DOI: 10.1002/anie.201308216

Organic Electronics

α-Oligofurans: An Emerging Class of Conjugated Oligomers for Organic Electronics

Ori Gidron and Michael Bendikov†*

conjugation · fluorescence · heterocycles · oligomerization · organic electronics

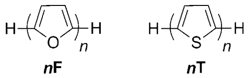
In memory of Michael Bendikov

While the field of organic electronics has developed extensively in recent years, it remains limited by number of materials available. Further expansion requires the innovation of new types of π-conjugated backbones, but suitable candidates are discovered only very rarely. The recent introduction of a new class of conjugated materials, long α-oligofurans, was therefore greeted with considerable interest. α-Oligofurans possess many of the properties required to excel in applications as organic electronic materials, can be manufactured from renewable resources, and are expected to be biodegradable. This Minireview provides an account of long oligofurans from the perspectives of their synthesis, molecular properties, chemical reactivity, and use in electronic devices.

1. Introduction

Organic electronics, a field of science involving mainly π-conjugated materials, has evolved rapidly since conductivity in organic crystals[1] and polymers[2] was first discovered. Recent years have seen burgeoning growth in applications for organic materials in electronic devices, such as organic solar cells,[3] organic field-effect transistors (OFETs),[4] and organic light-emitting diodes (OLEDs),[5] as well as in highly efficient organic light-emitting transistors (OLETs),[6] flexible displays, and specific chemical sensors.

The main requirements for organic electronic materials are a low HOMO–LUMO gap (which also leads to absorption/emission in the visible or NIR range), good solid-state packing, stability, solubility (which is important for their processability), rigidity/planarity, and high luminescence (for light-emitting applications). Despite extensive research, only a limited number of families of conjugated materials are found to comply with these requirements. Among the workhorses in this field are α-oligothiophenes (***n*T**, in particular the α-sexithiophene **6T**)[7] and oligoacenes (particularly pentacene),[8] which have been extensively studied and employed in organic electronic devices. However, **6T** is almost completely insoluble in common organic solvents.[9] An additional downside of oligothiophenes is the low rigidity (high flexibility) of their π-conjugated backbones: while **6T** is planar in the solid state, gas-phase measurements suggested that bithiophene is twisted with a torsional angle of about 20–35°.[10] The low rigidity of the thiophene–thiophene bond limits conjugation through the oligothiophene chain and so restricts functionalization of the backbone (thus, the addition of solubilizing groups, particularly in an head-to-head manner, often deplanarizes these molecules and impairs their conjugation).[11] There is thus an acute need for new types of conjugated materials with superior properties.

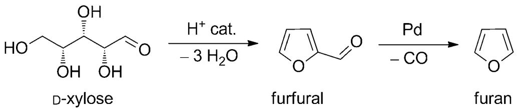


Discovered in 1870,[12] furan is the one of the simplest heteroaromatic compounds. It is less aromatic than thiophene,[13] which contributes to its greater reactivity. For example, furan can serve as a diene in Diels–Alder cycloadditions, whereas thiophene is practically inert to such reactions. Unlike thiophene- or acene-based materials, furan can be obtained entirely from renewable resources (such as D-xylose; Scheme 1).[14] In fact, furfural, a chief furan precursor, was first manufactured industrially by the Quaker Oats company in 1922 from biowaste.[15] In addition, unlike most other building blocks of organic electronic materials, furan and many furan-based derivatives are biodegradable.[16]

---

[*] Dr. O. Gidron, Prof. Dr. M. Bendikov
Department of Organic Chemistry
Weizmann Institute of Science, 76100 Rehovot (Israel)
E-mail: ogidron@ethz.ch

[†] Deceased: July 2, 2013.



Scheme 1. Synthesis of furan from D-xylose.[14d,24]

Short oligofurans up to **4F** were reported about 30 years ago,[17] and only one example of a substituted α-oligofuran consisting of five rings[18] was known prior to the 2010 synthesis of long α-oligofurans (***n*F**).[19–22] As can be seen in Figure 1, oligofurans have a 0.3–0.4 eV higher HOMO–LUMO gap than oligothiophenes. As a result, only oligofurans with six or more furan rings possess a HOMO–LUMO gap below 3 eV (which is the typical range for organic semiconductors).[23] Thus, achieving the preparation of oligofurans with $n \geq 6$ was a necessary prerequisite for their application as organic electronic materials.

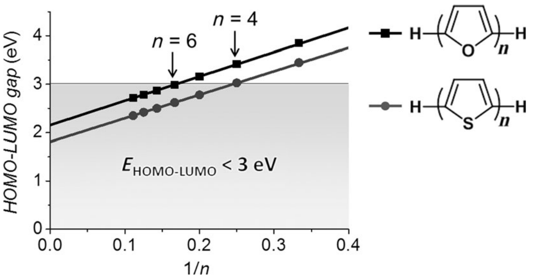


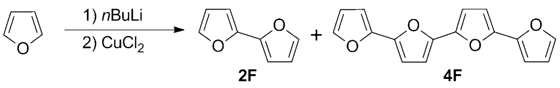
Figure 1. Calculated (B3LYP/6-31G(d)) HOMO–LUMO gaps vs. $1/n$ (n = number of rings) for ***n*F** and ***n*T**.[23]

In this Minireview, we describe recent progress in the study of long α-oligofurans, starting with their synthesis and characterization. We then compare the molecular properties of oligofurans with those of other materials (specifically oligothiophenes), thus focusing on properties such as molecular ordering, planarity, aromaticity, photophysical properties, conjugation, and charge delocalization, which are considered important for π-conjugated systems. We also look at the reactivity of oligofurans in Diels–Alder cycloadditions, which can serve as a test case for the reactivity of long, linear conjugated systems in general. Finally, the first steps towards using oligofurans and oligofuran-containing polymers in practical electronic devices, such as OFETs, solar cells, and OLETs, are discussed.

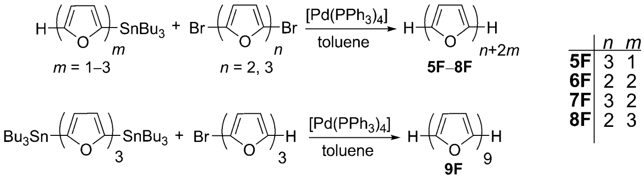
2. Synthesis and Molecular Properties

2.1. Synthesis of Oligofurans

The group of Kaufmann was the first to describe the synthesis of **2F** and **4F** using the Ullmann reaction (Scheme 2),[17] and later used a Negishi coupling to yield the substituted **5F**.[18] Ishida et al., used a Stille coupling to synthesize **3F**.[25] Attempts to obtain longer oligofurans resulted in unstable and inseparable mixtures.[26] In 2010, we found that the Stille coupling of α,ω-dibromooligofurans with monostannyloligofurans gives long oligofurans (**5F–8F**) in good yields (Scheme 3).[19] In addition, the better solubility of the reaction intermediates allows the synthesis of very long, unsubstituted oligofurans, such as **9F** (Scheme 3), while the unsubstituted thiophene analogue, **9T**, is unknown. A different approach to substituted oligofurans was recently reported by the group of Zhang, and proposed a new type of tandem radical cyclization of acetylenes with substituted diazo reagents by a Co^{II}-based metalloradical catalyst (Scheme 4).[27] By using this method, specifically functionalized oligofurans containing up to four rings were prepared.



