Communication

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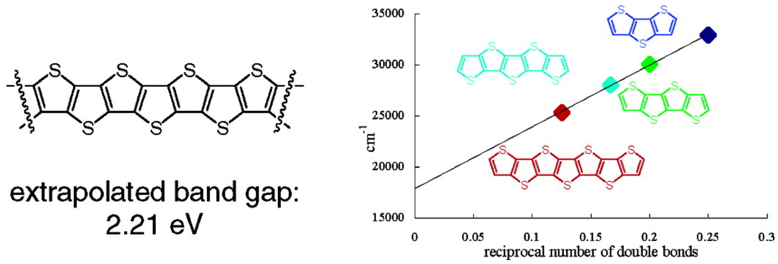

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Synthesis and Structure of Fused α-Oligothiophenes with up to Seven Rings

Xinnan Zhang, Adrien P. Côté, and Adam J. Matzger*

Department of Chemistry and the Macromolecular Science and Engineering Program, University of Michigan, 930 North University, Ann Arbor, Michigan 48109-1055

Received May 21, 2005; E-mail: matzger@umich.edu

α-Oligothiophenes are one of the most prominent organic semiconducting materials and have been widely studied both as compounds of interest in electronic devices and as models for understanding polythiophenes.[1] In particular, α-sexithiophene (Figure 1) and its derivatives have been employed as the active layer in organic electronic devices.[2] However, deviation from planarity may decrease conjugation in α-oligothiophenes through torsion about single bonds or S-syn defects. Such effects do not arise in fully fused conjugated oligomers, such as pentacene, because of its rigid structure.[3] Although pentacene exhibits outstanding charge carrier mobility,[4] its environmental stability[5] raises concerns about device lifetime. Furthermore, theoretical studies predict that the molecular packing is not optimized for maximum charge carrier mobility.[6] This raises the possibility of creating α-oligothiophenes that are fully fused because stability will be vastly improved relative to acenes and molecular packing may change from a herringbone to π-stacked structure. This latter effect is expected to arise from the relatively high C/H ratio, which reduces the role of C−H···π interactions in the crystal.[7] Although the synthesis of an impressive array of fully fused β-oligothiophenes has been accomplished, annelation in this manner gives rise to relatively large optical band gaps ($\lambda_{\max}$ = 260 nm for n = 7).[8] In contrast, fully fused α-oligothiophenes, oligothienoacenes (Figure 1), have planar structures with extended conjugation, which suggests potential applications in electronic devices should a suitable synthetic route be achieved. They are also of considerable interest as models for the hypothetical thienoacene (C_2S) polymer.

The synthesis of fully fused α-oligothienoacenes with up to five rings has previously been reported.[9,10] However, the synthetic route is inefficient and not applicable to longer thienoacenes because of the extremely poor solubility of the longer oligomers. Here, we introduce new synthetic methodology designed to efficiently prepare oligothienoacenes (Figure 1). This route allowed production of pentathienoacene (**1**) in large scale and with improved yield. In addition, heptathienoacene (**2**), which contains seven fused rings, was also successfully prepared. Significantly, diffraction data indicate that compounds **1** and **2** adopt face-to-face (π-stacked) packing motifs in contrast to the packing arrangement of α-oligothiophenes (face-to-edge or herringbone packing).[1]

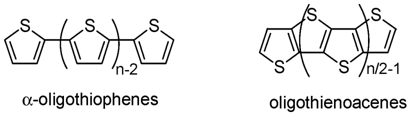
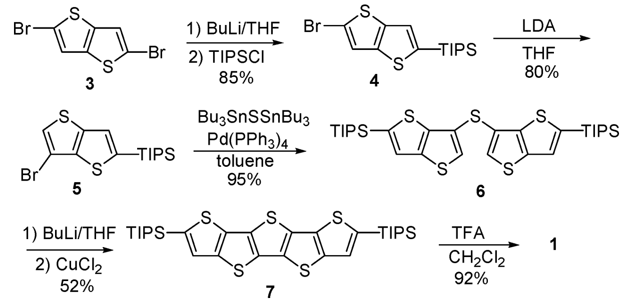
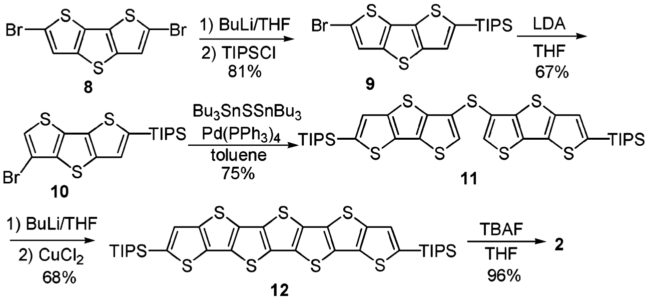


Figure 1. Chemical structures of α-oligothiophenes (n = 4, α-quaterthiophene; n = 6, α-sexithiophene) and oligothienoacenes (n = 3, dithieno[3,2-*b*:2′,3′-*d*]thiophene; n = 5, pentathienoacene, **1**; n = 7, heptathienoacene, **2**).

