2,6-Bis(tributyltin)benzo[1,2-*b*:5,4-*b'*]dithiophene: a new synthon for organic semiconductors

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Dedicated to Prof. Ted Sorensen on the occasion of his 75th birthday

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Abstract

A new tin-functionalized benzo[1,2-*b*:5,4-*b'*]dithiophene building block was synthesized that can provide access to a series of further extended π−conjugated materials for Organic Field-Effect Transistors (OFETs) via Stille coupling protocol, as exemplified in two cases. The *syn*-configured benzodithiophene scaffold complements the well-established (*anti*) benzo[1,2-*b*:4,5-*b'*]dithiophene unit that has already been successfully employed in OFET devices. DFT-quantum theoretical calculations on a series of organic semiconductors support the selective modification of the band gap by either changing the HOMO, the LUMO, or both. The suitability of the tin-functionalized synthon to efficiently access a variety of organic semiconductor materials with different properties was also confirmed by the study of their photophysical features.

Keywords: Organic semiconductors, oligothiophenes, ring-annelated systems, pi-conjugation, organic field-effect transistors

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Introduction

Organic π-conjugated oligomers and polymers are of growing importance, particularly in the area of alternative and efficient energy applications.[1-6] Corresponding materials have recently been used increasingly as active materials in organic field effect transistors (OTFT, OFETs),[1,2] light emitting diodes (OLEDs),[3,4] photovoltaic cells,[5] and sensory materials.[6] Due to their highly intriguing photophysical properties, one of the most extensively studied classes of π−conjugated materials are thiophene-based oligomers and polymers.[4c,7] It has been shown that functionalization of organic materials has a significant influence on their photophysical properties; materials with well-defined small band gaps are known to be accessible.[8] A great deal of attention has thus been focused on modifications of the electronic nature of the materials to get properties suitable for the desired function (e.g., high charge mobility, or electroluminescence). The band gap width, i.e., the HOMO and LUMO energy levels, and the degree of π-conjugation can be adjusted via organic transformations to tailor the optoelectronic properties of these materials and to also influence their structure.[1,2,9] The solid-state morphology of conjugated materials, in particular, plays an important role in the performance characteristics of electronic devices.[2,10] In terms of potential applications for organic electronics, pentacene is one of the first organic materials successfully used in OTFTs showing high field effect mobility and properties comparable to classic transistors that rely on amorphous silicon as active material.[2] However, as a consequence of the low solubility and poor stability of pentacene in solution, a large number of investigations to circumvent these problems have been performed.[1,2]

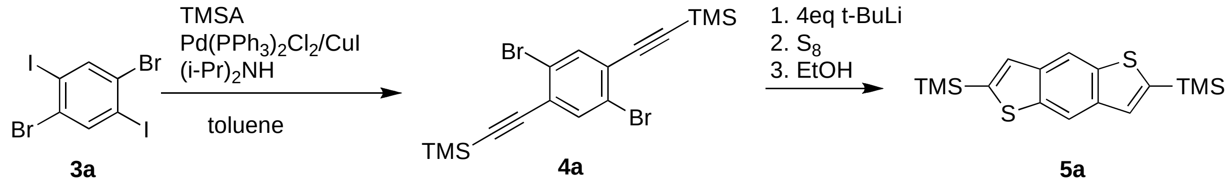
These and other investigations have revealed that fused bithiophenes with a rigidified and planar structure are generally advantageous for application in organic electronics, since they exhibit smaller HOMO-LUMO gaps and a higher degree of π-conjugation compared to simple oligo- or polythiophenes.[11-14] The benzo[1,2-*b*:4,5-*b'*]dithiophene (*anti*-BDT) building block **1** is one of the more popular components used in organic semiconductors.[15] The narrow HOMO-LUMO band gap and completely planar structure of **1** allow for herringbone (edge-to-face) arrangement in the solid state. In addition, intermolecular chalcogen-chalcogen contacts in the solid state can provide an improved carrier transport by intermolecular overlap. Its *syn*-isomer, benzo[1,2-*b*:5,4-*b'*]dithiophene (*syn*-BDT) **2**, on the other hand, is not as well known in this context.[16]

Figure 1. Benzo[1,2-*b*:4,5-*b'*]dithiophene (left) and benzo[1,2-*b*:5,4-*b'*]dithiophene (right).