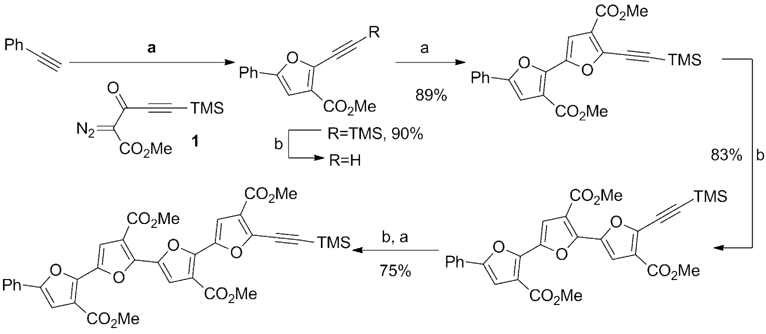
Scheme 2. Synthesis of **2F** and **4F** using the Ullmann reaction.[17]



Scheme 3. Synthetic route for long α-oligofurans.[19]

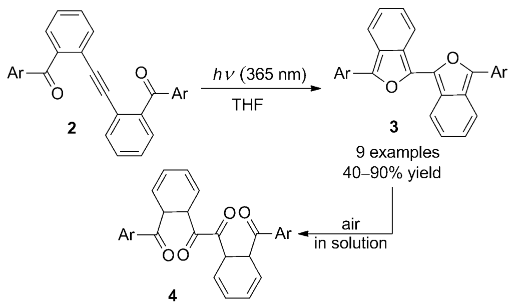
Michael Bendikov received a B.A., M.Sc., and Ph.D. in Chemistry from the Technion—Israel Institute of Technology under the direction of Prof. Y. Apeloig. In 2001, he joined Prof. F. Wudl at UCLA as a postdoctoral researcher. In 2004 he joined the Weizmann Institute of Science, and was promoted to Associate Professor in 2011. His research focused on the design of novel organic electronic materials and the application of physical organic chemistry tools to understand the properties of optoelectronic materials. Michael Bendikov passed away during the course of writing this Minireview.

Ori Gidron received his M.Sc. in Chemistry from the Weizmann Institute of Science (2007) under the supervision of Professor M. van der Boom. He then joined the group of Professor M. Bendikov at the Weizmann Institute of Science and received his Ph.D. in 2012, for which he was awarded the Dov-Elad Prize for Excellence in Chemical Research. In June 2013 he started a Marie-Curie (IEF) Postdoctoral Fellowship in the group of Professor F. Diederich at ETH Zürich.

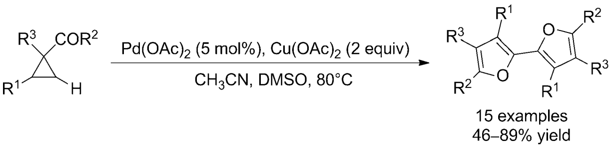


Scheme 4. Construction of functionalized α-oligofurans by iterative metalloradical cyclization of **1**. Reaction conditions: a) **1**, cobalt catalyst, *o*-dichlorobenzene, 80 °C; b) K_2CO_3, methanol.[27] TMS = trimethylsilyl.

Several groups developed different synthetic pathways for the shorter bifuran linker with different substituents. The Yamaguchi group synthesized 3,3′-diaryl-1,1′-bi(isobenzofuran)s (**3**) by photochemical exocyclic [2+2+2] cycloadditions from the acetylene **2** with various aryl groups in good yields (Scheme 5).[28] Despite the instability displayed by these compounds, which readily oxidized to **4**, it was possible to obtain single crystals which revealed good packing in the solid state. Recently, a new methodology for the synthesis of multisubstituted bifurans by the dimerization of cyclopropenes, using a copper-promoted cycloisomerization and palladium-catalyzed dimerization cascade, was reported (Scheme 6).[29]



Scheme 5. Synthesis of **3** by photochemical exocyclic [2+2+2] cycloaddition, and spontaneous oxidation to **4** in solution.[28]



Scheme 6. Copper/palladium-catalyzed oxidative dimerization of cyclopropenes to bifurans.[29] DMSO = dimethylsulfoxide.

2.2. Stability, Solubility, and Solid-State Packing

In the dark, long α-oligofurans were found to be quite stable in the solid state and in solution.[19] However, they readily degrade when exposed to a combination of light and oxygen.[19]

The solubility of oligofurans is significantly better than that of the corresponding oligothiophenes (the solubility of **6F** in chloroform is 0.7 mg mL^{-1}, compared with < 0.05 mg mL^{-1} for **6T**), and is important for solution processing of these materials.[19] This difference can be rationalized by the lower heat of melting of oligofurans (for example the heat of melting for **4F** and **4T** is 6.5 kcal mol^{-1} and 10.5 kcal mol^{-1}, respectively) and accounts for weaker interactions in the solid state.[30]

The single-crystal X-ray structure of **6F** shows the oligomer to be completely planar, with each furan ring *trans* to its neighboring rings (Figure 2 a).[19] The degree of molecular organization (packing) in the solid state strongly affects charge-transport properties.[31] In this respect, it is interesting to compare the crystal packing of oligofurans with that of benchmark molecules in organic electronics. Figure 2 b shows the crystal packing arrangements of pentacene,[32] **6F**,[19] and **6T**.[9] All three molecules have very similar herringbone packing motifs, but the molecular density is 17 % higher in **6F** than in **6T**. Such a difference should account for strong intermolecular interaction in oligofurans, thus resulting in good charge-transport properties in the solid state.

2.3. Planarity and Aromaticity

In conjugated systems, planarity is a prerequisite for obtaining good π-orbital overlap and effective electron delocalization. However, nonfused conjugated systems have very flexible π-conjugated backbones resulting from possible rotation around the (single) inter-ring bonds. Here lies perhaps one of the most significant differences between oligofurans and the majority of other conjugated systems, including oligothiophenes. Oligofurans have a stiffer conjugated backbone.[33] The calculated twisting potential for **6F** is significantly steeper than that for **6T** (Figure 3, left): twisting each inter-ring bond in **6F** to a 35° inter-ring twist angle

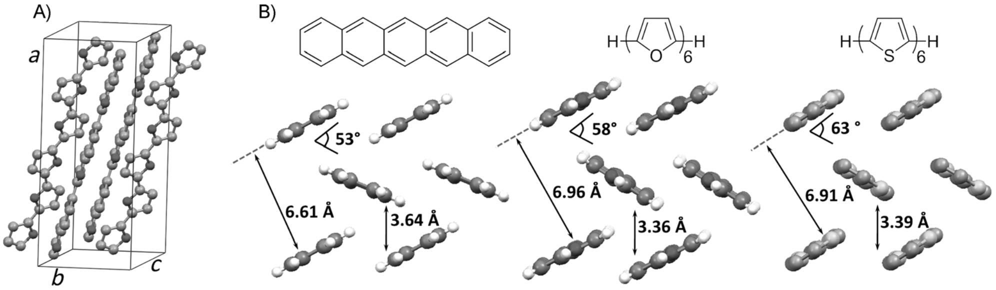


Figure 2. A) Unit cell of **6F**. B) Packing of pentacene[32] (left), **6F**[19] (centre), and **6T**[9] (right) showing their herringbone structure. Adapted with permission from Ref. [19]. Copyright (2010) American Chemical Society.

