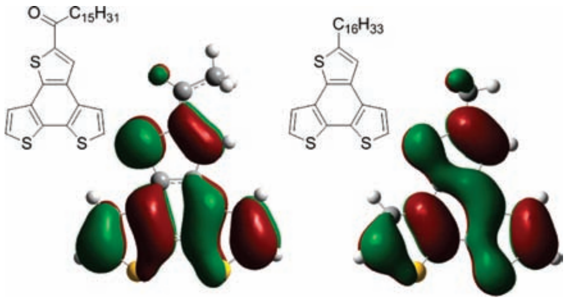
Received March 11, 2011

ABSTRACT



Several functionalized benzo[1,2-*b*:3,4-*b*′:5,6-*d*″]trithiophenes have been synthesized and characterized. The fully planar and highly electron-rich material shows great promise as the donor constituent in donor−acceptor type copolymers for use in organic electronics. As a proof of concept, a copolymer with the electron acceptor, 2,1,3-benzothiadiazole, has been prepared. Side-chain modifications have been employed to adjust both the electron-rich character of the monomer and the solubility and processability of the polymer.

The development of polymeric electron donor materials to be used in conjunction with fullerene acceptors for bulk heterojunction (BHJ) organic photovoltaic (OPV) devices has received much attention over recent years, and steady progress has been reported with power conversion efficiencies (PCEs) approaching 8%.[1,2] The most commonly used approach for obtaining suitable donor materials with broad absorption characteristics to match the solar spectrum and frontier energy levels adjusted to allow efficient electron transfer to the acceptor has been donor−acceptor (D−A) copolymers. Here an intramolecular charge transfer (ICT) transition broadens the absorption spectrum and narrows the HOMO−LUMO band gap. In addition to combining existing donor and acceptor moieties to form new D−A copolymers, it is also important to develop new donor and acceptor structures to improve the understanding and performance of OPVs. Here we report on an electron-rich benzotrithiophene structure that not only holds promise as a suitable donor constituent in D−A copolymers for use in heterojunction blend organic photovoltaics (OPVs) but also has the versatility to be employed in the pristine copolymer form as a hole transporting semiconductor in organic field effect transistors (OFETs).

Whereas benzodithiophene (**BDT**, Figure 1) has proven to be one of the most useful donor moieties in high performing photovoltaic devices with fullerene acceptors,[1b−e] very little has been reported in the literature on benzotrithiophenes, and so far only the C_{3h}-symmetrical isomer (**BTT-sym**) has been tested in optoelectronic materials applications.[3,4] In contrast to **BTT-sym** (where the sulfur atoms are arranged meta with regard to the benzene unit), the asymmetric analogue (**BTT-asym**) depicted in Figure 1 allows, in similarity to **BDT**, for a direct conjugation pathway between the two free α-positions with the

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10.1021/ol200643z

third fused thiophene bearing a solubilizing side chain and contributing extra electron density to the aromatic backbone. We believe that the extended aromatic core will be advantageous for intermolecular π-stacking and charge transport, and we furthermore note that Müllen and coworkers have found this particular bonding geometry to cause an optimal backbone curvature for a polymer when considering the trade-off between improving solubility (high degree of curvature advantageous) and maximizing charge mobility (high degree of linearity advantageous).[5]

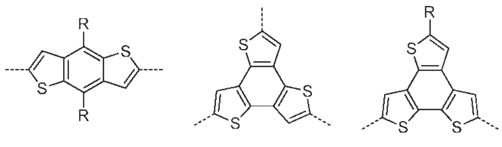
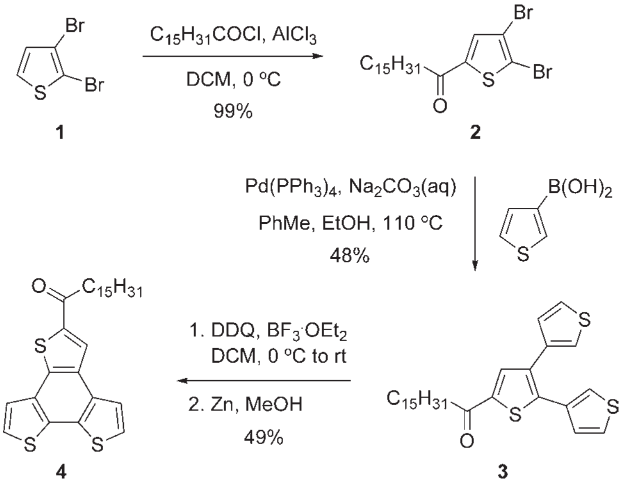


Figure 1. Structures of **BDT** (benzo[1,2-*b*:4,5-*b*′]dithiophene), **BTT-sym** (benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene), and **BTT-asym** (benzo[1,2-*b*:3,4-*b*′:5,6-*d*″]trithiophene).