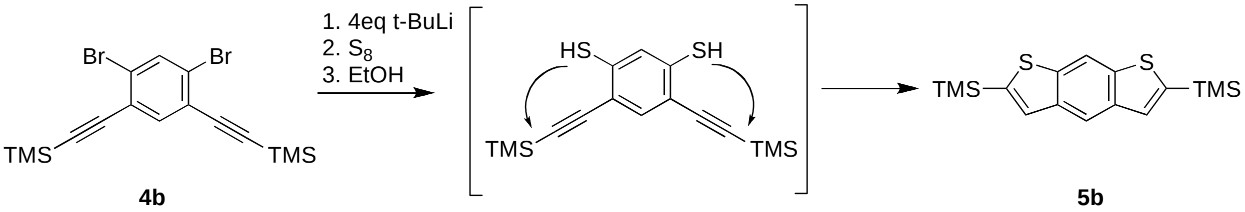
In this contribution we now report on the synthesis of a tin-functionalized *syn*-BDT that allows for the convenient synthesis of a series of extended π-conjugated materials via Stille cross-coupling protocol. This new synthon can provide efficient access to a variety of organic semiconductors, potentially applicable as OFET materials in organic electronics.

Results and Discussion

The first syntheses of *anti*-BDT **1** reported by Kossemehl *et al.*[17] and Katz *et al.*[18] are based on thiophene derivatives as precursors. Other synthetic routes start from the functionalized benzene core **3a** with TMS-acetylene *via* palladium catalyzed Cassar-Heck-Sonogashira coupling,[19] followed by intramolecular cyclization (Scheme 1).[20]



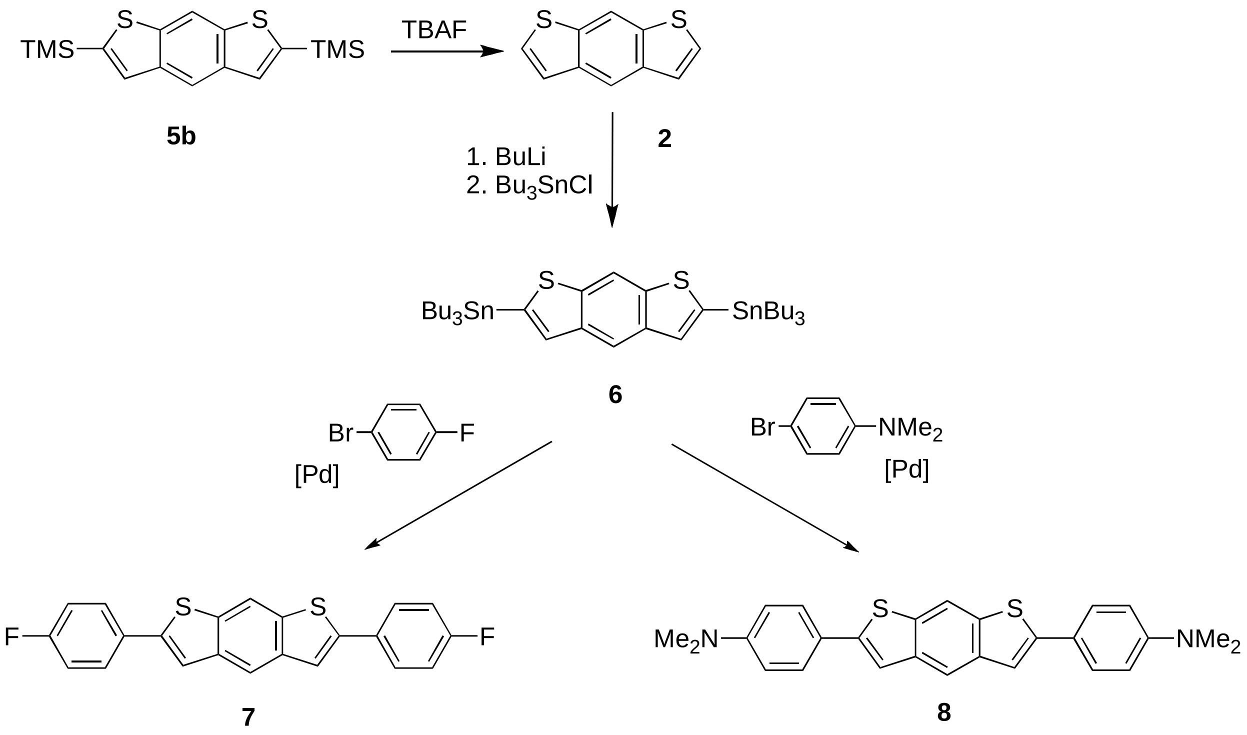
Scheme 1. Synthesis of the *anti*-BDT precursor **5a**.[15a,19]



