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α-Oligofurans

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α-Oligofurans: Molecules without a Twist**

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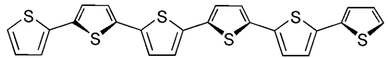
Organic electronics, the science of π-conjugated organic compounds and their applications, is a focus of chemistry, materials science, and engineering. Despite the thousands of π-conjugated compounds that are already available, the development of new materials is critical, as specifically desired properties (such as stability, solubility, high purity, molecular packing to maximize intermolecular interactions in the solid state, and the correct level of the frontier molecular orbitals) are difficult to obtain in the solid state. Enhanced solubility by introduction of alkyl or alkoxy chains will change packing and influence molecular conformation, but might also disrupt π–π interactions, leading to decreased intermolecular interactions, whereas the addition of donor or acceptor substituents will influence the gross electronic properties of organic semiconductors.

Substituted α-oligo- and α-polythiophenes,[1–3] and pentacenes[4,5] and C_{60} derivatives[6] are important for the development of organic thin-film transistors and photovoltaics.[7] In the case of thiophene-based materials, synthetic routes for oligomers of any size and also polymers with varying side-chain density, stereochemistry, and regiochemistries have been reported. However, the sexithiophene **1** is already almost completely insoluble in common organic solvents.[8] A single-crystal specimen of **1** could only be obtained through high-vacuum/high-temperature sublimation.[9] Whereas hexamer **1** is planar in the solid state, oligo- and polythiophenes adopt twisted conformations in solution, as can be attested to by their normally broad and featureless absorption spectra.[10–12] There have been more than 1000 articles published on oligothiophenes, and more than 4600 articles have been published on polythiophenes, but the corresponding polyfurans have attracted much less attention. Most publications dealing with polyfurans involve the electrochemical synthesis by electrolysis of the terfuryl monomer. As the oxidation potentials of furan, bifuryl, and terfuryl are very different, the synthesis of polyfuran by the electrolysis of furan is not very successful.[13] However, even polymer films obtained from terfuryl are insoluble in organic solvents and therefore cannot be characterized by classic polymer analytical methods (gel permeation chromatography, NMR spectroscopy, light scattering).

The first highly soluble and characterized polyfurans, poly(3-octylfuran)s **5** and **6**, were prepared by Curtis et al. in 2001 using either nickel or palladium catalysis (Scheme 1).[14] Starting from 2,5-dibromo-3-octylfuran **8**, metalation with Rieke zinc gave the intermediates **9a,b**, which upon reaction with $[(dppp)NiCl_2]$ (dppp = 1,3-bis(diphenylphosphino)propane) furnished the regioregular polyfuran **5**, whereas in the presence of $[(Ph_3P)_4Pd]$, only the regiorandom polymer **6** was obtained. The difference in regioregularity is not unusual in these polycondensation reactions and is attributed to the



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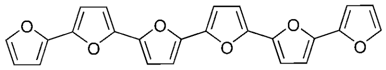

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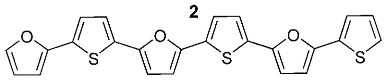

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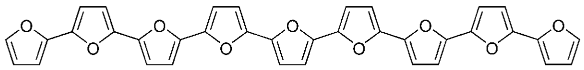

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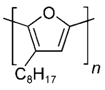

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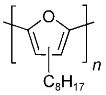

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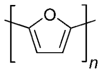

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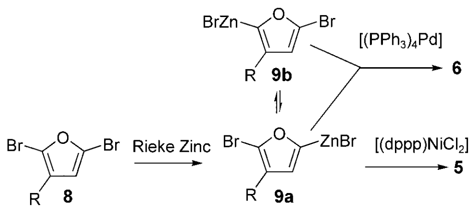

Scheme 1. Synthesis of soluble polyfurans **5** and **6** using nickel or palladium catalysis. R = octyl.[14]

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steric hindrance of the intermediate difurylnickel complexes. These nickel species only allow reductive elimination to give the head-to-tail product, whereas with the larger palladium center, all possible difurylpalladium species can be formed. Head-to-tail, head-to-head, and tail-to-tail dyads are possible.

