

Making Benzotrithiophene a Stronger Electron Donor

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ABSTRACT



- 3a: R = H, R' = H
 3b: R = H, R' = C₆H₁₃
 3c: R = H, R' = C₁₂H₂₅
 3d: R = C₆H₁₃, R' = H
 3e: R = C₆H₁₃, R' = C₆H₁₃

A new member of the benzotrithiophene family, benzo[2,1-*b*:3,4-*b'*:5,6-*c'*]trithiophene (3a), and its alkyl substituted derivatives (3b–e) were synthesized and characterized. Their photophysical, electrochemical, crystallographic, and self-assembly properties were described. Thin film structures varied widely with the exact nature of the alkyl substitution pattern, with decreasing self-assembly propensity with increasing alkyl chain length. The high HOMO levels and the coplanarity of these molecules show their potential as organic semiconductors and as donor components in donor–acceptor copolymers.

Considerable interest has been focused on thiophene-based π -conjugated organic materials due to their use as promising organic semiconductors.¹ The electron-donating character of thiophene- and fused thiophene-based derivatives qualifies them as donor units to construct donor–acceptor (D–A) copolymers, which has proven to be an effective strategy for tailoring the properties of conjugated polymers for applications in organic photovoltaics (OPV),² organic field-effect transistor (OFET),³ organic light-emitting diodes (OLEDs),⁴ and electrochromics.⁵

Many efforts have been made to develop electron-rich thiophene-containing donors such as thienothiophenes, benzodithiophenes, and β,β' -bridged bithiophenes (see Figure 1).^{2,3,6} In addition to employing these existing donors to construct D–A copolymers, it is also significant to design and synthesize new donors. In the past, several papers about a class of new donor units, namely, benzotrithiophenes (BTT), have been reported.⁷ BTT is a fused terthiophene with a sulfur-rich, planar and extended π -system. According

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to the positions of the sulfur atoms, there are seven possible isomeric members of the **BTT** family, as shown in Figure 2. Among these isomers, **ccc-BTT** (three *c*-fused thiophene rings, D_{3d} symmetry),^{7a,b} **bbb-BTT-1** (three *b*-fused thiophene rings, C_{3h} symmetry),^{7c-e} and **bbb-BTT-2** (three *b*-fused thiophene rings, asymmetry)^{7d} have been synthesized by oxidative photocyclization or intermolecular cyclic condensation. Especially, **bbb-BTT-1** was studied intensively and has been used as a core for the construction of star-shaped oligomers, polymers, and dendrimers.^{7f-h}

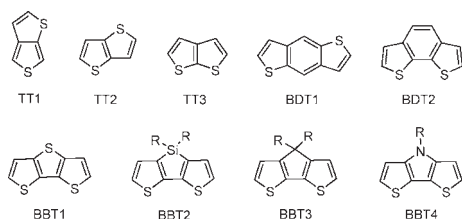


Figure 1. Molecular structures of several widely reported thiophene-fused donors. Thienothiophenes (**TT**): thieno[3,4-*b*]thiophene (**TT1**), thieno[3,2-*b*]thiophene (**TT2**), and thieno[2,3-*b*]thiophene (**TT3**). Benzodithiophene (**BDT**): benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDT1**) and benzo[2,1-*b*:3,4-*b'*]dithiophene (**BDT2**). β,β' -Bridged bithiophenes (**BBT**): dithienothiophenes (**BBT1**), dithieno[3,2-*b*:2',3'-*d*]silole (**BBT2**), cyclopentadithiophene (**BBT3**), and dithieno[3,2-*b*:2',3'-*d*]pyrrole (**BBT4**).

The alkyl substituted **bbb-BTT-2** has also been synthesized and used as a donor component in a D–A copolymer.⁷ⁱ

However, there is hardly any report on other **BTT** isomers containing one or two *c*-fused thiophene rings (i.e., **bcc-BTT**, **bbc-BTT1**, **bbc-BTT2** and **bbc-BTT3** in Figure 2), probably owing to the tougher synthesis compared with the isomers containing three *b*- or *c*-fused thiophene rings mentioned above. Furthermore, according to DFT calculations as shown in Figure 2, **bbc-BTT-3** with C_{2v} symmetry possesses a higher HOMO level than all other isomers, which provides a theoretical support for **bbc-BTT-3** as an electron-rich donor unit. Moreover, compared with the linear thiophene-based donors such as the above-mentioned benzodithiophene, the fully planar and extended aromatic system of **bbc-BTT-3** should facilitate the formation of highly ordered one-dimensional (1D) structures via a self-organization process, which is particularly important for OFET application.⁸ Additionally, this **BTT** isomer has four active positions, which allows further functionalization to extend the molecular system. In this contribution, we report the synthesis and characterization of a new member of the benzotrithiophene family, benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene (**bbc-BTT-3**), and a series of its derivatives with alkyl substituents. Their

optical, electrochemical, crystallographic and self-assembly properties are investigated. The results show that this **BTT** isomer can be used not only as organic semiconductor but also as a donor component in D–A copolymers.