Scheme 2. Synthesis of the *syn*-BDT precursor **5b**.

Modifying the latter literature procedure towards the *anti*-derivative **5a**,[15a] we were able to obtain the *syn*-derivative **5b** by iodination of 1,3-dibromo-benzene followed by Pd-catalyzed Cassar-Heck-Sonogashira coupling of TMS-acetylene;[19] subsequent treatment of **4b** with four equivalents of *tert.*-butyllithium provided the dilithiated intermediate that was quenched subsequently with sulfur and ethanol (Scheme 2). The resulting dithiol is not stable towards rearrangement and the trimethylsilyl functionalized *syn*-BDT **5b** is formed in situ through an intramolecular cyclization reaction, similar to the formation of the *anti*-isomer **5a**.

Notably, our first attempts to further functionalize this synthon for subsequent reactions, involved the bromination of the 2,6-positions. This functionalization was then to be utilized in a cross-coupling protocol to extend the degree of π-conjugation within our materials by introduction of various electron–donating or –withdrawing aromatic groups. However, bromination of **5b** with two equivalents of NBS in analogy to reported procedures for somewhat related dithienothiophenes[21] gave only an inseparable mixture of several brominated products. For that reason we shifted our focus towards an inversely functionalized building block suitable for cross-coupling reactions. Introduction of suitable functional groups, such as boryl (Suzuki-Miyaura) or stannyl (Stille), can usually be achieved by lithiation of the aryl and treating it with an alkoxy/hydroxy boronate or a chloro stannane.[22] To provide the necessary reactivity at our building block, desilylation with tetrabutylammonium fluoride (TBAF)[15b] was performed to provide **2** selectively. The parent *syn*-BDT compound **2** was then functionalized with two equivalents of tributyltin chloride after lithiation with n-butyllithium at -78ºC in THF to give **6** as light orange oil. This difunctionalization with tributyltin groups subsequently allowed for Stille coupling of **6** with halogenated arenes, as expected (Scheme 3).



Scheme 3. Synthesis and Stille coupling of **6**.

To provide for a representative scope of the utility of our distannylated synthon, we decided to couple **6**, with an electron-donating (p-C_6H_4-NMe_2), as well as an electron-withdrawing (p-C_6H_4-F) arene. As mentioned in the introduction, the structure of organic materials can significantly affect their performance in electronic devices and even small structural changes can have a significant effect on their optoelectronic properties. The Stille cross-coupling reactions were performed using standard conditions in toluene and $Pd(PPh_3)_4$ as catalyst.[23] After reflux conditions overnight, the products **7** and **8** could be isolated as light yellow, however, poorly soluble solids after evaporation of the solvent, washing with pentane and acetone, and subsequent sublimation. The ability to purify **7** and **8** via sublimation indicates that, although their solubility is limited, the materials can nevertheless be processed via vapor deposition techniques into future devices. Notably, **7** and **8** are also both stable under atmospheric conditions.

