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α-Oligofurans

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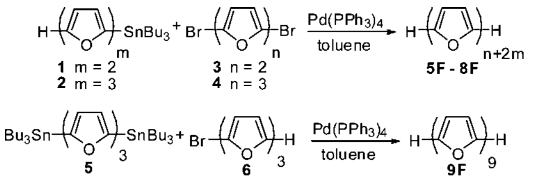
Organic molecules with long π conjugation have received much attention because of recent progress in solar cells, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), batteries, and sensors.[1] Stability, good solid-state packing, processability, rigidity/planarity, high fluorescence, and a HOMO−LUMO gap in the semiconductor region (which also leads to absorption/emission in the visible range) are among the main requirements for useful organic electronic materials. Among the workhorses in this field are long α-oligothiophenes [***n*****T**'s, in particular α-sexithiophene (**6T**)][2] and oligoacenes (in particular, pentacene),[3] which have been extensively studied because of their superior electronic properties, including relatively high field-effect mobility. There is an ongoing search for new compounds possessing most of the advantages of oligo- and polythiophenes but also having enhanced fluorescence, solubility, and rigidity. For example, polyselenophenes were recently introduced as an alternative to polythiophenes that shows better planarity and good electrochromic properties.[4] However, long α-oligofurans (***n*****F**'s), which are close oligothiophene analogues, are not known, and even short α-oligofurans have never been structurally characterized. It has been suggested that α-oligofurans comprising more than four rings (i.e., with more rings than **4F**) are unstable[5] since they are very electron-rich, and the longest reported substituted α-oligofuran consists of five rings.[6,7] α-Oligofurans include only first-row elements. Usually, organic electronic materials are not biodegradable, and extensive usage of these compounds may generate a significant amount of hazardous waste. Furan-only materials are biodegradable, and in addition, furans (in contrast to other types of conjugated materials) can be obtained from entirely renewable resources.[8]

In this paper, we report the synthesis and characterization of a series of unsubstituted and sufficiently stable α-oligofurans containing up to nine rings.[9−11] The α-oligofurans reported here are the first oligofuran-based materials to be comprehensively characterized, including single-crystal X-ray analysis. Importantly, long oligofurans are highly fluorescent (relative to oligothiophenes and alternating furan−thiophene oligomers), electron-rich, and exhibit tighter herringbone solid-state packing, greater rigidity, and greater solubility than oligothiophenes.

α-Oligofurans **5F**−**9F** were synthesized using Stille coupling of shorter oligomers (Scheme 1). Compounds **1** and **2** were obtained by lithiation of bifuran and terfuran with *n*-butyllithium followed by the addition of tributyltin chloride [see the Supporting Information (SI)]. The preparation of **3** and **4** was described previously.[12] Stille coupling between tributyltin oligofurans (**1** and **2**) and dibromooligofurans (**3** and **4**) afforded analytically pure compounds **5F**−**8F**. The coupling of α-dibromooligofurans with monotin oligofurans is the preferred synthetic route for **5F**−**8F**, since monobrominated oligofurans are unstable and tend to decompose when concentrated from solution. To obtain **9F**, the preferred route is coupling of **5** with **6**, since the coupling of **4** with **2** results in a complex reaction mixture (for the synthesis of compounds **5** and **6**, see the SI). **5F**−**9F** were characterized by a combination of ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HRMS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV−vis spectroscopy, fluorescence, and cyclic voltammetry (CV). In addition, compound **6F** was characterized by single-crystal X-ray crystallography.

Scheme 1. Synthetic Route to Long α-Oligofurans



	m	n
5F	1	3
6F	2	2
7F	2	3
8F	3	2

The oligofurans were found to be relatively stable. For example, **6F** is stable in air up to 250 °C on the basis of the onset of the TGA curve (see the SI). Long α-oligofurans are stable in powdered form and even as a dioxane solution when exposed to air (including moist air) at room temperature for up to at least a few weeks. However, as expected, α-oligofurans are unstable with respect to a combination of light and oxygen, since 2,5-disubstituted furans, especially those with electron-donating groups, are known to react with singlet oxygen to form unsaturated esters via ring opening of furan endoperoxide.[13] Other light-induced decomposition pathways are also possible.