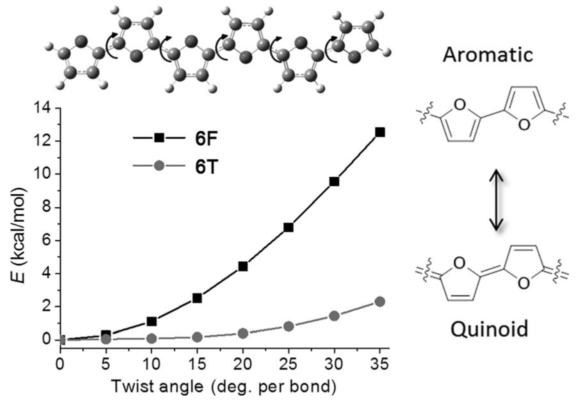


Figure 3. Calculated (B3LYP/6-31G(d)) relative energy versus twist angle for spiral twisting of **6F** and **6T** (left) and aromatic and quinoid resonance structures of oligofuran (right). Adapted with permission from Ref. [19]. Copyright (2010) American Chemical Society.

requires 12.5 kcal mol^{-1}, while similar twisting in **6T** requires only 2.3 kcal mol^{-1}.[19,34] Since furans are less aromatic than thiophenes,[13] the differences in the twisting potentials can be explained by the more quinoid character of oligofurans (Figure 3, right). This difference is evidenced by both the calculated bond length alternation (BLA) patterns of oligofurans,[23] and by shorter average inter-ring C–C bond lengths (obtained from X-ray data); 1.433 Å for **6F** compared with 1.442 Å for **6T**. The smaller size of the oxygen atom compared with the sulfur atom can also contribute to the significant difference in rigidity, as it reduces the steric repulsion between the heteroatom and the β-hydrogen atom in the adjacent ring.

2.4. Photophysical Properties

The rigid π-conjugated backbone of oligofurans affects their photophysical properties. Unlike oligothiophenes, the vibronic shoulders of oligofurans are clearly observed in UV-Vis spectra, even at room temperature (Figure 4a). Their Stokes-shift values are significantly smaller than those of oligothiophenes (around 0.25 eV for **3F**–**9F** and around 0.40 eV for **3T**–**9T**), with both factors indicating their greater rigidity. The group of Becker first reported improved fluorescence quantum yields for short oligofurans (78% in **3F**) compared with the those of the corresponding oligothiophenes (6.6% in **3T**).[35,36] Long oligofurans also exhibit strong fluorescence (Figure 4b,c and Table 1),[19] which is important for their application in optoelectronic devices. The higher quantum yield can be rationalized by the difference in the nonradiative decay constant (k_{NR}), which is an order of magnitude larger for oligothiophenes compared with that of the corresponding oligofurans.[35] For example, k_{NR} is 0.17 ns^{-1} for **4F** and 1.77 ns^{-1} for **4T** in acetonitrile. This difference mostly stems from the greater rigidity towards out-of-plane vibrations of oligofurans compared with those of oligothiophenes.[30]

Table 1: Photophysical and electrochemical data for oligofurans.[19]

	ε_{max}[a] [M^{-1} cm^{-1}]	λ_{abs}[a] [nm]	λ_{flu}[a] [nm]	Φ_f[a,b]	E_{ox}[c] [V]
3F	–	331	–	0.78 (0.07)	0.91
4F	37900[30]	364	391, 413	0.80 (0.18)	0.78
5F	51000	388	421, 449	0.74 (0.36)	0.71
6F	53000	404	442, 472	0.69 (0.41)	0.67
7F	56000	417	455, 485	0.67	0.66
8F	56000	423	467, 499	0.66	0.67
9F	–	430	473, 507	0.58	–

[a] Measured in 1,4-dioxane. [b] Fluorescence quantum yields for the corresponding **nTs** (taken from Ref. [36]) are given in parentheses. [c] Oxidation potentials measured in propylene carbonate with 0.1 M tetra-*n*-butylammonium tetrafluoroborate, reference electrode Ag/AgCl, Fc/Fc$^+$ = 0.34 V vs. SCE under these conditions, scan rate: 100 mV s^{-1}.

2.5. Conjugation and Charge Delocalization

The extent of charge delocalization and conjugation in oligofurans directly affects their electronic and electrical properties, and is therefore critical for their applications as active materials in optoelectronic devices. The low aromaticity and high rigidity of oligofurans demonstrated above should favor considerable conjugation and charge delocalization, despite a larger HOMO–LUMO gap compared to that of the oligothiophenes.

Charge delocalization in oligofurans was studied using a mixed valence system containing diferrocenyl-capped oligofurans, which were compared with the corresponding

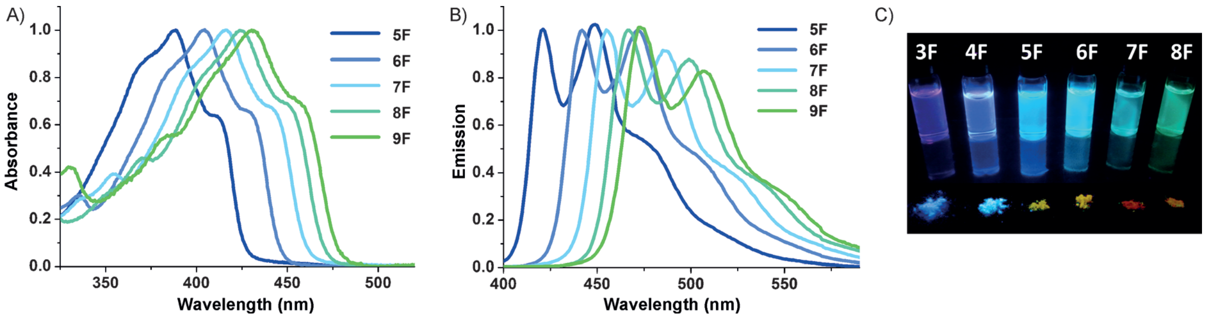


Figure 4. a) Normalized absorbance and b) fluorescence spectra of **5F**–**9F** in 1,4-dioxane.[19] c) Photograph of irradiated samples of **3F**–**8F** in 1,4-dioxane solutions and as powders. Adapted with permission from Ref. [19]. Copyright (2010) American Chemical Society.