To determine the effects of the cross-coupled units onto the energy levels of the π-extended materials, we investigated the photophysical properties of **7** and **8** in comparison to the parent system **2**, as well as the stannylated synthon **6**. These features generally help to indicate a change in the band gap energies, as well as the nature of the excited states of the materials. The observation of fluorescence is generally a good indication that the materials have a promising band gap for organic electronics, and the wavelength of excitation/emission can be used to quantify the band gap energy. Furthermore, a small Stokes shift usually supports rigid structures that do not change much from the ground to the excited states, whereas a large Stokes shift indicates a significant portion of non-radiative processes involved upon excitation/relaxation.[25]

The BDT-core **2** itself, only shows very weak fluorescence in the UV-region of the optical spectrum, as expected. The rather small π-conjugated system does not allow for a strong emission due to the large optical band gap of 3.46 eV (estimated from the excitation spectrum) that also opens up many non-radiative relaxation pathways; on the other hand, the very small Stokes shift underscores the fairly rigid structure of **2**.[24] Introduction of the tin-groups, however, affords a noticeable fluorescence of **6**, which can be attributed to the acceptor character of the tin centers, supported by the reduced optical band gap of 2.90 eV. Compound **6** shows a blue fluorescence with an emission maximum at 450 nm and a maximum wavelength of excitation at 376 nm. The strongly increased Stokes shift of $\Delta\lambda$ = 74 nm in **6**, as compared to **2** (cf.: $\Delta\lambda$ = 19 nm), on the other hand, supports a significant amount of non-radiative pathways present in the system, due to the heavy-atom effect of the tin. In other words, although the tin-centers reduce the band gap, likely due to the participation of the Sn valence 5p atomic orbitals, the photophysical properties of **6** are still on the weak side, due to the quenching of the heavy tin atoms present in the system. In the case of the cross-coupled organic semiconductor materials **7** and **8**, however, the photophysical properties are now very pronounced with both materials showing a strong blue fluorescence in solution, but also in the solid state. Both materials exhibit optical band gaps in solution that are smaller than the one observed for **2** (**7**: 3.22 eV; **8**: 3.04 eV), but that are surprisingly larger than the tin-functionalized compound **6**. This can likely be attributed to a disruption of the π-conjugation, due to twisting of the terminal phenyl groups from planarity (see below), which is also supported by Stokes shifts of $\Delta\lambda$ = 42 nm for **7** and $\Delta\lambda$ = 43 nm for **8**. Importantly, the fluorescence data for **7** and **8** show some significant differences that arise from the character of the terminal end groups. Whereas the excitation and emission spectra for **7** show distinct vibronic side bands, indicating a very rigid molecular scaffold overall, the spectra for compound **8** show only one broad signal each. Furthermore, the value for the optical band gap of acceptor-substituted **7** is slightly blue-shifted from the value for the donor-compound **8** (see Table 1). Remarkably, both compounds show even increased fluorescence emissions in the solid state, which is rather unusual, as intermolecular interactions in the solid state usually result in a quenching of the fluorescence. However, this *aggregation-enhanced fluorescence* has been observed before in the literature,[25] and can be attributed to a hindered rotation of the cross-coupled phenyl groups due to close packing of the molecules in the solid state, eliminating non-radiative pathways. The close packing of the molecules in the solid state is also supported by the red-shifted values for excitation and emission compared to the corresponding values in solution. It should be mentioned that the red shift is significantly more pronounced in **8** where it amounts to $\Delta\lambda_{ex}$ = 71 nm and $\Delta\lambda_{em}$ = 65 nm (cf. **7**: $\Delta\lambda_{ex}$ = 49 nm and $\Delta\lambda_{em}$ = 43 nm) and leads to the smallest optical bandgap of the materials reported herein (2.65 eV). Furthermore, the excitation spectrum for **7** is extremely broad, covering the spectrum from 300 – 385 nm; excitation at λ_{ex} = 300, 350, and 385 nm, respectively, results in essentially the same emission spectrum. This observation can be attributed to a continuum of rotational isomers being present in the solid state.