The two polyfurans **5** and **6** differ in their NMR spectra but more so in their optical spectra, even though they feature the same backbone. Curtis et al. explained the differences in the optical properties as a consequence of the unusual planarization of the backbone of **5** in solution, which is apparently not possible for **6**, owing to the head-to-head diads that enforce a significant twist. The absorption maximum for **5** is $\lambda_{max} = 537$ nm in solution, whilst that of **6** is 372 nm. Furthermore, the UV/Vis spectrum of **5** is structured, whereas that of **6** is broad and featureless, similar to that of regioregular polythiophenes in good solvents. What is the difference between thiophene and furan and what governs the difference in behavior in their respective polymers? Both heterocycles have a similar degree of aromaticity according to calculated nucleus-independent shifts determined by Schleyer et al. Furan has a NICS(I) value of −9.4, while thiophene has a NICS(I) value of −10.2; that is, is only somewhat more aromatic than furan, but not significantly so.[15] From the calculated geometries of the corresponding dimers **10** and **11** (Figure 1), the central bond is shorter in the bifuran **10** than in the bithiophene **11**. DFT calculations show that the two thiophene rings in **11** are twisted by 22.6° with respect to each other, whereas the bifuran **10** is planar. The twisting in **11** is due to the steric interaction between the sulfur atom and the 3′-hydrogen of the adjacent ring; in **10** this is apparently not the case, as oxygen is smaller. Bithiophene **11** is less electron-rich than **10**, yet it has the smaller HOMO–LUMO gap owing to a lower-lying LUMO. Similar computational results were obtained for thiophene itself and for the larger oligothiophenes, and also for furan and its oligomers/polymers. Therefore, furans are more electron-rich than the corresponding thiophenes, but the thiophenes have smaller HOMO–LUMO gaps.

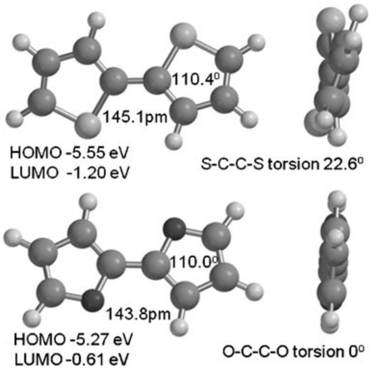
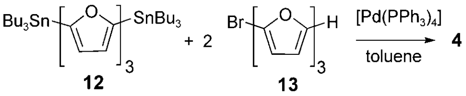


Figure 1. Calculated geometries of 2,2′-bithiophene (top; **11**) and 2,2′-bifuryl (bottom; **10**). The structures were calculated using Spartan for Windows (B3LYP 6-31G**//B3LYP 6-31G**).

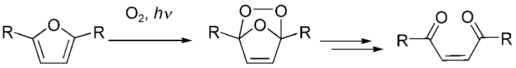
The somewhat lower aromaticity of furan leads to a shorter inter-ring bond in **10** with a slightly higher bond order. In combination with the lesser steric hindrance between the smaller oxygen atom and the 3′-hydrogen of the second ring, the planar form becomes (as calculated) more stable in oligo- and polyfuranes than the twisted forms predominant for oligo- and polythiophenes in solution. In the solid state, however, both oligothiophenes and oligofurans are planar, as the packing forces in the crystal apparently overcome the steric repulsion in the oligothiophenes.

Polyfurans have been described and some calculations carried out on the lower oligomeric furans; oligomers up to the tetramer have been sythesized by Kauffmann and Lexy.[16–18] Only recently, the groups of Komatsu and Bendikov independently prepared larger unsubstituted oligomers of furan (**2**, **4**) and mixed furan–thiophene hexamers such as **3**. Komatsu et al. observed in 2005 that **3** was considerably more soluble in common solvents than the analogous sexithiophene **1**.[8,9] Synthesis of unsubstituted oligofurans, tetramer through nonamer, was reported in 2010 by Bendikov et al.[19] A combination of metalation and Stille couplings gives the nonamer **4** in the last step, in which **12** is coupled with two equivalents of **13** in the presence of $[(Ph_3P)_4Pd]$ (Scheme 2). The nonamer **4** is surprisingly soluble in common organic solvents and is reasonably stable.



Scheme 2. Synthesis of unsubstituted nonafuran **4** using palladium catalysis.[19]

All of the furan oligomers can be stored either as powders or in solution at room temperature in dioxane without any noticeable decomposition for several weeks. The hexamer **2** only starts to decompose above 250 °C according to thermal gravimetric analysis. However, in the presence of air and light, one or several of the furan rings are photooxidized to dicarbonyl compounds (Scheme 3). All of the oligofurans are highly fluorescent and have structured absorption and emission spectra even in good solvents (Figure 2), suggesting that the molecules adopt a planar conformation or are at least considerably less twisted than the corresponding oligothiophenes. The fluorescence quantum yields of oligofurans (0.6–0.8) are impressive and are higher, by factors between two and ten, than those reported to date for the unsubstituted oligothiophenes (up to the hexamer **1**).