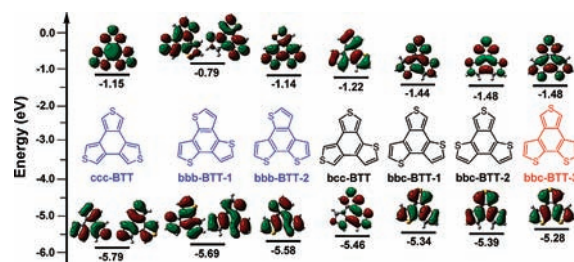


Figure 2. Molecular structures of seven benzotrithiophene isomers: benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]trithiophene (**ccc-BTT**), benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**bbb-BTT-1**), benzo[2,1-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**bbb-BTT-2**), benzo[1,2-*b*:3,4-*c'*:5,6-*c''*]trithiophene (**bcc-BTT**), benzo[1,2-*b*:4,3-*b'*:5,6-*c''*]trithiophene (**bbc-BTT-1**), benzo[1,2-*b*:4,3-*b'*:5,6-*c''*]trithiophene (**bbc-BTT-2**), benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene (**bbc-BTT-3**) and their calculated frontier orbitals (DFT-B3LYP 6-31 G*). Among them, HOMO level of **ccc-BTT** is doubly degenerate and LUMO is nondegenerate; both HOMO and LUMO levels of **bbb-BTT-1** are doubly degenerate; energy levels of all the others are nondegenerate. The HOMO (lower) and LUMO (upper) orbital energies are given in eV.

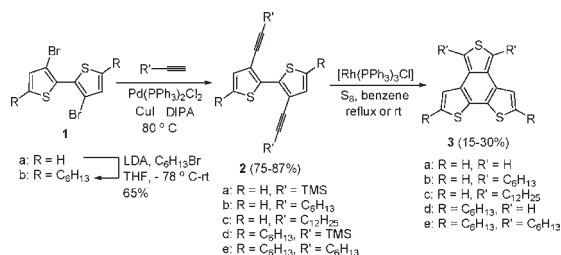
The target compound **bbc-BTT-3** (**3a**) and its alkyl substituted derivatives **3b–e** were synthesized according to the procedures depicted in Scheme 1. Starting from 3,3'-dibromo-2,2'-bithiophene (**1a**), which was synthesized according to a literature procedure,^{6c} alkylated dibromothiophene **1b** was obtained by selective lithiation with LDA and subsequent addition of *n*-hexylbromide. The TMS or alkyl substituted alkynes were introduced by Sonogashira reactions to achieve **2a–e** in high yields. Then, they were treated with tris(triphenylphosphine) rhodium(I) chloride (Rh(PPh₃)₃Cl, Wilkinson catalyst) to produce rhodium complex intermediates that were converted to the target compounds **3a–e** by adding sulfur powder to form the third thiophene ring.⁹ We found that (i) Rh(PPh₃)₃Cl needed to be added in equimolar amounts with substrates **2a–e**; (ii) the ring-closure reactions from **2a** and **2d** with TMS groups to **3a** and **3d** required refluxing in benzene while the reactions from **2b**, **2c** and **2e** with alkyl chains to **3b**, **3c** and **3e** proceeded smoothly in benzene at room temperature; and (iii) for the purification of **3a**, the TMS groups were removed mostly during the silica-gel column separation and three species **3a** (20%), 4-trimethylsilylbenzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene with one TMS (4%), and 4,6-di(trimethylsilyl)-benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene with two TMS (8%) were obtained, which made target product **3a** achievable directly by the column separation. The substances with remaining TMS groups can be treated with trifluoroacetic acid in CHCl₃ at room

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temperature to remove TMS to give **3a**. The purification and removal of TMS for **3d** were performed in the same manner. **bbb-BTT-1** and **bbb-BTT-2** were accessible by oxidative photocyclization, as mentioned above, but this method could not be applied to **bbc-BTT-3** as described by Kagan and Perrine et al.^{7d} Therefore, the approach we present here is so far the only feasible way to synthesize functionalized **bbc-BTT-3**.

