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Planar *β*-Linked Oligothiophenes Based on Thieno[3,2-*b*]thiophene and Dithieno[3,2-*b*:2′,3′-*d*]thiophene Fused Units

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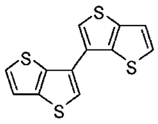
ABSTRACT



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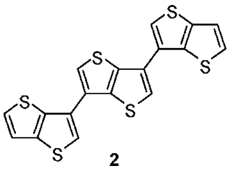

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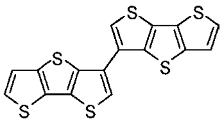

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A series of planar *β*-linked oligothiophenes based on thieno[3,2-*b*]thiophene and dithieno[3,2-*b*:2′,3′-*d*]thiophene fused units were synthesized. The optical data indicate a blue shift of the absorption maximum in comparison to the α-linked analogues due to cross-conjugation between fused rings. The crystal structures of 3,3′-bi(thieno[3,2-*b*]thiophene) and 3,3′;6′,3”-ter(thieno-[3,2-*b*]thiophene) reveal edge-to-face *π*-stacked dimer motifs, whereas the crystal structure of 3,3′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) consists of face-to-face *π*-stacked molecules.

In the growing field of organic semiconductors, thiophene-based materials play an important role. Oligothiophenes and polythiophenes have been synthesized with promising optical and electrical properties for use in organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs).[1,2] For example, the α-linked hexamer of thiophene, sexithiophene, and its derivatives have been successfully used as the active component in OLEDs[3] and OFETs.[4−6] The performance of sexithiophene and related oligomers, especially in OFETs, may be hampered by their nonideal solid-state arrangement. Oligothiophenes generally present the so-called herringbone motif in the solid state, an arrangement that does not optimize $\pi-\pi$ overlap between adjacent molecules.[7] Theoretically, face-to-face π-stacking facilitates charge transport, thus increasing charge-carrier mobilities because a closer approach between π-clouds allows superior π-overlap.[8]

Understanding the relationship between the electronic structure of a given molecule, its crystal structure, and how this relates to charge-transport characteristics is a current challenge impeding the purposeful design of materials with superior performance.[9] With this goal, we have recently applied the approach of systematically varying the degree of fusion to a series of oligothiophenes, and it was found that moving from single-bonded thiophene units toward fully fused thienoacenes changes the packing from herringbone to face-to-face π-stacking.[10] One driving force for this trend is the removal of C−H$\cdots\pi$ interactions accompanying the excision of C−H bonds.

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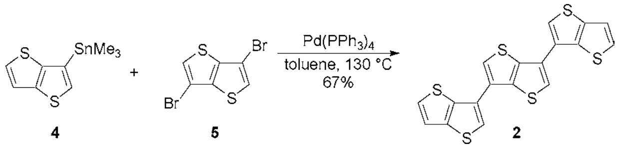
Scheme 1. Synthesis of the β-Linked Trimer of Thieno[3,2-*b*]thiophene (**2**)



It has been observed in polycyclic aromatic hydrocarbons that the ratio between carbons and hydrogens available for intermolecular interactions plays an important role in determining solid-state packing.[11,12] Low C/H ratios result in the occurrence of $C-H\cdots\pi$ intermolecular interactions, which are associated with the formation of herringbone packing in the solid state. In contrast, high C/H ratios, which reduce the role of $C-H\cdots\pi$ interactions in the crystal, favor the formation of π-stacking that is characterized by $\pi\cdots\pi$ interactions in the solid state. Applying this principle to oligothiophenes leads to the hypothesis that β-linked oligothienoacenes can be considered good candidates for materials able to π-stack in the solid state. The introduction of fused-ring moieties and the presence of intramolecular sulfur−hydrogen interactions (vida infra) decrease the number of hydrogens available for intermolecular interactions, which effectively increases the C/H ratio and should result in $\pi-\pi$ stacking in the solid state.