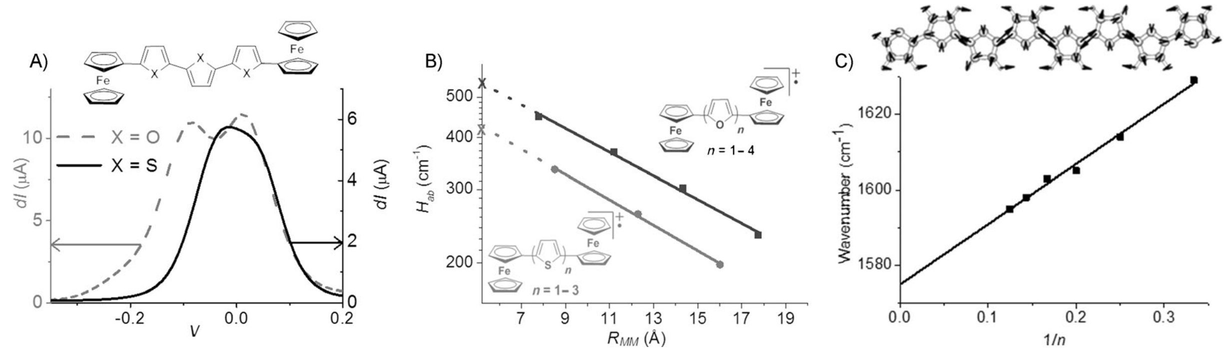


Figure 5. a) Square-wave voltammetry of diferrocenyl-capped **3 F** and **3 T**. b) Hush coupling constant H_{ab} as a function of metal–metal distance (R_{MM}) for oligofuran- and oligothiophene-bridged systems. Adapted from Ref. [37] with permission. c) Top: eigenvector associated with the strongest Raman feature of **8 F** (calculated at the B3LYP/6-31G(d) level). Bottom: experimental dependence of Я mode on the reciprocal chain length in oligofurans. Adapted from Ref. [38] with permission from The Royal Society of Chemistry.

oligothiophenes (Figure 5).[37] Electrochemical experiments showed better electronic communication between oligofuran-bridged systems, as evidenced by the larger difference between the oxidation potentials of the two terminal ferrocenes (Figure 5 a). Spectroscopic studies revealed that the electronic coupling integral (H_{ab}) is 30–50 % greater for oligofuran-bridged systems compared with that of oligothiophene-bridged systems, thus indicating better energy matching between the ferrocene units and oligofurans (Figure 5 b). While both the difference in oxidation potentials and H_{ab} depend on the energy matching between the terminal ferrocene units and the conjugated bridge, the distance decay factor (attenuation factor), β, is considered to be independent of the effect of the terminal ferrocenyl units. The β value is similar for oligofurans (0.066 A^{-1}) and oligothiophenes (0.070 A^{-1}), thus indicating a similar extent of delocalization, despite the higher HOMO–LUMO gaps in oligofurans. The obtained β value for oligofurans is small relative to other conjugated systems, thus indicating strong delocalization in oligofurans. Computational studies suggested a slightly larger extent of delocalization in furan-bridged systems when compared with thiophene-bridged systems.[37]

Conjugation in the oligofurans **3 F**–**8 F** and polyfuran was studied by Raman spectroscopy, measuring the Я ("Ya") mode, which corresponds to C−C/C=C stretching of the π-conjugated backbone (Figure 5 c).[38] The strongest Raman feature arising from the collective "breather" Я mode continuously downshifts with increasing chain length. The experimental data indicate that π-conjugation in this series does not reach saturation with chain length of at least up to the octamer, and extends over about 14–15 furan units in the polymer.[38]

2.6. Oligofurans as Building Blocks in Conjugated Systems

Given the favorable molecular properties of oligofurans discussed above, and the growing interest in oligofuran-containing materials, it is important to identify and study the smallest oligofuran unit bearing these properties. Comparing two structural isomers (Figure 6),[30] it was found that an oligofuran unit as small as bifuran is responsible for the increased fluorescence, greater solubility, and greater rigidity, previously observed in long oligofurans.[19] Importantly, a single furan ring is insufficient to obtain these properties. Consequently, incorporation of the short bifuran unit into organic electronic materials should be considered in the rational design of structurally complex tailor-made π-conjugated organic electronic materials.[30]

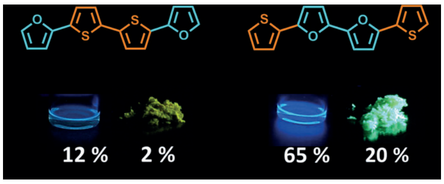
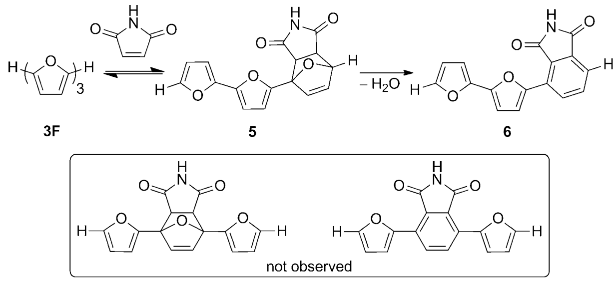


Figure 6. Irradiated (at λ = 365 nm) samples of bithiophene- (left) and bifuran- (right) containing molecules in 1,4-dioxane solutions and in solid (crystalline) form. Quantum efficiencies are denoted below each sample. Adapted from Ref. [30] with permission from The Royal Society of Chemistry.

2.7. Reactivity in Diels–Alder Cycloadditions

Considered a classic textbook reaction, the reactivity of furan towards dienophiles was one of the first cycloaddition reactions studied by Diels and Alder more than 80 years ago.[39] However, the reactivity of long conjugated systems has rarely been explored[40] because of their limited synthetic availability and low solubility. Recently, the reactivity of oligofurans towards dienophiles was studied (both experimentally and computationally) as a test case for the reactivity of long conjugated systems (Scheme 7).[41] Interestingly, terminal-ring cycloadducts of oligofurans (such as **3 F** and **5 F**) are both kinetically and thermodynamically favored. For example, the reaction of terfuran (**3 F**) and maleimide proceeds at room temperature to yield the terminal cycloadduct **5** exclusively, which in turn aromatizes to the thermodynamic product **6** (Scheme 7).[41]

DFT calculations show that terminal cycloaddition is both kinetically and thermodynamically preferred over cycloaddition to the central ring (Figure 7). Interestingly, the reactivity



Scheme 7. Diels–Alder cycloaddition of **3 F** and maleimide.[41]

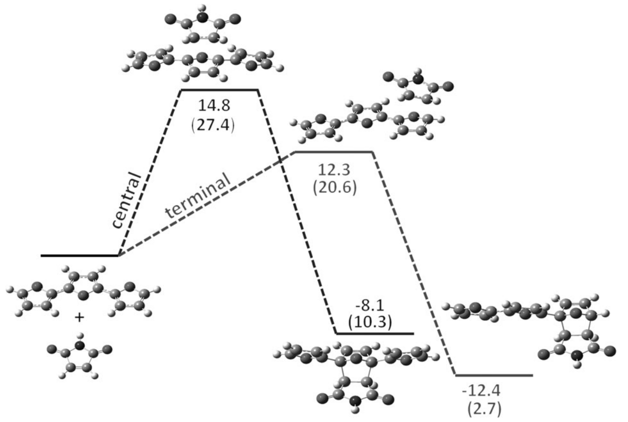


Figure 7. Pathway for the reaction of **3 F** with maleimide calculated at M06-2X/6-31G(d) (in kcal mol^{-1}; values at B3LYP/6-31G(d) are given in parentheses). Reprinted with permission from Ref. [41]. Copyright (2010) American Chemical Society.