As shown in Scheme 1, the aromatic core was synthesized in three steps in a good overall yield; starting from 2,3-dibromothiophene (**1**), a solubilizing side chain was incorporated by a Friedel–Crafts acylation and the resulting ketone (**2**) was subjected to a Suzuki–Miyaura cross-coupling with thiophene-3-boronic acid to assemble the trithiophene system (**3**), which was subsequently ring-closed oxidatively with DDQ to form the benzo[1,2-*b*:3,4-*b*′:5,6-*d*″]trithiophene (**4**).[6] Compound **4** could also be obtained by dibrominating **3** with NBS in DMF followed by a copper-mediated Ullmann coupling, but the yield was very low due to the competing debromination and a low-yielding purification process.

Scheme 1. Synthesis of the Benzotrithiophene Core



When a shorter acyl chloride ($C_8H_{17}COCl$) was used in the first step, a single crystal of the resulting nonanoyl-functionalized BTT core was obtained from slow evaporation of a dichloromethane/methanol solution, and X-ray diffraction confirmed unambiguously the formation of this novel aromatic molecule. The crystallographic structure depicted in Figure 2 illustrates as expected the fully planar geometry of the aromatic core. Moreover, we note that the bonding geometry for extending the conjugated system through the two unsubstituted α-positions is associated with a *ca.* 140° bend, which is similar to the best performing material in the aforementioned study of backbone curvature in polythiophenes.[5]

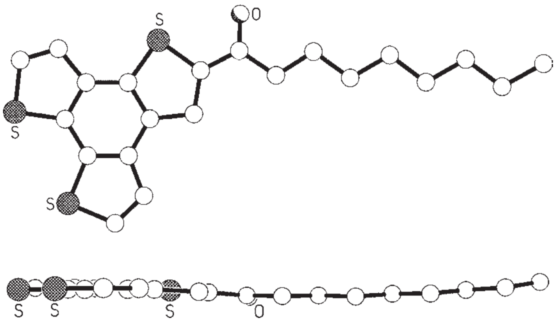


Figure 2. Molecular structure of one (A) of the six crystallographically independent molecules present in the crystals of **nonanoyl-BTT** in top view (top) and side view (bottom). See Supporting Information for more details on the crystallography.

As illustrated in Scheme 2, the acyl-functionalized BTT (**4**) is easily converted to the corresponding alkyl-BTT (**5**) using the Huang–Minlon modification of the Wolff–Kishner reduction. With the aim of incorporating these two new structures into π-conjugated materials, we were particularly interested in the dibrominated species (**6**–**7**). The electron-withdrawing acyl substituent slightly deactivates **4** toward bromination, but the reaction proceeded smoothly and regioselectively with NBS in DMF at 50 °C to give **6** in a moderate yield. The bromination of **5** with the electron-donating alkyl substituent, on the other hand, proved very difficult to control; even at 0 °C formation of isomers prevailed and different solvents, reaction times, and temperatures did not improve this unexpected problem with regioselectivity.

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(5) Rieger, R.; Beckmann, D.; Mavrinskiy, A.; Kastler, M.; Mullen, K. *Chem. Mater.* **2010**, *22*, 5314.

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Scheme 2. Initial Synthetic Strategy for Obtaining Two Dibrominated Benzotrithiophene Derivatives

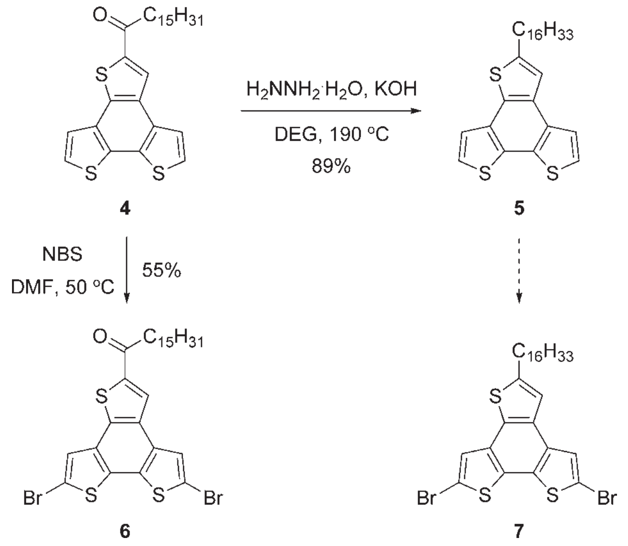


Figure 3 displays the molecular geometry and the HOMO energy distribution calculated for **5** at the B3LYP/6-31G* level; the charge density is clearly higher at the two free α-positions than at the three *β*-positions as expected. This supports the assumption that an electrophilic substitution reaction should be selective at the two free α-positions, in clear contradiction to our experimental observations.