Oligothiophenes containing β-linkages have not been extensively studied in part due to the lack of efficient synthetic methodologies[13] and because the β-linkage between thiophene units creates a cross-conjugated relationship between rings that, beyond the dimer, has the potential to strongly deplanarize the molecule. This tendency can be partially overcome through extensive ring fusion but for longer oligomers leads to helical cross-conjugated materials.[13−16] Constructing β-linked oligothiophenes from larger subunits could potentially avoid helix formation and enhance planarity. Therefore, a series of planar β-linked oligothiophenes containing fused thiophene units—3,3′-bi(thieno[3,2-*b*]-thiophene) (**1**), 3,3′;6′,3″-ter(thieno-[3,2-*b*]thiophene) (**2**), and 3,3′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (**3**)—were synthesized to elucidate the effect of the β-linkage on the properties of these materials. The analysis of the optical and solid-state behavior reveals marked differences in conjugation and solid-state packing relative to the α-linked isomers.

Oligomers **1**−**3** were synthesized by Stille coupling of the appropriate stannyl and bromo compounds catalyzed by Pd(PPh$_3$)$_4$. The first target oligomer, compound **1**, was obtained from the cross-coupling reaction of 3-bromothieno-[3,2-*b*]thiophene and 3-trimethylstannylthieno[3,2-*b*]thiophene (**4**) (see Supporting Information).[17] Compound **2** was obtained from the cross-coupling reaction of **4** with 3,6-dibromothieno[3,2-*b*]thiophene (**5**) (Scheme 1). The key building block, compound **5**, was prepared by the halogen dance reaction of 2,5-dibromothieno[3,2-*b*]thiophene with LDA.[18] It is commonly observed for oligothiophenes that an increase in ring fusion is accompanied by a decrease in solubility. This can be addressed by the introduction of removable solubilizing groups. Trimethylsilyl (TMS) groups were employed in the synthesis of **3** to ease the purification process and to improve the overall yield (Scheme 2). Compound **3** was readily obtained from the protodesilylation of **11** using tetrabutylammonium fluoride (TBAF). This precursor was obtained from the Stille coupling reaction of **9** and **10**. The β-bromo substitution in **9** was obtained by bromination of **7** utilizing NBS, followed by the halogen dance reaction of **8** with LDA. The TMS groups at the outside α-positions play an important role in eliminating competing deprotonation at these sites, resulting in an improvement of the ring-closure reaction of **6** to produce **7**. The synthesis of sulfide **6** was achieved by the Pd-catalyzed coupling of S(SnBu$_3$)$_2$ with 2 equiv of (4-bromothiophen-2-yl)-trimethyl-silane. This synthetic route[19] represents an improvement over the traditional method of sulfur linkage insertion where lithium−halogen exchange is followed by quenching with a sulfur(II) source because it avoids β−α anion migration and the resulting mixture of undesired α- and β-linked isomers as byproducts. Both β-linked oligomers, **2** and **3**, were purified by vacuum sublimation due to low solubility.

The electronic properties of **1**−**3** were studied by UV−vis and fluorescence spectroscopies and compared to the corresponding α-linked oligothiophenes, which are detailed in Table 1. In the α-linked nonfused ring series, the longest-wavelength absorption maximum (λ_{max}) depends primarily on the number of double bonds. An increase in the number of double bonds leads to a red shift of the absorption maximum. For example, α-terthiophene is 50 nm red-shifted relative to α-bithiophene which is 64 nm red-shifted relative to thiophene (λ_{max} = 240 nm). As the number of double bonds increases, the λ_{max} of absorption undergoes a dramatic bathochromic shift. However, β-terthiophene is 7 nm blue-shifted relative to β-bithiophene which is 21 nm red-shifted relative to thiophene. The nonfused β-linked oligothiophenes

Scheme 2. Synthesis of the β-Linked Dimer of Dithieno[3,2-*b*:2′,3′-d]thiophene (**3**)

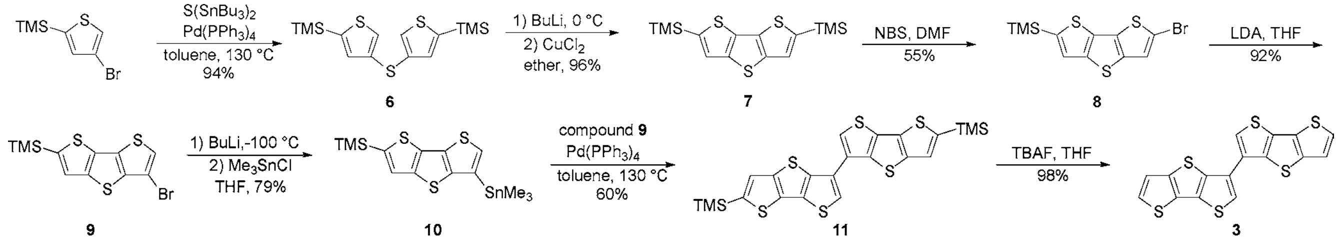


Table 1. Longest Wavelength of Absorption and Emission Maxima of a Series of β-Linked Oligothienoacenes, the Corresponding α-Linked Isomers, and Monomeric Units in CH_2Cl_2 Solution