Table 1. Fluorescence data (10^{-5} M in CH_2Cl_2) for the *syn*-BDT derivatives **2**, **6-8**

Compound	$\lambda_{ex}{}^a$ [nm]	$\lambda_{em}{}^b$ [nm]	Rel. intensity	Optical bandgap^c
2	330	349	weak	3.46 eV
6	376	450	medium	2.90 eV
7	298, 314, 336	378, 397, 416(sh)	strong	3.22 eV
7^d	300-385	416, 440, 469(sh), 500(sh)	very strong	3.13 eV
8	375	418	strong	3.04 eV
8^d	446	483	very strong	2.65 eV

(a) λ_{max} for excitation; (b) λ_{max} for emission; (c) Estimated from the onset of the excitation spectra; (d) In the solid state.

To get a better understanding of the electronic structures and band gaps of the extended organic semiconductors, as well as the electronic distribution within the respective materials, we performed quantum chemical DFT calculation at the B3LYP/6-31G* level on the parent *syn*-BDT **2**, as well as the cross-coupled products **7** and **8**. The calculated frontier orbitals for the corresponding minimized structures are shown in Figure 1. As can be seen, the homoaryl species **7** and **8** show a slight twist from co-planarity with torsion angles of 24.8º for **7**, and 28.6º for **8**. However, this torsion is not very pronounced so that a significant degree of π-conjugation is still present in the HOMO as well as the LUMO, and the orbitals are well delocalized over the whole molecule. To investigate, whether it would be possible to achieve a fully co-planar structure without twisted end-groups, we have also calculated the structure of the pyridyl-functionalized species **9.** A fully coplanar orientation can indeed be observed here, as the steric demand of the pyridyl group is reduced due to the absence of a hydrogen substituent at the nitrogen position of the ring. We have also observed this structural feature in an earlier study involving phosphorus-based oligothiophenes.[26] Notably, the frontier orbitals of **9** are also well distributed over the whole molecule.

As can been seen further, the LUMO in **2** and **7-9** has a similar shape of all four compounds, however, extended throughout the cross-coupled sections in **7-9**. This supports a general basic electronic structure for all four compounds that can be tuned by the respective aryl groups. The same is true for the HOMOs, with the exception of **8**. Here the shape of the HOMO is actually the shape of the HOMO-1 in the other compounds. Due to considerable π-conjugation of the amino-nitrogen atoms in *para*-position, and the greatest loss of symmetry in **8**, HOMO (now HOMO-1 at -4.797 eV) and HOMO-1 (now HOMO at -4.746 eV) switch places.

Remarkably, extension of the π-conjugated system of the *syn*-BDT core with different aryl substituents is found to selectively manipulate the band-gap of the materials. Depending on the planarity of the systems, as well as the nature of the aryl group being either electron donating, or electron accepting, HOMO and/or LUMO levels can be manipulated selectively. Compared to the energies of the frontier orbitals of the BDT-core (HOMO: -5.491 eV; LUMO: -0.881 eV) the extended all co-planar material **9** shows a raised HOMO level at -5.244 eV as well as a depressed

LUMO-level at -1.563 eV, effectively reducing the band gap to 3.681 eV (from E_{bg} = 4.610 eV). This is in very good agreement with the general electronics of π-conjugated organic materials, due to the presence of an increased number of π-electrons.[6a] In the case of the homoaryl species; only one of the frontier orbitals is affected in each case. Substitution with an electron-donating functional group, such as -NMe_2 in **8**, increases the HOMO substantially to -4.746 eV (ΔE = 0.745 eV, see above), whereas the LUMO at -0.908 eV is almost not changed at all (ΔE = 0.027 eV). The opposite is true for compound **7** with the electron-withdrawing F-substituents. Here the LUMO experiences a significant drop in energy down to -1.461 eV (ΔE = 0.580 eV), and the HOMO remains unaffected at -5.487 eV (ΔE = 0.004 eV). These observations are also consistent with the general theory of organic conjugated materials.[6,7] As a net result, the band gaps of compounds **7** (E_{bg} = 4.026 eV) and **8** (E_{bg} = 3.838 eV) are both smaller than the one for the BDT-core.