Scheme 1. Synthetic Routes of Compounds **3a–e**



All the compounds showed good thermal stability as measured by thermogravimetric analysis (TGA). The temperatures with 5% weight loss for **3a–e** were 241, 262, 318, 335, and 338 °C, respectively (see Figure S1, SI). Differential scanning calorimetry (DSC) measurements showed only one peak upon cooling of compounds **3a**, **3c** and **3e** (no signal was detected for **3d**), implying a phase transition to a crystalline state. For compound **3b**, however, two phase transitions at 7.5 and 29.5 °C during the cooling process were observed indicating the formation of a liquid crystal at room temperature, which was further proven by birefringence phenomenon as observed under polarized light (see details in SI).

The UV–vis absorptions and PL emissions of compounds **3a–e** are shown in Figure 3 and the data are listed in Table 1. The longest wavelength absorption of **3a** occurs at 360 nm, which reflects an evident red-shift compared to other reported **BTT** isomers (286 nm for **bbb-BTT-1**, 320 nm for **ccc-BTT** and 335 nm for **bbb-BTT-2**),^{7a,d} indicating that **3a** possesses an enhanced π -electron delocalization and a narrower energy gap, in agreement with the results from DFT calculations. The maxima of absorptions of **3b–e** are bathochromically shifted compared with **3a**, particularly the tetraalkylated **3e** exhibits a red-shift of 32 nm, which is attributed to the weak electron-donating effect of alkyl chains. The maxima of emission wavelengths of **3a–e** shift from 395 to 442 nm dependent on the positions and numbers of alkyl chains. Compounds **3b** and **3c** show the same emission spectra. All compounds emit blue light, which is tunable by the alkyl chains from deep blue to light blue. Moreover, **3a** is the only member of the reported **BTT** isomers that emits fluorescence in the visible range.

Cyclic voltammetry (CV) was carried out to detect the HOMO levels of compounds **3a–e** (see details in SI). The HOMO energy levels are estimated from the onsets of the oxidation peaks to be -5.30 , -5.29 , -5.29 , -5.22 , and -5.14 eV for **3a–e**, respectively. The LUMO energy levels are estimated from the optical gaps that are determined

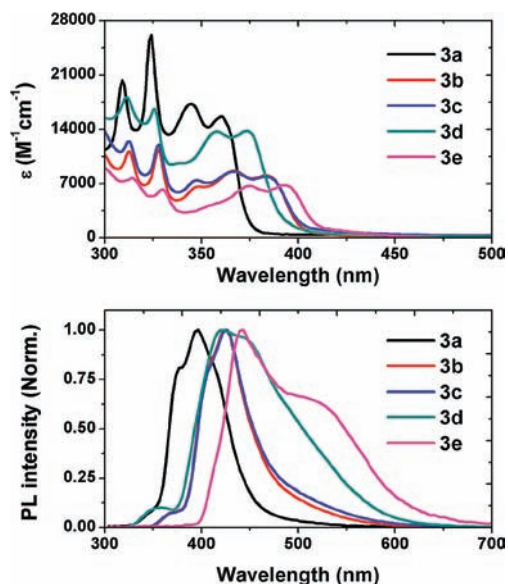


Figure 3. UV–vis absorption (top) and fluorescence (bottom) spectra of compounds **3a–e** in chloroform solution (10^{-5} M).

from the onsets of absorption spectra and the results are summarized in Table 1. The HOMO levels of **3a**, **3b** and **3c** are almost the same while the other two show higher values. The high lying HOMO level of **3e** leads to easy oxidation in air as witnessed by the color change of its solution. This indicates that the alkyl chains at 4,6-positions (**3b** and **3c**) have a small influence on the HOMO level while those at 2,8-positions (**3d** and **3e**) shift the HOMO level upward. The enhanced π -electron delocalization and high HOMO levels as well as the good solubility of **3b** and **3c** with long alkyl chains strongly suggest their use as donor components in D–A copolymers.⁷¹ Such work is underway in our group.

Single crystals, obtained by slow evaporation of a solution of **3b** or **3c** from a dichloromethane/ethanol mixture, have been analyzed by X-ray diffraction. The crystallographic structures are depicted in Figure 4. Both of them illustrate as expected the nearly planar geometry of the conjugated core. The dihedral angle in the central six-membered ring is only 2.91° for **3b** and 1.97° for **3c**. The alkyl chains at the 4,6-positions lie in the same plane with the skeleton and stretch out along an angle of *ca.* 55° with respect to the C_2 symmetry axis. Moreover, when introducing **3b** or **3c** into a polymer main chain through 2,8-positions, a *ca.* 130° bend between the C2–C8 connection should cause a backbone curvature, which could guarantee an optimum compromise between solubility and formation of highly ordered films, as described in our previous findings.^{6a} For **3b** and **3c**, the crystals form layer-by-layer structures but no π – π stacking exists owing to the steric effect of the long alkyl chains. An overlap in space occurs between aromatic cores and aliphatic chains rather than between aromatic cores of adjacent layers (see Figure S4, SI). In each layer, the distance between two aromatic cores increases with increasing length of the alkyl