of oligofurans and oligothiophenes remains constant with increasing chain length (and it might be assumed that the same trend will be observed in other conjugated heterocyclic systems), and might explain the relative stability of very long conjugated oligomers and polymers.[41] This trend is in sharp contrast with that of other aromatic systems, such as oligoacenes, where reactivity increases with increasing chain length, and the central ring is the most reactive.[42]

3. Electronic and Optoelectronic Devices Based on Oligofurans

3.1. Theoretical Aspects

Oligofurans of different lengths were studied computationally, including several investigations of their charge-transport properties, using DFT methods.[23,43–46] Hutchison et al. addressed the importance of the heteroatom in oligothiophenes, oligofurans, and oligopyrrols.[43] Their calculations indicated larger hole-transfer rates for oligofurans compared to those of oligothiophenes, despite their lower intermolecular π-cloud overlap.[43b] Two reports have used the crystal structure reported in Reference [19] to predict computationally the FET mobility of oligofurans.[45,46] Mohakud et al. calculated that the hole and electron mobility of **6F** is almost five times higher than that of **6T** (with μ_h values of 0.153 and 0.035 cm^{2}V^{-1}s^{-1} for **6F** and **6T**, respectively).[45,47] Huang et al. calculated the effective electronic coupling and reorganization energies in oligofurans.[46] They also looked at the possible hopping pathways in the crystal lattice, and concluded that charge mobility should be more direction-dependant in **6F** than in **6T** because **6F** exhibits shorter interplane distances than **6T** in one direction while other interplane distances are similar. Indeed, the calculated maximum hole mobility in the *b* axial direction is nearly 17 times larger in **6F** (0.167 cm^{2}V^{-1}s^{-1}) than in **6T** (0.009 cm^{2}V^{-1}s^{-1}), while in the *c* axial direction the calculated mobility of **6F** (0.010 cm^{2}V^{-1}s^{-1}) is only slightly larger than that of **6T** (0.006 cm^{2}V^{-1}s^{-1}).[46] Thus, the theory predicts that the charge-carrier mobilities in oligofurans should be similar to or even larger than that in oligothiophenes.

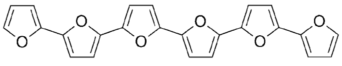
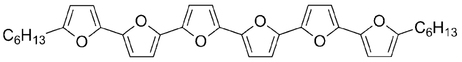
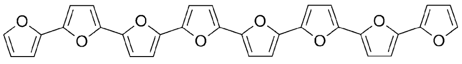
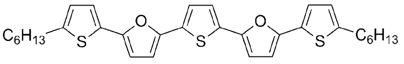
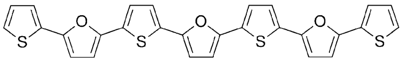
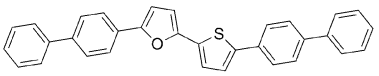
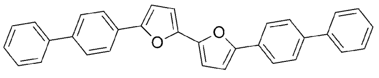
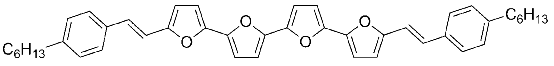
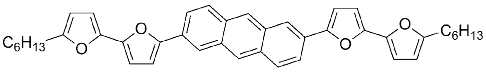
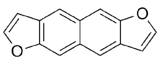
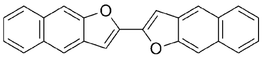
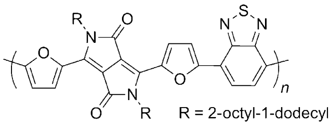
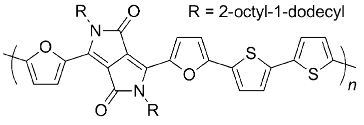
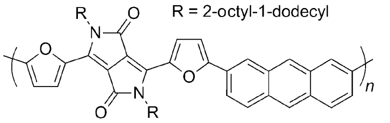
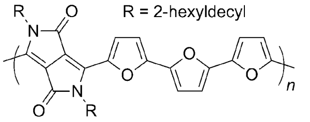
3.2. Devices Based on Long Oligofurans and Oligofuran-Containing Polymers

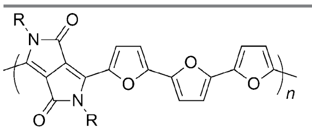
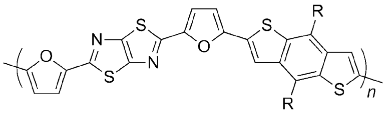
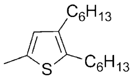
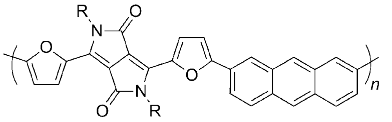
Table 2 lists representative example devices (OFET and organic solar cells) with furan-containing oligomers and polymers. Recently, we reported the OFET characteristics and film morphology of oligofurans and compared them with their benchmark thiophene analogues.[48,49] Generally, the FET mobility values for oligofurans were found to be similar in both classes of materials, when measured under similar conditions (with typical range of $\approx 10^{-2}$ cm^{2}V^{-1}s^{-1} and on/off ratio of $\approx 10^5$ for polycrystalline films). The output curves for oligofuran-based OFETs (Figures 8a and b) indicate good (ohmic) contact with the electrodes. Oligofurans have higher HOMO energies and consequently display lower contact resistance with the gold electrodes (e.g., HOMO = −4.55 eV for **6F** and −4.80 eV for **6T** at the B3LYP/6-31G(d) level). These works[48,49] provided evidence that, contrary to accepted opinion,[43b,50] the presence of a large polarizable element, such as sulfur, is not a prerequisite for successful OFET materials based on conjugated heterocyclic molecules.

OFET devices containing DH-**6F** and DH-**7F** as the active layer revealed the appearance of greenish-yellow electroluminescence upon biasing the devices (when the gate voltage was "on").[48,49] This observation combined with a high on/off ratio and a low threshold voltage in oligofuran-based OFETs sets a starting point for future development of OLETs.[48,51,52] To that end, the group of Tanigaki has recently studied furan-based biphenyl end-capped oligomers BPFF and BPFT (Table 2).[53] Single-crystal FET devices of both BPFF and BPFT were shown to have good hole mobility (Table 2), while the BPFT device displayed good electron mobility and electroluminescence.

Recently, several groups have used oligofuran-containing polymers as active materials in solar cell and OFET devices.[54–58] The increased solubility of oligofurans is one of the advantages for their applications in solar cells. The group of Frećhet prepared an oligofuran/diketopyrrole copolymer (PDPP3F-D) and used it in solar cells with an efficiency of up to 3.8 % (Table 2).[55] The group of Janssen also used an oligofuran based-polymer, PDPP3F-H, to produce solar cells with efficiencies of up to 1.9 %.[56] The furan-containing

Table 2: Structure and properties of oligofurans and furan-containing oligomers and polymers used for OFETs and organic solar cells. Values within parentheses are for the corresponding oligothiophene analogues.