In addition to the altered HOMO/LUMO levels, the introduction of various aryl substituents can also be used to significantly influence the dipole moment of the materials. The dipole moment in general has a major impact on the packing properties of the materials in the solid state, which has been found to be of central importance for the ultimate device performance, as already mentioned.[1,2] Due to the *syn*-arrangement of the two thieno-units in BDT **2**, the central core already has a notable dipole moment of μ = 1.52 D. Incorporation of the 4-fluorophenyl group in **7** results in a reduced dipole moment of μ = 1.22 D, which is likely due to the vector of the symmetrically arranged fluorine atoms somewhat dominating the structure. The 4-dimethylanilino functionalized species, on the other hand shows a slightly increased dipole moment (μ = 2.13 D) compared to that of BDT, whereas compound **9** has the largest dipole in this series (μ =4.64 D), which can be attributed to the asymmetric nature of the pyridyl groups, exhibiting vectors in the same direction as the thieno groups. It can be expected that the polar nature of the materials could act as a guiding template for a highly ordered solid-state structure and result in some desirable organization to optimize the charge carrier properties of the materials. However, more detailed studies are required to verify this assumption.

In conclusion, we have synthesized a new tin-functionalized *syn*-BDT sython that was used to create extended organic semiconductor materials. Investigation of the photophysical properties, as well as DFT-quantum mechanical studies have revealed that the electronic structure of the materials can be efficiently manipulated using various electron–donating or –withdrawing groups, as well as heteroarenes, such as pyridine.