Good solubility is required for processing of organic electronic materials from solution. We found that the solubility of oligofurans is significantly better than that of the corresponding oligothiophenes (the solubility of **6F** is 0.7 mg/mL, compared with only <0.05 mg/mL for **6T**), which allows crystallization from heptane.[14] Longer oligothiophenes are completely insoluble, while **5F**−**8F** are reasonably soluble; ^{13}C NMR spectra of **5F**−**6F** can be measured in solution, and **9F** can be extracted using a Soxhlet extraction (see the SI). The single-crystal X-ray structure of **6F**[15] shows the oligomer to be completely planar with herringbone packing, as observed for **6T**[16] (Figure 1). The average inter-ring C−C bond lengths in **6F** (1.428 Å) are significantly shorter than in **6T** (1.442 Å). This may indicate a less aromatic and more quinoid structure for **6F**. The exo-bond C−C−C angle is ∼5° larger in **6F** than in **6T** (C8−C9−C10 = 133.4 and 129.0°, respectively; see the SI). Importantly, **6F** is more tightly packed than **6T**, since **6F** contains only first-row atoms. The distance between planes in **6F** is 2.57 Å, which is significantly shorter than that in **6T** (2.89 Å), although in both structures there is practically no direct π−π overlap between adjacent molecules. Also, the molecular density (obtained by dividing the number of molecules per unit cell by the unit cell volume) is 17% higher in **6F** than in **6T** (0.00221 Å^{-3} for **6F** vs 0.00189 Å^{-3} for **6T**; however, the molecular weight and size of

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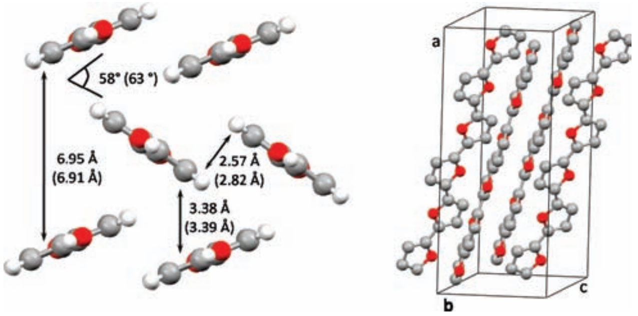

Figure 1. (left) Herringbone structure and (right) packing of **6F**. Color scheme: gray, C; white, H; red, O. Values in parentheses are for **6T**.[16]

Table 1. Photophysical and Electrochemical Data for Oligofurans

	$\varepsilon_{max}{}^{a}$ (M^{-1} cm^{-1})	$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{flu}{}^{a}$ (nm)	$\Phi_f{}^{a,b}$	$E_{ox}{}^{c,d}$ (V)	HOMO^e (eV)
3F	28700^f	331	352, 371^f	0.78^f (0.07)	0.91 (0.79)	−4.91
4F	28600^f	364	391, 413	0.80 (0.18)	0.78 (0.72)	−4.73
5F	51000	388	421, 449	0.74 (0.36)	0.71 (0.67)	−4.62
6F	53000	404	442, 472	0.69 (0.41)	0.67 (0.66)	−4.55
7F	56000	417	455, 485	0.67	0.66 (0.66)	−4.51
8F	56000	423	467, 499	0.66	0.67 (0.68)	−4.48
9F	–	430	473, 507	0.58	–	−4.45

[a] Measured in dioxane. [b] Fluorescence quantum yields for the corresponding ***n*T**s (taken from ref 20) are given in parentheses. [c] Oxidation potentials were measured in propylene carbonate (PC) with 0.1 M tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) and a Ag/AgCl reference electrode (Fc/Fc^+ = 0.34 V vs SCE under these conditions) at a scan rate of 100 mV/s. [d] Values in parentheses are from differential pulse voltammetry (DPV) measurements (see the SI). [e] Calculated values [B3LYP/6-31G(d)].[22] [f] Data were taken from ref 9 and measured in MeCN.