OFET Compound	Name	μ_h [cm^{2}V^{-1}s^{-1}]	on/off ratio	V_T [V]	Ref.	Notes
	**6 F**	6.4×10^{-4} (0.04)	10^5 (4×10^5)	−14 (−12)	[48] ([48])	"wirelike" film morphology
	DH-**6 F**	0.05 (0.098)	2×10^5 (5×10^5)	−15 (−10)	[48] ([48])	electroluminescent
	**8 F**	0.066	8×10^5	−14	[48]	
	DH-SOSOS	1.4×10^{-2}	10^4	-26	[20c]	
	SOSOSOS	1.3×10^{-3}	10^4	−23	[20b]	
	BPFT	0.27	–	−45	[53a]	$\mu_e = 0.013$ electroluminescent
	BPFF	0.32	–	−7	[53a]	
	DSH-**4 F**	0.07 (0.05–0.075)	10^4 (10^3 10^4)	−3 (−10 −15)	[49] ([60])	
	**2 F**-Ant	0.025	10^4	−12	[49]	
	NDF	0.6	4×10^6	−2.7	[61a]	
	BNF	0.21	–	–	[61b]	
	PDPP-FBF	0.20	≈10^3	–	[62]	annealed at 200 °C $\mu_e = 0.56$
	PDBFBT	1.54	10^6	–	[57b]	annealed at 200 °C
	PDPP-FAF	0.07	10^5	−16.3	[57d]	
	PDPP3 F-H	3×10^{-3} (4×10^{-2})	–	–	[56]	$\mu_e = 8\times10^{-5}$ ($\mu_e = 1\times10^{-2}$)

Organic Solar Cells Compound	R	Name	V_{oc}	J_{sc} [mA cm^{-2}]	FF	PCE [%]	Ref.	Notes
	2-ethylhexyl 2-hexydecyl	PDPP3 F-H PDPP3 F-D	0.66 0.73	5.4 9.1	0.54 0.58	1.9 3.8	[56] [55]	1:1 polymer/[70]PCBM 1:3 polymer/[70]PCBM
		PBDTTDFTT	0.83	7.67	0.48	3.06	[63]	1:1 polymer/[70]PCBM
	2-octyl-1-dodecyl	PDPP-FAF	0.69	7.8	45	2.5	[57d]	1:2 polymer/[70]PCBM

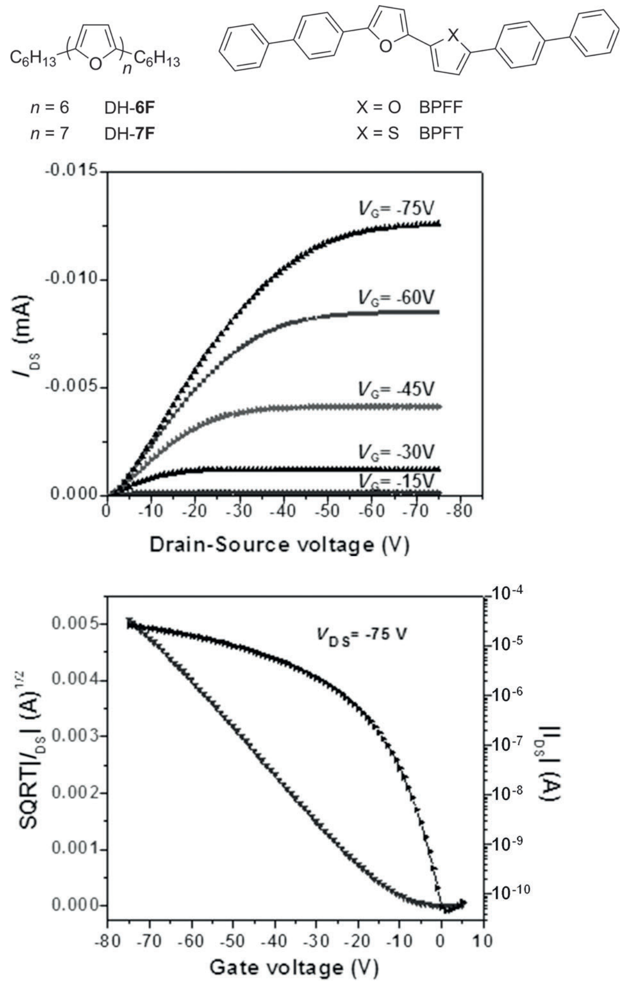


Figure 8. a) Output and b) transfer characteristics of OFETs based on DH-**6F**.[48]

polymer PDBFBT displayed a high mobility of 1.54 $cm^2V^{-1}s^{-1}$.[56b] These reports demonstrate that the incorporation of a furan unit in a wide variety of conjugated polymers is a convenient tool for tailoring their properties.

4. Summary and Outlook

In this Minireview, we have highlighted the important features of the recently introduced family of long α-oligofurans. Compared with other π-conjugated materials (specifically, oligothiophenes), they possess some important advantages for the design of new organic electronic materials: a) High rigidity of the π-conjugated backbone, which allows good conjugation by maintaining the planarity of the backbone. This rigidity is predicted by DFT and confirmed experimentally by the presence of vibronic shoulders in their absorption spectra and by their small Stokes shifts. b) Strong fluorescence, which can increase the efficiency of optoelectronics, such as OLEDs and OLETs, and should also be advantageous for sensors. c) Extensive conjugation and charge delocalization, which is an important factor for charge transport in molecular and polymer films, as well as for possible applications of oligofurans as molecular wires. d) Good field-effect mobility enables the application of oligofurans in OFETs and solar cells. e) Increased solubility enables oligofurans to be processed from solution and also allows chemical reactions to be performed with relatively long oligofurans. f) Availability from renewable resources and potential biodegradability, which is important for the economic and sustainability aspects of possible mass-production.

The quest for possible applications of oligofurans is still in its infancy, but already oligofurans and oligofuran-containing polymers have shown promise as active materials in OFETs and in organic solar cells. Other applications are clearly expected to follow. Re-investigation of polyfurans[59] and study of the cation radicals of long α-oligofurans are the next steps required to understand this new family of compounds and to explore their applications in the field of organic electronics.

We thank the Minerva Foundation for financial support. M.B. was a member ad personam of the Lise Meitner-Minerva Center for Computational Quantum Chemistry.