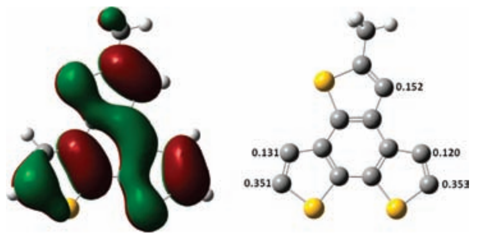


Figure 3. Energy-minimized structure (B3LYP/6-31G*) of a methyl-substituted BTT with a visualization of the HOMO energy distribution (left) and numerical charge densities on sites available for direct bromination (right).

To understand this unanticipated problem with regioselectivity in more depth, we decided to identify the brominated species that formed during the reaction. To our surprise, we found that when treated with only 1 equiv of NBS, one monobrominated isomer (**8**, Figure 4) formed almost exclusively. Upon further bromination, this species would react to give several compounds with the two depicted dibromides, **7** and **9**, formed predominantly; the ratio between **7** and **9** varied greatly with reaction temperature and time, but no better selectivity than 80:20 was achieved. These findings indicate that the 8-position (see Figure 4 for atom numbering) is most reactive toward electrophilic reagents and thereafter the 2- and 6-positions, which are almost equally reactive under the investigated reaction conditions. We emphasize that no experiments using more regioselective brominating agents were attempted at this point.

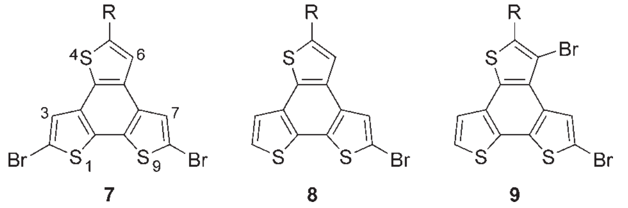


Figure 4. Mono- and dibrominated species observed: 2,8-dibromo-BTT (**7**), 8-bromo-BTT (**8**), and 6,8-dibromo-BTT (**9**).

The brominated species depicted in Figure 4 were unambiguously identified by NMR spectroscopy as illustrated in Figure 5. The 8-bromo-derivative (**8**) showed two singlets in the aromatic region of the ^{1}H NMR spectrum (Figure 5, top left) from H^6 and H^7 and two close-lying doublets from H^2 and H^3. In ^{13}C NMR (Figure 5, top right), the aromatic region containing the hydrogen- and bromine-bearing carbon atoms has four C−H carbons and one C−Br carbon (112 ppm) as expected. A nuclear Overhauser effect (NOE) between the two proton singlets (H^6 and H^7) and a heteronuclear multiple bond correlation (HMBC) between H^7 and C^8 confirm that the structure is indeed the 8-bromo-derivative (**8**). The 6,8-dibromo-BTT (**9**, Figure 5 middle) has one aromatic singlet shifted far downfield in the ^{1}H NMR spectrum (H^7), and the coupled AB spin system (H^2 and H^3) has almost merged to a singlet (7.4 ppm). The ^{13}C

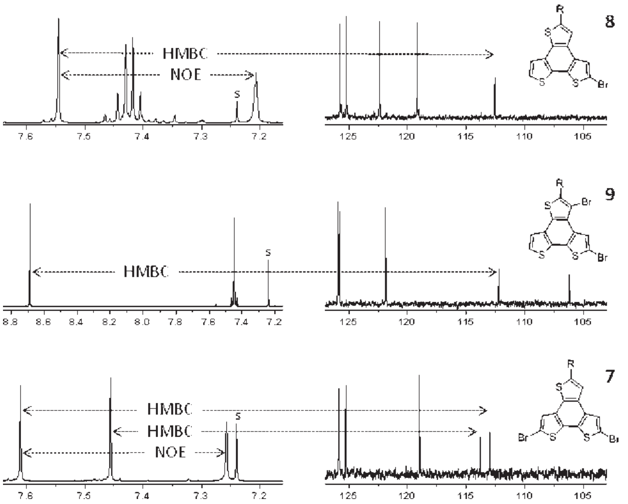
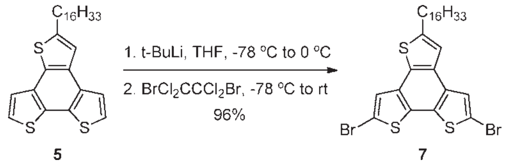


Figure 5. ^{1}H NMR (left) and ^{13}C NMR (right) of the identified products from the NBS bromination with observed long-range couplings indicated (see Supporting Information for all 2D NMR spectra).