Scheme 3. Photooxidation of furan oligomers.[19]

Figure 3 shows the packing arrangement of **1**, **2**, and pentacene in the crystal. The oligomers **1** and **2** are structurally quite similar to each other, and their overall packing motif is almost superimposable. There are however some subtle but important differences in the packing arrange-

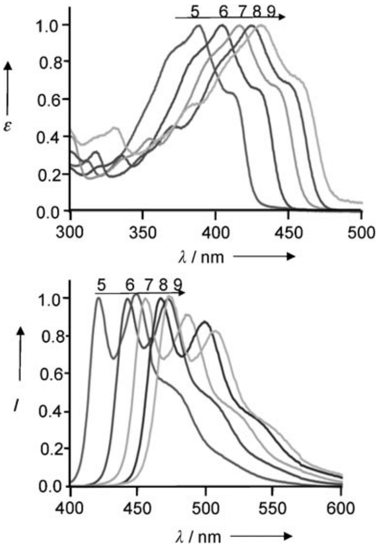


Figure 2. Absorption (top) and emission spectra (bottom) for the oligofurans. The number over the spectra represents the number of the furan rings in the oligomer. (Courtesy of M. Bendikov.)[19]

ment of **1** and **2**, as **2** is more tightly packed than **1** and the distance between the nearest neighbors of two parallel packet molecules of **2** are 257 pm as compared to 282 pm for **1**. The angle between two non-parallel molecules of **2** is 58°, that is, smaller than that of **1** (63°). Also noticeable is the similarity of the packing of **1** and **2** with that of pentacene. Considering that **1** is an important molecule in organic electronics, and that field-effect transistors and light-emitting diodes have been fabricated,[20–22] and that the structure of **1** has been investigated on every conceivable surface,[23] we would expect that the easy access to **2**–**4** will be met with greatest interest. It can be assumed that organic electronic devices prepared from **2**–**4** could surpass those made from **1**, as the tighter packing combined with their more electron-rich nature might be an advantage for increased charge-carrier mobilities. The use of **2**–**4** in organic electronic applications, such as thin film transistors or light-emitting diodes, is envisioned.

The partial or full exchange of sulfur for oxygen in conjugated five-ring oligomers and polymers leads to surprising changes in their chemistries and in their physical and spectroscopic behavior:

a) Furan-based materials have different conformational preferences from their thiophene relatives and adopt planar as opposed to twisted geometries, even in solution.
b) Oligo- and polyfurans are more electron-rich than the respective thiophenes, and are therefore more easily oxidized. At the same time, their optical features are blue-shifted from those of the oligothiophenes.
c) The oligofurans are much more soluble than their oligothiphene congeners.

Overall, these properties make the oligofurans complimentary to the oligothiophenes, and by analogy, furan-based materials should have a great but untapped potential in organic electronics.

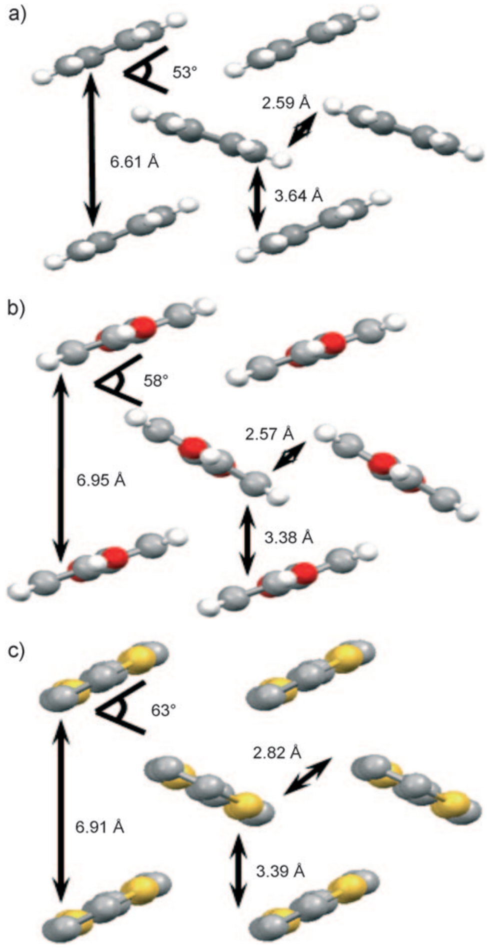


Figure 3. Comparison of the X-ray crystal structure and packing of a) pentacene, b) the oligofuran **2**, and c) the oligothiophene **1** with salient packing details. C gray, H white, O red, S yellow. (Courtesy of M. Bendikov.)[19]

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