

Effect of Ring Fusion on the Electronic Absorption and Emission Properties of Oligothiophenes

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Abstract: A series of fused-ring oligothiophenes were synthesized by a combination of Stille and oxidative coupling reactions. Compounds with the same number of double bonds, but varying in extent of planarization, display a similar longest wavelength absorption maximum in solution. However, the introduction of sulfur linkages into these oligothiophenes leads to a blue shift of the maximum emission wavelength and a correspondingly smaller Stokes shift.

Oligothiophenes have received much attention as organic materials due to their excellent electronic and optical properties.¹ α -Sexithiophene (Figure 1), the α -linked hexamer of thiophene, and its derivatives have been successfully employed as active components in organic field-effect transistors^{2–4} and light-emitting devices.⁵ Compared to pentacene, an important small molecule semiconductor that is rigidly planar,⁶ oligothiophenes can easily twist from planarity, thus disrupting conjugation and potentially affecting band gap in the solid state.⁷ An intriguing approach for the design of conjugated small molecules is to combine the stability of the thiophene ring with the planarity of linear acenes to produce thienoacenes (Figure 1).⁸ As of yet, only isolated examples of conjugated oligomers containing fused-ring thiophenes have been reported, and therefore, clear trends in the effect of this structural perturbation on the electronic properties of oligothiophenes have not yet emerged. The synthesis and characterization of oligomers of 3,6-dimethylthieno[3,2-*b*]thiophene has been accomplished.⁹ However, the steric repulsion between the β -methyl groups prevents coplanarity of adjacent thieno[3,2-*b*]thiophene

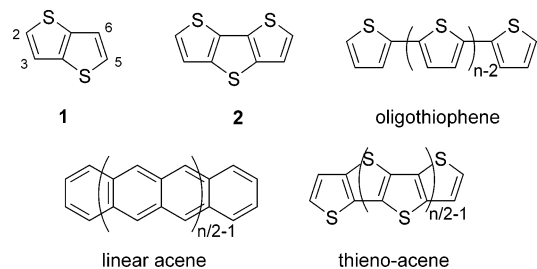


FIGURE 1. Chemical structures of thieno[3,2-*b*]thiophene (1), dithieno[3,2-*b*:2',3'-*d*]thiophene (2), oligothiophenes ($n = 3$, α -terthiophene, 3; $n = 4$, α -quaterthiophene, 4; $n = 6$, α -sexithiophene), linear acenes ($n = 5$, pentacene), and thienoacenes.

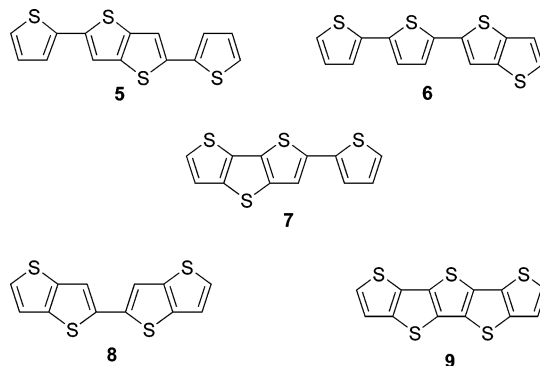


FIGURE 2. Chemical structures of fused-ring oligothiophenes used to explore the influence of planarization on the electronic absorption and emission spectra of thiophene materials.

units.¹⁰ In addition, the α -linked dimer of dithieno[3,2-*b*:2',3'-*d*]thiophene (2) and its alkylated derivatives have proven to be effective as the active layer in organic thin film transistors.^{11,12} Higher thienoacenes with $n = 4$ and 5 have also been reported, and in the case of the former a crystal structure has been obtained which indicates planarity of these fused-ring systems.¹³ However, perhaps because of the lack of convenient synthetic routes, devices utilizing these compounds have not been studied.¹⁴

To systematically explore the effect of increasing degree of ring fusion on the inherent electronic properties of α -oligothiophenes, we have synthesized a series of oligomers in which two or more of the thiophene rings are replaced by thieno[3,2-*b*]thiophene (1) and dithieno[3,2-*b*:2',3'-*d*]thiophene (2) units (Figure 2). These compounds, in combination with the fully planar pentathienoacene^{14,15} (9), provide the first well-defined series

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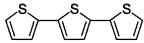
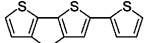
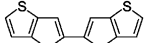
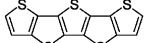
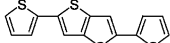
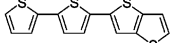
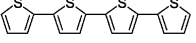
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TABLE 1. Longest Wavelength Electronic Absorption and Emission Maxima of a Series of Oligothiophenes in CH₂Cl₂ Solution

oligomer	double bonds	absorption λ_{\max} (nm)	emission λ_{\max} (nm)
3 	6	354	433
7 	6	352	414
8 	6	350	412
9 	6	357	388
5 	7	371	439
6 	7	370	453
4 	8	390	482

in which to probe the effect of ring fusion on the electronic spectra of oligothiophenes. These results provide a basis for the design of new materials with specified electronic properties.