Scheme 1. Synthesis of Fully Fused Oligothienoacene **1**



Scheme 2. Synthesis of Fully Fused Oligothienoacene **2**



The solubility of oligothienoacenes is generally low, causing isolation difficulties and contributing to low yields. In our synthetic method, TIPS (triisopropylsilyl)[11] groups were introduced by Li−Br exchange of dibromide **3**[12] followed by quenching with TIPS−Cl (Scheme 1). The β-bromo substitution was obtained by the halogen dance reaction[13] of **4** with LDA to afford **5**. The synthesis of sulfide **6** was achieved by the Pd-catalyzed coupling of $Bu_3SnSSnBu_3$ with 2 equiv of **5** in excellent yield (95%).[14] This constitutes a significant improvement over the traditional method of introducing sulfur linkages via Li−Br exchange followed by quenching with bis(phenylsulfonyl)sulfide, which leads to substantial amounts of the α,β-linked isomer as a byproduct. By blocking the terminal α-positions with TIPS groups, competing deprotonation at the outside α-positions is eliminated and the yield of oxidative ring closure is 52% for **7** and 68% for **12** (Scheme 2), excellent results considering that unsubstituted **6** yields **1** in 0−20% yield. Pentathienoacene (**1**) was isolated in high yield after protodesilylation with TFA and is a fully fused analogue of α-terthiophene containing only six double bonds and with a relatively large HOMO−LUMO gap.[9,15] The solubilization strategy allowed us to prepare a longer oligothienoacene, heptathienoacene (**2**), with extended conjugation and a lower band gap (Scheme 2). TIPS-substituted heptathienoacene, **12**, was obtained in a similar manner as **7** from dibromide **8**.[16] Protodesilylation of **12** with TFA led to an inseparable mixture of **2** and mono-TIPS-substituted **2** as evidenced by EI-MS. However, both TIPS groups were smoothly removed upon treatment with tetrabutylammonium fluoride (TBAF). The solubility of **2** is exceedingly low in common organic solvents, and both it and **1** could be further purified by sublimation.

TIPS-substituted oligomers **7** and **12** produced single crystals suitable for X-ray structural analysis. This confirmed the backbone

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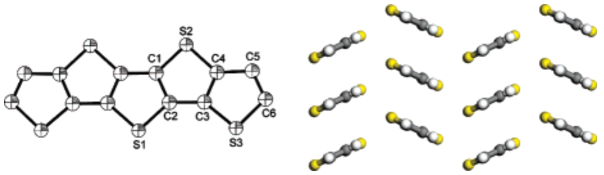

Figure 2. (left) ORTEP diagram with ellipsoids at 50% probability and (right) packing motif of **1**.

structure but yielded distorted molecular geometries, a likely consequence of accommodating the bulky TIPS groups (see Supporting Information). To elucidate the molecular packing of oligothienoacenes, the single-crystal X-ray structure of **1** was solved, which confirmed that the design of a π-stacked packing motif was successful (Figure 2). Negligible atomic deviation ($<$0.007(5) Å) from the mean plane of the fused ring system was observed, and molecules were found to π-stack at a distance of 3.518(2) Å, closely following the crystallographic [1 0 1] and [$-$1 0 1] directions. Furthermore, comparison of the indexed powder diffractograms of **1** and **2** revealed that these compounds are isostructural, with **2** exhibiting a *b*-axis 35% longer than that of **1** with all other parameters remaining equal to that measured for **1** from the single-crystal X-ray data. This relationship between **1** and **2** suggests that their π-stacking motifs are also highly correlated as revealed by the similar d_{101}-spacings (**1**: 3.71(3) Å; **2**: 3.68(6) Å) measured for each compound.

The electronic properties of **1** and **2** were studied by UV−vis and fluorescence spectroscopies and compared to the corresponding nonfused oligothiophenes (see Supporting Information). α-Terthiophene and **1**, both of which contain six double bonds, show similar longest λ_{max} of absorption (354 and 357 nm, respectively), although they have a different number of sulfur linkages.[15] This trend was also observed for the longer oligomers; fully fused quaterthiophene **2** displayed similar λ_{max} of absorption (396 nm) compared to that of the nonfused α-quaterthiophene (390 nm). In all cases, the absorption envelope of the fused oligomers is much narrower, and vibronic transitions are clearly visible, consistent with absorption from a single conformation. Although the longest λ_{max} of absorption is similar in oligomers with the same number of double bonds, the emission spectra of fused oligothienoacenes are dramatically blue-shifted compared to the corresponding nonfused α-oligothiophenes. The emission peaks of **2** (413 and 433 nm) shift to shorter wavelength compared to α-quaterthiophene (452 and 480 nm). Therefore, a smaller Stokes shift was observed when comparing spectra of the fully fused ring system to the nonfused oligothiophenes. This is consistent with a closer geometric match between the ground state and excited state for the rigid systems. As expected, the longest λ_{max} of **2** is red-shifted compared to that of **1** in both absorption and emission, which indicates that introduction of two more double bonds leads to extended conjugation and a decreased HOMO−LUMO gap. A linear dependence of the longest λ_{max} on the reciprocal number of double bonds of oligothienoacenes ($n = 3-7$) was observed. The band gap of polythienoacene is expected to be approximately 561 nm (2.21 eV) by extrapolating to the infinite chain. This value is close in energy to that of polythiophene (571 nm, 2.17 eV) estimated by the same method.[17] It is important to note that the extrapolated band gap for the fully fused polymer is at odds with a recent report claiming its synthesis through condensation of the corresponding thienyl sulfoxide.[18,19]

In summary, a general synthetic approach to fully fused α-oligothiophenes has made it possible to efficiently prepare oligothienoacenes with up to seven fused rings. X-ray diffraction data indicate that compounds **1** and **2** adopt a π-stacked packing motif. Efforts are underway to determine the semiconducting properties of **1** and **2** in organic field effect transistors.

Acknowledgment. This work was supported by National Science Foundation (CHE-0316250). A.P.C. thanks NSERC for a postdoctoral fellowship.

Supporting Information Available: Experimental procedures, CIF files and structural details of compounds **1**, **7**, and **12**, powder X-ray and spectral data for compounds **1**, **2**, **7**, **12**, α-terthiophene, and α-quaterthiophene, cyclic voltammetry of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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