Received: September 18, 2013

---

[1] F. Wudl, D. Wobschal, E. J. Hufnagel, *J. Am. Chem. Soc.* **1972**, *94*, 670 – 672.
[2] a) H. Shirakawa, E. J. Louis, A. G. Macdiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Commun.* **1977**, 578; b) C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. Macdiarmid, *Phys. Rev. Lett.* **1977**, *39*, 1098 – 1101.
[3] Y. Lin, Y. Li, X. Zhan, *Chem. Soc. Rev.* **2012**, *41*, 4245 – 4272.
[4] Z. Bao, J. Locklin, Eds. *Organic Field Effect Transistors*, CRC, Boca Raton, FL, **2007**.
[5] a) I. F. Perepichka, D. F. Perepichka, H. Meng in *Handbook of Thiophene-Based Materials*, Wiley, Hoboken, **2009**, pp. 695 – 756; b) S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem, K. Leo, *Nature* **2009**, *459*, 234 – 238.
[6] a) A. Hepp, H. Heil, W. Weise, M. Ahles, R. Schmechel, H. von Seggern, *Phys. Rev. Lett.* **2003**, *91*, 157406; b) R. Capelli, S. Toffanin, G. Generali, H. Usta, A. Facchetti, M. Muccini, *Nat. Mater.* **2010**, *9*, 496.
[7] a) D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, **1999**; b) A. Mishra, C.-Q. Ma, P. Bäuerle, *Chem. Rev.* **2009**, *109*, 1141 – 1276; c) *Handbook of Thiophene-Based Materials* (Eds.: I. F. Perepichka, D. F. Perepichka), Wiley-VCH, Weinheim, **2009**.
[8] a) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460; *Angew. Chem. Int. Ed.* **2008**, *47*, 452; b) D. Chun, Y. Cheng, F. Wudl, *Angew. Chem.* **2008**, *120*, 8508; *Angew. Chem. Int. Ed.* **2008**, *47*, 8380; c) B. Purushothaman, M. Bruzek, S. R. Parkin, A.-F. Miller, J. E. Anthony, *Angew. Chem.* **2011**, *123*, 7151; *Angew. Chem. Int. Ed.* **2011**, *50*, 7013.
[9] G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J. L. Fave, F. Garnier, *Chem. Mater.* **1995**, *7*, 1337 – 1341.
[10] a) S. Samdal, E. J. Samuelsen, H. V. Volden, *Synth. Met.* **1993**, *59*, 259; b) M. Takayanagi, T. Gejo, I. Hanazaki, *J. Phys. Chem.* **1994**, *98*, 12893.
[11] G. Barbarella, M. Zambianch, A. Bongini, L. Antolini, *Adv. Mater.* **1993**, *5*, 834.
[12] H. Limpricht, *Ber. Dtsch. Chem. Ges.* **1870**, *3*, 90 – 91.

[13] a) J. A. Joule, K. Mills, *Heterocyclic Chemistry*, 5th ed., Blackwell Publishing, **2010**, chap. 15; b) M. K. Cyrañski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, *J. Org. Chem.* **2002**, *67*, 1333; c) A. Stanger, *J. Org. Chem.* **2006**, *71*, 883.

[14] a) M. N. Belgacem, A. Gandini, *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, **2008**, chap. 6; b) A. Gandini, *Macromolecules* **2008**, *41*, 9491 – 9504; c) J. B. Binder, R. T. Ronald, *J. Am. Chem. Soc.* **2009**, *131*, 1979 – 1985; d) A. Gandini, *Green Chem.* **2011**, *13*, 1061 – 1083.

[15] H. E. Hoydonckx, W. M. Van Rhijn, W. Van Rhijn, D. E. De Vos, P. A. Jacobs in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2000**.

[16] a) M. Okada, K. Tachikawa, K. Aoi, *J. Appl. Polym. Sci.* **1999**, *74*, 3342 – 3350; b) F. Koopman, N. Wierckx, J. H. de Winde, H. J. Ruijssenaars, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 4919 – 4924; c) "Agricultural and Synthetic Polymers. Biodegradability and Utilization": A. Gandini, *ACS Symp. Ser.* **1990**, *433*, 195.

[17] T. Kauffmann, H. Lexy, *Chem. Ber.* **1981**, *114*, 3667.

[18] J. M. Kauffman, G. Moyna, *J. Heterocycl. Chem.* **2002**, *39*, 981 – 988.

[19] O. Gidron, Y. Diskin-Posner, M. Bendikov, *J. Am. Chem. Soc.* **2010**, *132*, 2148.

[20] For highlight on oligofurans see: U. H. F. Bunz, *Angew. Chem.* **2010**, *122*, 5159; *Angew. Chem. Int. Ed.* **2010**, *49*, 5037.

[21] Alternating furan/thiophene oligomers containing up to only seven rings were also reported: a) Y. Miyata, T. Nishinaga, K. Komatsu, *J. Org. Chem.* **2005**, *70*, 1147 – 1153; b) Y. Miyata, M. Terayama, T. Minari, T. Nishinaga, T. Nemoto, S. Isoda, K. Komatsu, *Chem. Asian J.* **2007**, *2*, 1492; c) F.-T. Luo, A. C. Bajji, *J. Chin. Chem. Soc.* **2000**, *47*, 257.

[22] Recently, another interesting class of oligofurans, namely long β-oligofurans, was reported (T. Fallon, A. C. Willis, A. D. Rae, M. N. Paddon-Row, M. S. Sherburn, *Chem. Sci.* **2012**, *3*, 2133 – 2137). These compounds are nonplanar, and show no significant increase in conjugation with increasing length. Unfortunately, space constraints place them beyond the scope of this Minireview.

[23] S. Sharma, M. Bendikov, *Chem. Eur. J.* **2013**, *19*, 13127 – 13139.

[24] a) K. J. Jung, A. Gaset, J. Molinier, *Biomass* **1988**, *16*, 89 – 96.

[25] H. Ishida, K. Yui, Y. Aso, T. Otsubo, F. Ogura, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2828.

[26] G. Distefano, D. Jones, M. Guerra, L. Favaretto, A. Modelli, G. Mengoli, *J. Phys. Chem.* **1991**, *95*, 9746.

[27] X. Cui, X. Xu, L. Wojtas, M. M. Kim, X. P. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 19981 – 19984.

[28] H. Zhang, A. Wakamiya, S. Yamaguchi, *Org. Lett.* **2008**, *10*, 3591 – 3594.

[29] C. Song, D. Sun, X. Peng, J. Bai, R. Zhang, S. Hou, J. Wang, Z. Xu, *Chem. Commun.* **2013**, *49*, 9167 – 9169.

[30] O. Gidron, N. Varsano, L. J. W. Shimon, G. Leitus, M. Bendikov, *Chem. Commun.* **2013**, *49*, 6256 – 6258.

[31] M. Mas-Torrent, C. Rovira, *Chem. Rev.* **2011**, *111*, 4833 – 4856.

[32] D. Holmes, S. Kumaraswamy, A. J. Matzger, K. P. C. Vollhardt, *Chem. Eur. J.* **1999**, *5*, 3399.

[33] Previously, Curtis et al. noted that chemically prepared regioregular poly(3-octylfuran) adopt a planar conformation, while regioirregular poly(3-octylfuran) are not planar. See J. K. Politis, J. C. Nemes, M. D. Curtis, *J. Am. Chem. Soc.* **2001**, *123*, 2537 – 2547.

[34] We note that calculating the twisting energies at higher levels of theory results in similar trend of rigidity. For example, the energy required for a 35° inter-ring twist angle, calculated at the MP2/cc-pVTZ//B3LYP/6-31G(d) level of theory is 8.17 kcal mol^{-1} for **6F** and 1.25 kcal mol^{-1} for **6T**.

[35] The photophysical properties of **2F** – **4F** were studied in detail: J. Seixas de Melo, F. Elisei, C. Gartner, G. G. Aloisi, R. S. Becker, *J. Phys. Chem. A* **2000**, *104*, 6907.

[36] R. S. Becker, J. S. deMelo, A. L. Macanita, F. Elisei, *J. Phys. Chem.* **1996**, *100*, 18683 – 18695.

[37] O. Gidron, Y. Diskin-Posner, M. Bendikov, *Chem. Eur. J.* **2013**, *19*, 13140 – 13150.