Synthesis of the planarized oligomers was achieved by a modular approach using a combination of cross-coupling strategies and oxidative couplings (see the Supporting Information). The key building blocks, thieno[3,2-*b*]thiophene¹⁶ (**1**) and dithieno[3,2-*b*:2',3'-*d*]thiophene¹⁷ (**2**), were synthesized according to the literature procedures starting from 3-bromothiophene. The oligomers **5**–**7** were synthesized by Stille coupling of appropriate stannyl and bromo compounds catalyzed by Pd(PPh₃)₄ and CuI. Compound **5** has been reported previously; however, no spectroscopic data was measured.¹⁸ One of the greatest challenges was the purification of the oligomers because homocoupling of the stannyl and bromo compounds occurred as side reactions in all syntheses. α -Bithieno[3,2-*b*]thiophene (**8**) was prepared by an oxidative coupling of the lithiated **1**. The choice of metal proved critical in obtaining the product free of impurities. Employing CuCl₂ as coupling reagent led to the formation of chlorinated¹⁹ **1** in approximately 30% yield as evidenced by GC–MS. Substitution of Fe(acac)₃ as oxidative coupling reagent avoids halogenation products.¹⁹ Compounds **5**–**8**

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**FIGURE 3.** Chemical structures of methylene-bridged bithiophene **10** and a double-bridged terthiophene **11**.

were purified by one or more sublimations until they were greater than 99% pure by gas chromatography. α -Quaterthiophene (**4**)^{20,21} was used as a reference oligomer for the spectroscopic studies described below.

The optical data of the oligothiophenes²² and appropriate reference compounds are summarized in Table 1. Oligomers **3**, **7**, **8**, and **9** all have six double bonds but differ in the number and position of sulfur linkages. The nonfused oligomer **3**²³ displays a λ_{\max} in the absorption spectrum at 354 nm. It is generally recognized that increasing the planarity of aromatic systems leads to more extensive conjugation and a corresponding decrease in the HOMO–LUMO gap. Such a red shift in wavelength absorption of a planarized methylene-bridged bithiophene **10**,²⁴ and a double-bridged terthiophene **11**²⁵ (Figure 3) has been reported. The λ_{\max} of methylene-bridged bithiophene **10** is red-shifted (311 nm) compared to α -bithiophene (302 nm). Terthiophene **11** displays a bathochromic shift ($\Delta\lambda_{\max} = 22$ nm) when compared to the unconstrained model compound **3**.

The above arguments suggest that oligomers **7** and **8**, which have more sulfur linkages and increased planarity, will display spectra bathochromically shifted relative to **3**. In fact, these oligomers display longest wavelength absorption maximum values very close to **3**: 352 and 350 nm, respectively (Figure 4). Furthermore, the completely fused-ring compound **9** is also remarkably unperturbed relative to the unconstrained reference compound (**3**) with an absorption at 357 nm (Figure 4). This trend is also evident in the α -linked dimer of **2**,¹¹ which has an equal number of double bonds as α -quaterthiophene (**4**) and displays an absorption maximum at the same wavelength (390 nm). The insensitivity of the position of the absorption maximum to the extent of ring fusion likely results from a cancellation of effects. Planarization is acting to narrow the HOMO–LUMO gap while the increased sulfur substitution is widening it. Because the LUMO of α -terthiophene has the appropriate symmetry for interacting with the sulfur atoms introduced at the positions in **9**, this effect is presumed to result from a destabilization of this orbital. A related effect is also evident in thiophenol, which has a π – π^* absorption band at 238