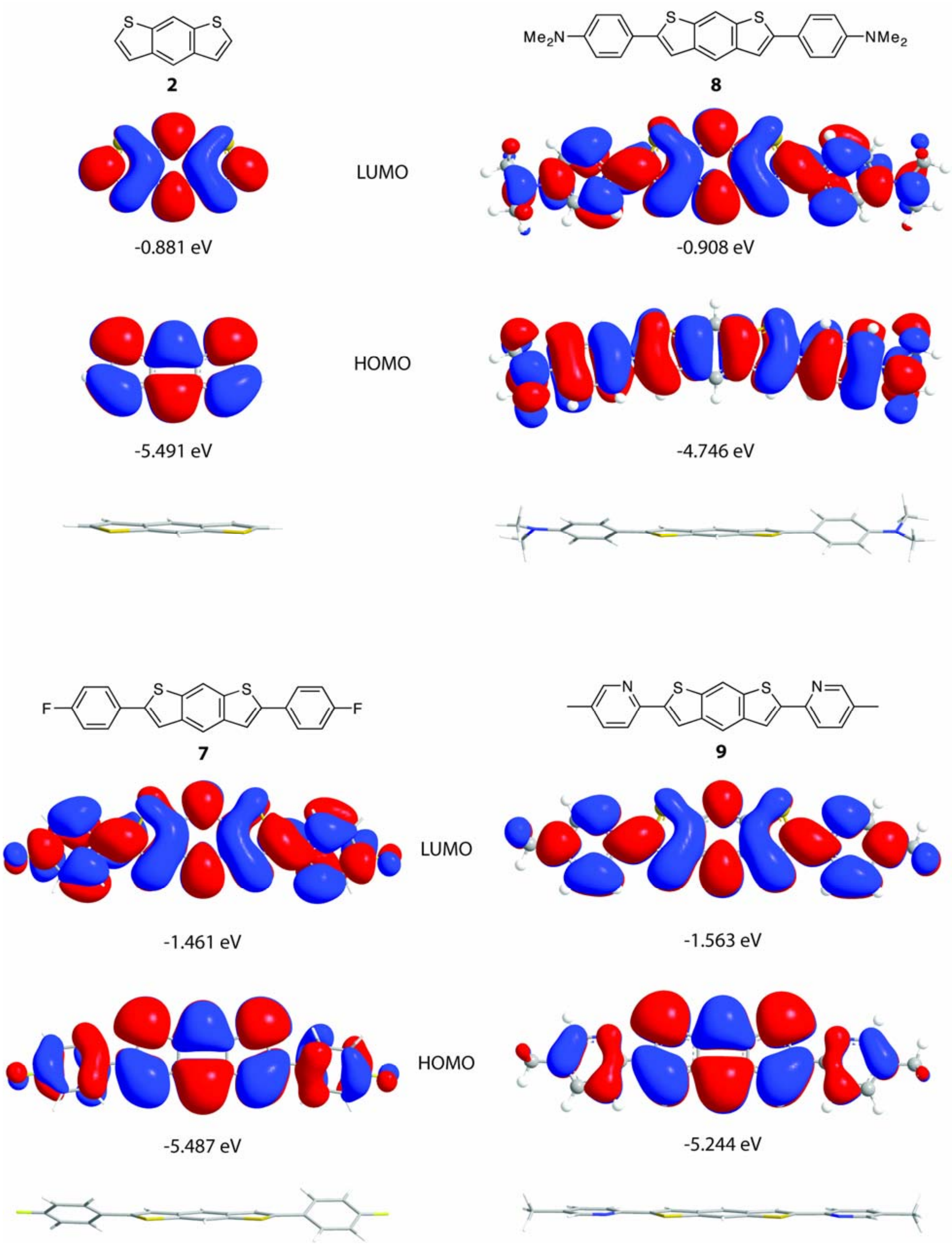


Figure 1. Frontier orbitals (B3LYP/6-31G*) and molecular geometry of compounds **2**, **7-9**.

Experimental Section

General Procedures. Reactions were carried out in dry glassware and under inert atmosphere of purified nitrogen using Schlenk techniques. Solvents were dried over appropriate drying agents and then distilled. *t*-BuLi (1.5 M in pentane, Acros), *n*-BuLi (2.5 M in hexanes, Acros), sulfur, tetrabutylammonium fluoride (TBAF), 4-bromo-dimethylaniline, 4-bromo-fluorobenzene (all Sigma-Aldrich), and $Pd(PPh_3)_4$ (Strem), were used as received. Tributyltin chloride (Sigma-Aldrich) was distilled prior to use. 1,5-Dibromo-2,4-bis(2'-trimethylsilylethynyl)benzene was prepared by literature methods.[21] ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC-200, or DMX-300 MHz-spectrometer. Chemical shifts were referenced to external TMS. EI mass spectra were recorded on a Finigan SSQ 7000 spectrometer; fluorescence data were recorded on a Jasco FP-6600 spectrofluorometer. DFT-calculations were performed using the Gaussian 03 software package.[27]

2,6-Bis(trimethylsilyl)benzo[1,2-*b*:5,4-*b'*]dithiophene (5b). *t*-BuLi (1.5 M in pentane, 37 mL, 54.6 mmol) was added dropwise to a solution of 1,5-dibromo-2,4-bis(2'-trimethylsilylethynyl)-benzene[22] (5.847 g, 13.65 mmol) in ether (250 mL) at -78 ºC. The solution was stirred at this temperature for 30 min and was then allowed to slowly warm to room temperature. Elemental sulfur (0.88 g, 27.3 mmol) was then added in one portion and the resulting mixture was allowed to stir for another 30 min. Ethanol (450 mL) was then added and reaction mixture was allowed to stir for 1 h. The solvents were then removed under reduced pressure and the resulting residue was taken up in pentane and filtered through silica. The pentane was then removed under reduced pressure and ethanol was added to this residue yielding a grey precipitate (product), which was filtered off. Yield 44%; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.34 (s, 1H), 8.21 (s, 1H), 7.51 (s, 2H), 0.41 (s, 18H).