β-linked oligomer and momomeric units	absorption λ_{max} (nm)	emission λ_{max} (nm)	α-linked oligomer	absorption λ_{max} (nm)	emission λ_{max} (nm)
β-bithiophene	261	318	α-bithiophene	304	364
β-terthiophene	254	340	α-terthiophene	354[a]	433[a]
thieno[3,2-*b*]thiophene (**12**)	279	–			
β-dimer of thieno[3,2-*b*]thiophene (**1**)	294 303[b]	345	α-dimer of thieno[3,2-*b*]thiophene (**13**)	350[a]	412[a]
β-trimer of thieno[3,2-*b*]thiophene (**2**)	303 313[b]	350	α-trimer of thieno[3,2-*b*]thiophene (**14**)	403[c]	477[c]
dithieno[3,2-*b*:2′,3′-*d*]thiophene	304	335			
β-dimer of dithieno[3,2-*b*:2′,3′-*d*] thiophene (**3**)	300 310[b]	367	α-dimer of dithieno[3,2-*b*:2′,3′-*d*] thiophene	390[d] 2	459[d]

[a] Ref 22. [b] Shoulder. [c] Ref 21. [d] In chloroform solution; ref 24.

do not follow the trend observed in the α-linked analogues, as the electronic absorption properties of the β-linked series are more dependent on the molecular conformation of the oligomers. β-Terthiophene possesses a nonplanar conformation due to severe steric interactions introduced by the β-linkages as corroborated by DFT calculations (see Supporting Information), whereas the α-linked isomer is essentially planar.[20] However, the introduction of the fused-ring moieties thieno[3,2-*b*]thiophene and dithieno[3,2-*b*:2′,3′-*d*]thiophene results in an improvement in molecular planarity and rigidity.

The β-linked fused-ring oligomer series based on thieno[3,2-*b*]thiophene units follows the same general trend as the α-linked nonfused ring series: as the number of double bonds increases, the λ_{max} of absorption shifts to longer wavelengths (Figure 1). The α-linked trimer of thieno[3,2-*b*]thiophene[21] (nine double bonds) is 53 nm red-shifted relative to the α-linked dimer of thieno[3,2-*b*]thiophene[22] (six double bonds). However, **2** is only 9 nm red-shifted relative to **1**. The difference in the degree of the red shift can be attributed to the fact that the conjugation is limited through the β-linkage, whereas the trend is suggestive of no substantial deplanarization along the series.

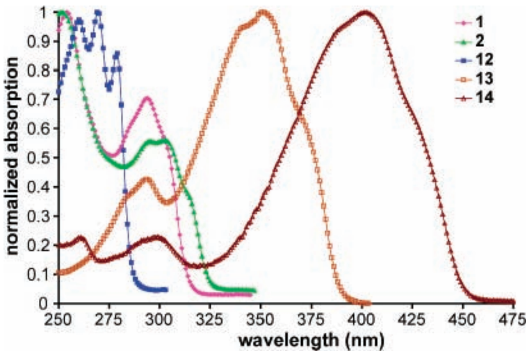


Figure 1. Comparison of UV−vis absorption spectra of α- and β-linked oligomers based on thieno[3,2-*b*]thiophene.