6T are slightly larger than those of **6F**). The herringbone angle of 58° in **6F** is midway between the values for pentacene[17] (53°) and **6T**[16] (63°).[18] It is interesting that the X-ray structures[15] of **3F** and **4F** exhibit more complicated packing, without herringbone packing, and are much less ordered than those of **3T** and **4T**,[19] which exhibit herringbone packing (see the SI).

The oligofurans are highly fluorescent, with quantum yields ranging from 58% for **9F** to 74% for **5F** (Table 1 and Figure 2).[21] The quantum yield slightly decreases with increasing chain length.[9] The Stokes shift values are ~0.25 eV for **3F**−**9F** and are substantially smaller than those for the corresponding oligothiophenes **3T**−**6T** (~0.40 eV), possibly indicating that oligofurans are more rigid. The solid-state fluorescence of **6F** shows peaks that are red-shifted by 0.35 eV relative to their value in solution (see the SI). In addition to the smaller Stokes shift and closer packing mentioned above, the rigidity of oligofurans can be seen from the calculated twisting potentials (Figure 3).[22] The energy required to twist **6F** is significantly greater than that for **6T**. For example, twisting **6F** to a 36° twist angle requires 12.5 kcal/mol, while similar twisting in **6T**[23] requires only 2.3 kcal/mol (we applied the same methodology for the calculation of the twisting energy as was described in ref 23). Such large differences in twisting potential should also allow introduction of different substituents onto the oligofuran backbone without disturbing its planarity. For comparison, even a small increase in twisting potential leads, in some cases, to significant changes in the structure and electronic properties of substituted oligoselenophenes relative to oligothiophenes.[4d,24] The rigidity of α-oligofurans also affects their internal reorganization energy, λ (see the SI). The difference in the twisting potential can be explained by the less aromatic and more quinoid character of oligofurans relative to oligothiophenes and is supported by the difference in the calculated average inter-ring C−C bond lengths. For example, the average calculated inter-ring C−C bond lengths in **6F** and **6T** are 1.432 and 1.443 Å, respectively, which correlates nicely with the experimental values mentioned above. The smaller size of the oxygen atom compared with sulfur atom, which leads to less steric demand in oligofurans than in oligothiophenes, may also contribute to the significant difference in the rigidity.

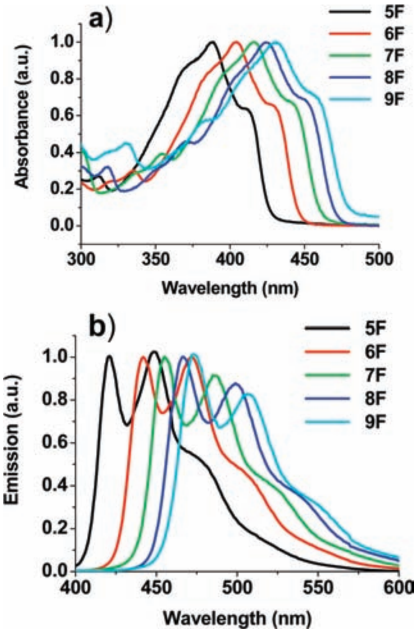

Figure 2. Normalized (a) absorbance and (b) fluorescence spectra of **5F**−**9F** in dioxane.

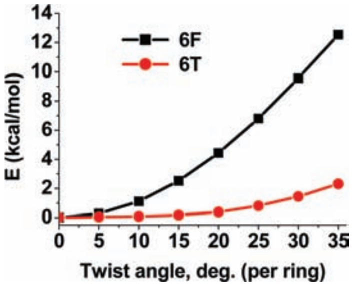

Figure 3. Calculated [B3LYP/6-31G(d)] relative energies required for spiral twisting of **6F** and **6T** as functions of twist angle.