Table 1. Optical, Electrochemical, and Thermal Data for Compounds **3a–e**

compd	ϵ^a ($M^{-1}cm^{-1}$)	λ_{max}^{absb} (nm)	λ_{max}^{PLb} (nm)	E_{ox}^{onset} (V)	E_{HOMO}^c (eV)	E_g^{optd} (eV)	E_{LUMO}^e (eV)	T_d^f (°C)
3a	15700	360 (340) ^g	395 (378)	0.88	-5.30	3.31	-1.99	241
3b	8000	383 (367)	425	0.87	-5.29	3.09	-2.20	262
3c	7900	383 (367)	425	0.87	-5.29	3.09	-2.20	318
3d	13800	373 (358)	423 (445)	0.80	-5.22	3.17	-2.05	335
3e	6800	393 (375)	442 (510)	0.72	-5.14	3.03	-2.11	338

^a Measured at λ_{max}^{abs} . ^b Measured in 10^{-5} M chloroform solution, upon excitation at λ_{max}^{abs} for every compound. ^c Estimated based on the empirical formula $E_{HOMO} = -(4.8 - E_{Fc}^{onset} + E_{ox}^{onset})$. ^d Optical energy gap calculated according to the absorption edge. ^e Calculated based on the formula $E_{LUMO} = -(E_{HOMO} - E_g^{opt})$. ^f Temperature of decomposition corresponding to 5% weight loss from TGA analysis under N_2 with a heating rate of $10^\circ C/min$. ^g Peaks that appear as shoulders or weak bands are indicated in parentheses.

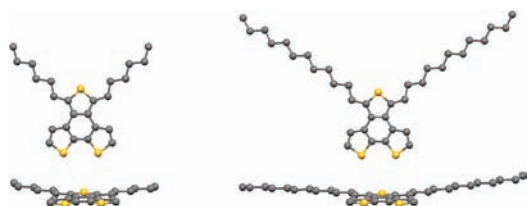


Figure 4. X-ray crystallographic structures of compounds **3b** (left) and **3c** (right) in top view (top) and side view (bottom). Hydrogens have been omitted for clarity.

chains. These suggest that the alkyl chains hinder the intermolecular π - π interactions.

The influence of alkyl chains on the molecular packing in compounds **3a–c** was also investigated in thin solid films prepared by drop-casting. A solution of **3a** in THF with a concentration of 0.6 mg/mL was drop-casted onto a plain SiO_2 silicon-wafer substrate at room temperature. The images obtained from optical microscopy studies are shown in Figure 5. Interestingly, more than hundreds of micrometers long microfibers are obtained from **3a** without substituents. The formation of such highly ordered 1D fibers is especially significant for the implementation in OFETs.⁸ In contrast, no such fibrous structures could be observed for **3b** and **3c** with alkyl chains when processing them under the same conditions. Instead, inhomogeneous and disordered patches appear. These results clearly reveal that the self-assembly propensity of these compounds decreased gradually with increasing length of alkyl chains. This could be attributed to the long alkyl chains preventing the approaches between molecules.

In summary, we have synthesized a new isomer of benzo-trithiophene, benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene **3a** and a series of its alkyl substituted derivatives **3b–e**. Theoretical calculations show that **3a** possesses a higher HOMO level and a narrower energy gap compared with other **BTT** isomers.



Figure 5. Optical microscopy images of the films of compounds **3a** (left), **3b** (middle), and **3c** (right) drop-casted from THF on a plain SiO_2 silicon-wafer substrate.

Optoelectronic and crystallographic studies indicate that this new isomer of **BTT** and its alkyl substituted derivatives are highly electron-rich and nearly planar aromatic systems. In particular, the compounds **3b** and **3c** with alkyl chains at 4,6-positions of benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene can provide good solubility and backbone curvature when introduced into polymer main chains, making them promising candidates as donor components to construct D–A copolymers. Interestingly, a highly ordered 1D fiber could be obtained from **3a** by the drop-casting method. The introduction of such fibrous microstructure into OFETs is currently under investigation. Our results demonstrate that benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene could be used as a new donor unit for the development of functionalized materials applied in the field of organic optoelectronics.

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Supporting Information Available. Full experimental details and characterization data. CIF files for the X-ray analysis of **3b** and **3c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.