We have previously noted that α-linked fused and nonfused ring oligothiophenes with an equal number of double bonds have similar longest-wavelength absorption maxima.[22] For example, α-terthiophene and the α-linked dimer of thieno[3,2-*b*]thiophene, both with six double bonds but a different degree of ring fusion, have similar λ_{max} of absorption, 354 and 350 nm, respectively, but markedly different λ_{max} of emission. In this pair, the introduction of the sulfur linkages (ring fusion) has little effect on the λ_{max} of absorption but a substantial effect on the emission maxima. The α-linked dimer of thieno[3,2-*b*]thiophene presents a smaller Stokes shift due to the introduction of ring fusion which reduces the degrees of freedom and conformational reorganization in the excited state. In the β-linked series, compounds with the same number of double bonds but

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different degrees of ring fusion have different λ_{max} of absorption. For example, β-terthiophene and **1** have λ_{max} of absorption at 254 and 294 nm, respectively. In this case, the λ_{max} is not determined merely by the number of double bonds as in the α-linked series but rather by planarization effects. However, the introduction of sulfur linkages (ring fusion) to oligomers with an equal number of double bonds results in smaller Stokes shifts as observed for α-linked oligomers. In general, the main effect of the introduction of the β-linkages on the optical properties is a blue shift of the λ_{max} of absorption and emission when compared to the corresponding α-linked isomers. This is primarily attributed to the cross-conjugation introduced by the β-linkage, which effectively limits π-electron delocalization between building units.[23]

To investigate the solid-state properties of these β-linked oligomers, specifically the role of intermolecular interactions and the packing motif, single-crystal structures for **1**−**3** were determined. The structure of **1** reveals a nearly planar molecular conformation with a packing arrangement consisting of edge-to-face π-stacked dimers (sandwich-herringbone packing, Figure 2). The two thieno[3,2-*b*]thiophene units adopt an anti conformation with a dihedral angle of 177.4°. The close intramolecular S···H distances are 2.59 and 2.52 Å, values considerably shorter than the sum of the van der Waals radii of sulfur and hydrogen (3.00 Å) and consistent with the presence of internal S···H interactions. Furthermore, the π-stacked dimers are separated by 3.55 Å. A comparison of the crystal structure of **1** with its α-linked analogue reveals a marked difference in solid-state packing: the former presents an edge-to-face π-stacked dimer motif, whereas the α-linked analogue shows herringbone packing.[10] This is likely a result of the decreased role of C−H···π interactions in the crystal structure of **1**. The introduction of an additional thieno[3,2-*b*]thiophene unit yields compound **2** but does not induce a significant change in conformation or packing motif. Compound **2** is nearly planar in the crystal and adopts an edge-to-face π-stacked dimers motif. These molecules are stacked at a distance of 3.45 Å. Short C−H···π and S···S intermolecular interactions exist between adjacent edge-to-face molecules at 2.94 and 3.52 Å, respectively, and intramolecular S···H contacts range from 2.51 to 2.54 Å. The atypical solid-state packing of **1** and **2**, edge-to-face π-stacked dimers, represents an interesting packing motif to explore in the context of OTFT performance.

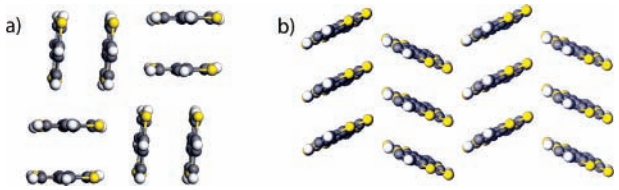

Figure 2. Crystal structure diagram of β-linked dimers of (a) thieno[3,2-*b*]thiophene (**1**) and (b) dithieno[3,2-*b*:2′,3′-*d*]thiophene (**3**), illustrating packing motifs.

Differing from the packing motif of **1** and **2**, the crystal structure of **3** adopts columns of face-to-face π-stacked molecules separated by a distance of 3.57 Å (Figure 2). In addition, the two dithieno[3,2-*b*:2′,3′-*d*]thiophene units adopt an anti conformation with a dihedral angle of 180°. Short intermolecular S···S distances of 3.49 Å and intramolecular S···H contacts of 2.53 Å are observed. This solid-state arrangement is similar to the α-linked isomer;[24] however, the π-stacked columns in the crystal structure of **3** are staggered (see Supporting Information).

Oligomers **1**−**3** all present π−π interactions in the solid state, making these materials attractive candidates for device applications. These packing motifs are attributed to the presence of short intramolecular S···H contacts and the inclusion of fused moieties which result in a higher C/H ratio, thus favoring π−π interactions.[11,12] Further experiments in which the charge-carrier mobilities of **1**−**3** are compared to the corresponding α-linked isomers may provide useful insight into the effect of packing motif on device performance.

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Supporting Information Available: Experimental procedures, equilibrium geometry calculations for **2** and β-terthiophene and UV−vis and NMR spectra and CIF files for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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