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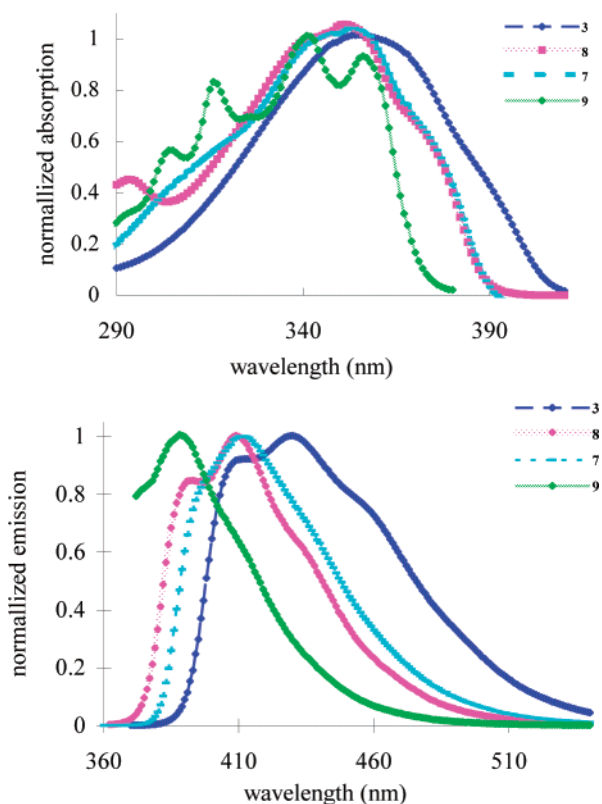


FIGURE 4. Comparison of UV–vis absorption and emission spectra of oligothiophenes with an equal number of double bonds in CH_2Cl_2 solution.

nm,²⁶ a value substantially shorter than that of benzene (252 nm). An additional trend evident in the spectra of the oligomers with six double bonds, that is not apparent in the position of the longest wavelength absorption maximum, is that increasing rigidity along the series **3** to **7**, **8** to **9** results in a narrowing of the absorption envelope and a general blue shift of the profile. Compound **3** has a long wavelength absorption tail associated with transitions occurring from a planar conformation. The general broadness of the band suggests important contributions from absorption of nonplanar conformers. In contrast, **9** is rigidly planar and therefore has an absorption profile that is more narrow with a clearly observable vibronic structure. Partially planarized oligomers **7** and **8** display intermediate broadening.

In oligomers **5** and **6**, the number of double bonds increases to seven and a correspondingly longer wavelength absorption is observed (371 and 370 nm, respectively). α -Quaterthiophene (**4**), which has eight double bonds, has a λ_{max} in the absorption spectrum at 390 nm. Significantly, these data show that both fused and nonfused ring oligothiophenes with an equal number of double bonds have similar longest wavelength absorption maxima. As expected, an increase in the number of double bonds leads to a red shift of the absorption spectrum.

Although the longest wavelength absorption maximum in this oligomer series depends primarily on the number

of double bonds, dramatic changes are observed in the emission spectra even for molecules differing only in the extent of ring fusion. Although compounds **3**, **7**, **8**, and **9** have similar absorptions, the emission maxima span nearly 50 nm (Figure 4). Oligomer **3**, which has three thiophene rings, displays the longest wavelength emission maximum of the series: 433 nm. The introduction of one sulfur linkage leads to ca. 20 nm blue shift in emission. Fused-ring oligomers **7** and **8** show emission maxima at 414 and 412 nm respectively. Compound **9**, which has one more sulfur linkage, displays the shortest emission λ_{max} of the series (388 nm). This trend indicates that for compounds with an equal number of double bonds, increasing the number of sulfur linkages leads to a substantial blue shift of the emission maximum. This dramatic difference in Stokes shifts can be explained by noting that a higher degree of ring fusion increases the rigidity in the oligomers, thus reducing the degrees of freedom and the conformational reorganization in the excited state. A closer geometric match between the ground and excited-state results in a smaller Stokes shift.

Although isomers **7** and **8** show similar emission maxima at 414 and 412 nm, a significant difference is observed between isomers **5** and **6** (439 nm, 453 nm). This effect is consistent with a greater degree of conjugation for the bithiophene-containing oligomer, **6**, in the excited state. Introducing another double bond and removing all ring fusion yields **4** and causes an additional bathochromic shift in the emission spectrum (482 nm).

In summary, a series of oligothiophenes were synthesized that differ in the extent of ring fusion. The optical data indicate that with the same number of double bonds in a molecule, the introduction of sulfur linkages into oligothiophenes leads to a minor shift in the electronic absorption spectra and a dramatic blue shift of the emission maximum. Increasing the number of double bonds leads to a red shift of both absorption and emission. Understanding these trends is critical for the design of new emissive materials in which fused thiophene rings replace the simple α -linked thiophenes.²⁷ Efforts are underway to determine the effect of ring fusion on the crystal packing of these oligomers and to produce longer chain fused-ring oligothiophenes with diminished HOMO–LUMO gaps for device applications.

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Supporting Information Available: Synthetic procedure and spectral data for compounds **5**–**8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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