[38] C. C. Ferrón, M. C. R. Delgado, O. Gidron, S. Sharma, D. Sheberla, Y. Sheynin, M. Bendikov, J. T. L. Navarrete, V. Hernández, *Chem. Commun.* **2012**, *48*, 6732.

[39] a) O. Diels, K. Alder, *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 554; b) For a review of Diels – Alder reactions with furan, see O. C. Kappe, S. S. Murphree, A. Padwa, *Tetrahedron* **1997**, *53*, 14179.

[40] K. Alder, M. Schumacher, *Justus Liebigs Ann. Chem.* **1950**, *570*, 178.

[41] O. Gidron, L. J. W. Shimon, G. Leitus, M. Bendikov, *Org. Lett.* **2012**, *14*, 502 – 505.

[42] W. C. Herndon, M. L. Ellzey, *J. Am. Chem. Soc.* **1974**, *96*, 6631 – 6642.

[43] a) G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 2339 – 2350; b) G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 16866 – 16881; c) G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Phys. Chem. B* **2005**, *109*, 3126 – 3138.

[44] S. S. Zade, M. Bendikov, *Org. Lett.* **2006**, *8*, 5243 – 5246.

[45] S. Mohakud, A. P. Alex, S. K. Pati, *J. Phys. Chem. C* **2010**, *114*, 20436.

[46] J.-D. Huang, S.-H. Wen, W.-Q. Deng, K.-L. Han, *J. Phys. Chem. B* **2011**, *115*, 2140.

[47] Note that the results reported in Ref. [45] could be affected by the fact that the geometries of the oxidized and reduced structures were optimized at the B3LYP/6-31G++(d,p) level, while the geometries of the neutral molecules were taken from the X-ray data and not optimized, except for the hydrogen atoms.

[48] O. Gidron, A. Dadvand, Y. Sheynin, M. Bendikov, D. F. Perepichka, *Chem. Commun.* **2011**, *47*, 1976 – 1978.

[49] O. Gidron, A. Dadvand, E. W.-H. Sun, I. Chung, L. J. W. Shimon, M. Bendikov, D. F. Perepichka, *J. Mater. Chem. C* **2013**, *1*, 4358 – 4367.

[50] K. Takimiya, Y. Kunugi, Y. Konda, N. Niihara, T. Otsubo, *J. Am. Chem. Soc.* **2004**, *126*, 5084.

[51] a) A. Hepp, H. Heil, W. Weise, M. Ahles, R. Schmechel, H. von Seggern, *Phys. Rev. Lett.* **2003**, *91*, 157406; b) F. Cicoira, C. Santato, A. Dadvand, C. Harnagea, A. Pignolet, P. Bellutti, Z. Xiang, F. Rosei, H. Meng, D. F. Perepichka, *J. Mater. Chem.* **2008**, *18*, 158.

[52] Recently, molecular assemblies (multilayers) of oligofurans or oligothiophenes coordinated with Pd^{II} complexes on ITO substrates were prepared. It was found that both assemblies possess similar features, with assemblies incorporating oligofuran exhibiting a lower density and being blue shifted relative to oligothiophene-based assemblies. See: A. Hayoun Barak, G. de Ruiter, M. Lahav, S. Sharma, O. Gidron, G. Evmenenko, P. Dutta, M. Bendikov, M. E. van der Boom, *Chem. Eur. J.* **2013**, *19*, 8821 – 8831.

[53] a) K. Oniwa, T. Kanagasekaran, T. Jin, M. Akhtaruzzaman, Y. Yamamoto, H. Tamura, I. Hamada, H. Shimotani, N. Asao, S. Ikeda, K. Tanigaki, *J. Mater. Chem. C* **2013**, *1*, 4163 – 4170; b) H. Tamura, I. Hamada, H. Shang, K. Oniwa, M. Akhtaruzzaman, T. Jin, N. Asao, Y. Yamamoto, T. Kanagasekaran, H. Shimotani, S. Ikeda, K. Tanigaki, *J. Phys. Chem. C* **2013**, *117*, 8072 – 8078.

[54] For a review of polymers containing furan units, see: B. C. Streifel, J. D. Tovar, *Encyclopedia of Polymer Science and Technology*, Wiley, Hoboken, **2013**, DOI: 10.1002/0471440264.pst578.

[55] C. H. Woo, P. M. Beaujuge, T. W. Holcombe, O. P. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2010**, *132*, 15547 – 15549.

[56] J. C. Bijleveld, B. P. Karsten, G. J. M. Simon, M. M. Wienk, D. M. de Leeuw, R. A. Janssen, *J. Mater. Chem.* **2011**, *21*, 1600 – 1606.

[57] Additional works demonstrating the use of furan-containing polymers for OFETs and solar cells were recently published: a) L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K. C. Cha, Y. He, G. Li, Y. Yang, *J. Am. Chem. Soc.* **2012**, *134*, 10071 – 10079; b) Y. Li, P. Sonar, S. P. Singh, W. Zeng, M. S. Soh, *J. Mater. Chem.* **2011**, *21*, 10829; c) S. Qu, B. Wang, F. Guo, J. Li, W. Wu, C. Kong, Y. Long, J. Hua, *Dyes Pigm.* **2012**, *92*, 1384 – 1393; d) P. Sonar, S. P. Singh, E. L. Williams, Y. Li, M. S. Soh, A. Dodabalapur, *J. Mater. Chem.* **2012**, *22*, 4425 – 4435.

[58] Electrochromic devices of bifuran-containing polymers were also reported: a) M. Icli-Ozkut, H. Ipek, B. Karabay, A. Cihaner, A. M. Onal, *Polym. Chem.* **2013**, *4*, 2457 – 2463; b) N. Akbaşoğlu, A. Balan, D. Baran, A. Cirpan, L. Toppare, *J. Polym. Sci. Part A* **2010**, *48*, 5603 – 5610.

[59] a) S. Kaur, N. J. Findlay, F. C. Coomer, R. Berridge, P. J. Skabara, *Macromol. Rapid Commun.* **2013**, *34*, 1330 – 1334; b) For review on polyfurans see: M. J. González-Tejera, E. S. de La Blanca, I. Carrillo, *Synth. Met.* **2008**, *158*, 165 – 189.

[60] C. Videlot-Ackermann, H. Brisset, J. Ackermann, J. Zhang, P. Raynal, F. Fages, G. H. Mehl, T. Tnanisawa, N. Yoshimoto, *Org. Electron.* **2008**, *9*, 591 – 601.

[61] Fused acenofurans were studied with respect to their FET properties. For recent examples, see: a) M. Nakano, H. Mori, S. Shinamura, K. Takimiya, *Chem. Mater.* **2012**, *24*, 190; b) K. Niimi, H. Mori, E. Miyazaki, I. Osaka, H. Kakizoe, K. Takimiya, C. Adachi, *Chem. Commun.* **2012**, *48*, 5892 – 5894.

[62] P. Sonar, T. R. B. Foong, S. P. Singh, Y. Li, A. Dodabalapur, *Chem. Commun.* **2012**, *48*, 8383 – 8385.

[63] C. Hu, Z. Wu, K. Cao, B. Sun, Q. Zhang, *Polymer* **2013**, *54*, 1098 – 1105.