Benzo[1,2-*b*:5,4-*b'*]dithiophene (2). TBAF (2.28 g, 7.20 mmol) was dissolved in THF (20 mL). This solution was then transferred dropwise to a solution of 2,6-bis(trimethylsilyl)benzo[1,2-b:5,4-b']dithiophene (1.12 g, 3.60 mmol) in THF (55 mL) and the resulting mixture was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure and the resulting residue was taken up in chloroform (50 mL), washed with water (30 mL x 3) and dried ($MgSO_4$). The chloroform was then removed under reduced pressure and the resulting residue was washed with pentane to yield a beige solid. Yield 60%; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.38 (s *b*, 1H), 8.27 (s *b*, 1H), 7.45 (d, 2H, ^1J (H,H) = 6.0 Hz), 7.41 (d, 2H, ^1J (H,H) = 6.0 Hz).

2,6-Bis(tributyltin)-benzo[1,2-*b*:5,4-*b'*]dithiophene (6). *n*-BuLi (2.5M in hexanes, 1.20 mL, 3.0 mmol) was added to a solution of benzo[1,2-*b*:5,4-*b'*]dithiophene (0.286 g, 1.5 mmol) in THF (35 mL) at -78 ºC. After stirring for 1 h and allowing to warm to -25 ºC, tributyltin chloride (0.82 mL, 3.0 mmol) was added and the solution was allowed to slowly warm to room temperature. The solvent was removed under reduced pressure, the residue was taken up in pentane and purified by filtering off unreacted benzo[1,2-*b*:5,4-*b'*]dithiophene and distilling off unreacted tributyltin chloride under vacuum at 60 ºC. Yield 98%; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.34 (s, 1H), 8.21 (s, 1H), 7.43 (s, 2H), 1.65 (m, 12H), 1.35 (m, 12H), 1.17 (m, 12H), 0.95 (t, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 141.2, 139.7, 139.1, 132.6, 115.4, 114.1, 29.3, 27.3, 14.1, 10.8; EI MS *m/z (%)*: 768 *10* [M^+], 711 *19* [M^+-Bu], 654 *4* [M^+-2Bu], 597 *4* [M^+-3Bu], 530 *3* [M^+-4Bu], 483 *4* [M^+-5Bu], 426 *13* [M^+-6Bu], 57 *100* [Bu^+]; HRMS calcd. for $C_{34}H_{58}S_2Sn_2$ [M^+]: 768.2018; found: 768.2018.

2,6-Bis(4-fluorophenyl)benzo[1,2-*b*:5,4-*b'*]dithiophene (7). A mixture of 2,6-bis(tributyltin)-benzo[1,2-*b*:5,4-*b'*]dithiophene (0.458 g, 0.596 mmol) and 4-bromofluorobenzene (0.250 g, 1.431 mmol) were dissolved in toluene (20 mL). To this solution $Pd(PPh_3)_4$ catalyst (6 mol%) was added and the solution was refluxed at 115 ºC for 24 h. After reflux the solution was allowed to cool to room temperature and the solvent was removed under reduced pressure with the resulting residue being washed with pentane and then acetone. This brown solid was then sublimed under vacuum to yield the light yellow product. Yield 65%; EI MS *m/z* (*%*): 378 *100* [M^+], 360 *33* [M-F+H^+], 189 *18* [$C_{10}H_5S_2^+$]; HRMS calcd. for $C_{22}H_{12}S_2F_2$ [M^+]: 378.0349; found: 378.0337. No NMR data could be obtained due to the poor solubility of **7**.

2,6-Bis(4-*N,N*-dimethylaminophenyl)benzo[1,2-*b*:5,4-*b'*]dithiophene (8). Compound **8** was prepared by a similar method as compound **7** by coupling compound of **2** with 4-bromo-N,N-dimethylaniline. Yield 72%; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.75 (s, 1H), 7.63 (s, 1H), 7.43 (m, 2H), 7.32 (m, 4H), 6.82 (m, 4H), 3.19 (s, 12H); EI MS *m/z* (*%*): 429 *82* [M+H^+], 386 *100* [M-NMe_2+$2H^+$]; HRMS calcd. for $C_{26}H_{24}N_2S_2$ [M^+]: 428.1381; found: 428.1385. Only ^{1}H NMR could be obtained due to the poor solubility of **8**.

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