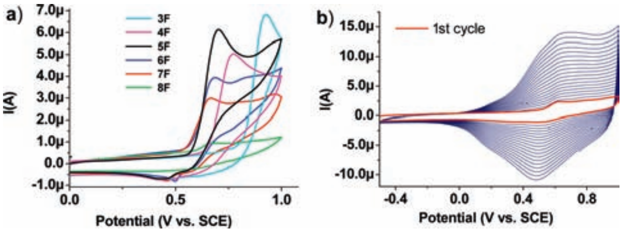

Figure 4. (a) CV of **3F**−**8F** in PC with 0.1 M $TBABF_4$ (scan rate 50 mV/s) and (b) repetitive CV scans of **6F** in 1,2-dichloroethane with 0.1 M $TBABF_4$ (scan rate 100 mV/s). Fc/Fc^+ = 0.34 V vs SCE under these conditions.

CV of **3F**−**8F** shows an irreversible oxidation peak that ranges from 0.91 V (vs SCE) for **3F** and 0.71 V for **5F** to 0.67 V for **8F** (Figure 4a and Table 1, calibrated using Fc/Fc^+ = 0.34 V vs SCE).[25] This is in agreement with the calculated difference of only 0.14 eV in the HOMO energies of **5F**−**8F** (Table 1).[22] Long oligofurans are significantly more electron-rich than oligoth-

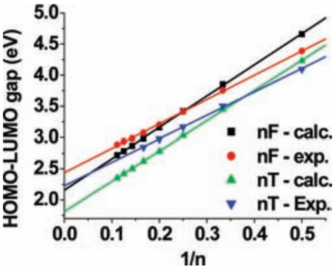

Figure 5. Calculated [B3LYP/6-31G(d)] and experimental HOMO−LUMO gaps vs the reciprocal of the number of oligomer units in α-oligofurans and α-oligothiophenes. Experimental values for oligothiophenes were taken from ref 20. The calculated [PBC/B3LYP/6-31G(d)] band gaps for polyfuran and polythiophene are 2.41 and 2.06 eV, respectively.[27]

iophenes, as evident from their relatively low oxidation potentials. For comparison, the oxidation potentials of **3T** and **4T** are 1.16 and 1.14 V, respectively, under similar conditions. In the cases of **4F**−**7F**, smooth polymer growth was observed during repetitive cycling (Figure 4b), in accord with an earlier report regarding terfuran.[26] The color of the formed film was yellowish-orange in the neutral state and changed to green upon doping.

Extrapolation of the experimental λ_{max} of oligofurans against the reciprocal of the number of monomer units ($1/n$) affords a linear correlation (Figure 5) with an intercept at 2.43 eV, which corresponds to the calculated [PBC/B3LYP/6-31G(d)] band gap of polyfuran[27] (2.41 eV). A similar correlation was observed for the experimental λ_{max} of oligothiophenes. The calculated[22] HOMO−LUMO gaps of oligofurans and oligothiophenes are given in Figure 5 and Table S3 in the SI.[27] It is interesting that the slope (both experimental and calculated) is slightly steeper (by 0.2 eV × n) for oligofurans than oligothiophenes, which may suggest that oligofurans are better-conjugated.

In summary, we have introduced a new class of organic materials, namely, long α-oligofurans, which fulfill the most important requirements for a wide range of applications. The formation of device-quality materials is often a trade-off between processability and function. The materials introduced here combine higher fluorescence, better packing, and greater rigidity with better processability (due to their greater solubility) than the corresponding oligothiophenes. These compounds have a unique combination of physical properties required for organic electronic materials and in addition can help shed light on the relatively unexplored polyfurans. The materials reported here are the first examples of well-characterized oligofuran-based materials. Importantly, furan-based materials should be biodegradable and can be obtained directly from renewable resources.

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Supporting Information Available: Experimental procedures; spectral data; X-ray structural data (CIF) for **3F**, **4F**, and **6F**; and details of electrochemistry and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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