NMR spectrum of **9** has three aromatic C–H carbons and two C–Br signals with C^8 (112 ppm) showing a long-range coupling (HMBC) to H^7. Finally, in the bottom part of Figure 5, the ^1H and ^{13}C NMR spectra of the desired 2,8-dibrominated derivative (**7**) show, as expected, three aromatic singlets from H^3, H^6, and H^7 with an NOE signal between H^6 and H^7, while both H^3 and H^7 show long-range couplings to the two bromine-bearing carbons (C^2 and C^8, 113–114 ppm).

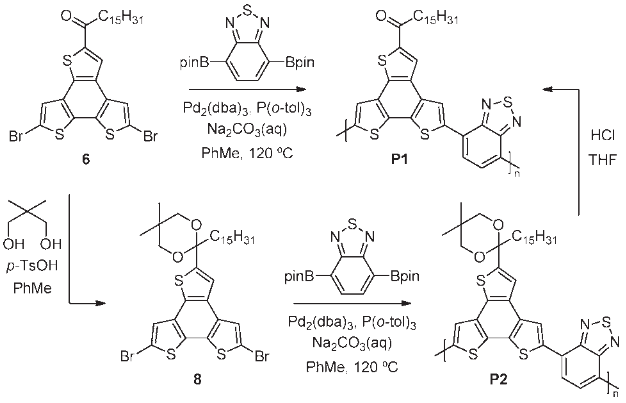
An alternative method for the synthesis of the target compound (**7**) was successfully developed by forming the 2,8-dilithiated BTT selectively with *tert*-butyllithium and subsequently reacting the dilithiated species with 1,2-dibromotetrachloroethane to form the 2,8-dibrominated compound (**7**) very cleanly and in excellent yield as depicted in Scheme 3.

Scheme 3. Improved Bromination Procedure



Attempts to copolymerize the dibrominated monomers **6** and **7** with the diboronic ester of 2,1,3-benzothiadiazole under Suzuki–Miyaura coupling conditions to obtain the acyl-functionalized copolymer **P1** (Scheme 4) and the alkyl-functionalized copolymer (not shown) have been complicated by a lack of solubility; both polymers were completely intractable even when only a moderate degree of polymerization (> 10) was achieved. In an attempt to extend the solubility of the growing polymer chain during polymerization and achieve a higher molecular weight polymer, we converted the ketone (**6**) to the more soluble neopentyl ketal (**10**) and, thus, succeeded in preparing **P1** from the ketal-derivative **P2**, as depicted in Scheme 4. It was also possible to solubilize the lower molecular weight **P1** polymer prepared from **6** by converting it to the fully soluble polymer **P2**. When synthesized from the ketone, **P1** was obtained with a number-average molecular weight, M_n, of 9.1 kDa; solubilizing the monomer (forming ketal-derivative **10**), on the other hand, gives access to **P1** with an M_n of 16.5 kDa. In solution, **P2** has an absorption maximum around 550 nm, and a red shift of 10–20 nm is observed when going from solution to the solid state (see Supporting Information for UV–vis spectra).

Scheme 4. Synthesis of Soluble Benzothiadiazole Copolymers



In conclusion, we have designed and synthesized an aromatic structure comprising three thiophene units fused to a central benzene ring to give a fully planar and highly electron-rich aromatic system with ideal backbone curvature for good charge mobility, making it a promising candidate as a donor component in D–A copolymers for OPVs. We are aware that the asymmetric nature of the molecule can result in the formation of an isotactic, or regiorandom, polymer, but we note from the crystallographic structure that the solubilizing substituent will be arranged perpendicular to the polymer backbone, so we do not expect the isotacticity to affect the morphology and packing unfavorably. Interestingly, the two monomers, **4** and **5**, are anticipated to have significantly different electron-donating abilities, as manifested in the different reactivities toward electrophilic reagents, which could provide a versatile means for fine-tuning the energy levels in the resulting D–A systems. This obviously also holds for the ketalization of the ketone; we can drastically change the solubility and simultaneously adjust the electron-donating effect significantly.

Acknowledgment. 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 246 International Collaborative Research Program of Gyeonggi-do, 247 Korea and the National Research Fund of Luxembourg.

Supporting Information Available. Experimental procedures and characterization data for **2–7** and **10**. 2D NMR spectra for **7–9** and UV–vis spectra for **P2**. Crystal data and full crystallographic information for **nonanoyl-BTT** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.