Extended Thienylenevinylene Oligomers as Highly Efficient Molecular Wires**

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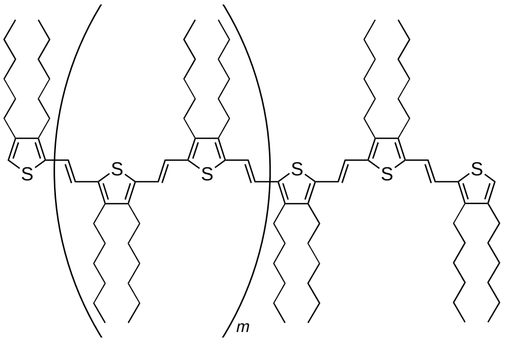
Linear π-conjugated oligomers with a well-defined chemical structure have been intensively investigated to simulate the electronic and electrochemical properties of the corresponding polydisperse polymers.[1] More recently, their possible use as molecular wires in molecular electronics or nanoscopic systems has attracted particular attention.[2] Although most of the work in these two areas has involved oligomers of intermediate chain length ($n = 2-10$),[1, 2] the synthesis of highly extended π-conjugated oligomers is of crucial importance for several reasons. On one hand, the use of π-conjugated oligomers as molecular wires in nanoscopic systems requires dimensions approaching the *present limit of nanopatterning techniques (namely the 100 Å gap regime).[2c] On the other hand, as the oligomeric model postulates that the properties of an oligomer series would approach those of the polymer as chain length increases, the analysis of the ultimate electronic properties of highly extended systems should permit assessment of the relevance of the oligomeric model and/or give evidence of novel properties.*

The recently synthesized hexadecamers of the oligothiophenes,[3] oligo(phenylenethynylene)s [4] and oligo(thiophenethynylene)s[5] series are the longest clearly characterized linear π-conjugated systems. Although the size of these molecules (65–120 Å) make them potentially interesting as molecular wires, these various classes of oligomers show a rapid saturation of effective conjugation with chain extension. In other words, the ultimate values of the oxidation potential and HOMO–LUMO gap are attained far before the maximum chain length (at $n = 10-12$ for oligothiophenes[1, 3] and $n = 8$ for oligo(phenylenethynylene)s and oligo(thienylenethynylene)s).[4, 5] As this saturation originates from π-electron confinement related to structural factors such as rotational disorder or resonance stabilization energy of the aromatic ring,[6] oligomeric systems in which such effects are minimized may even surpass the present limit.

Although the excellent electron transmission efficiency of oligo(thienylenevinylene)s (nTVs) has been demonstrated in nonlinear optical chromophores[7] or extended tetrathiafulvalene analogues,[8] this class of conjugated oligomers has been scarcely considered until now. nTVs up to $n = 7$ were first synthesized by Kossmehl et al. by a succession of formylation reactions and Wittig olefinations.[9] More recently a slightly different approach was reported by Nakayama et al.; however, the insolubility of nTVs did not allow the $n = 7$ limit to be surpassed.[10]

We recently described the synthesis of alkyl-substituted soluble nTVs.[11] The chain length dependence of the electrochemical and electronic properties gave no evidence of saturation up to the decamer ($n = 10$), but further chain extension was hampered by solubility problems.

We report here on the synthesis and characterization of novel soluble nTVs based on 3,4-dihexylthiophene (**2a**, **4a**, **6a**, **8a**, **12a**, and **16a**) and on the analysis of the chain length dependence of their electrochemical and electronic properties. Except for the dimer (**2a**) and tetramer (**4a**), all longer nTVs have been synthesized by twofold Wittig–Horner olefination of dicarbaldehydes with phosphonate **2e** (Scheme 1). Although McMurry dimerization[12] leads to doubling of the chain length at each iterative step,[10,11] we finally opted for the double Wittig–Horner route because of the increasing difficulty to achieve monoformylation selectively as the chain length increases.



6a, $m = 1$
8a, $m = 2$
12a, $m = 4$
16a, $m = 6$

Dithienylethylene **2a** was prepared by McMurry coupling of 3,4-dihexylthiophene carbaldehyde (**1b**). Mono- and dialdehydes **2b** and **2c** were prepared by Vilsmeier formylation of **2a** with appropriate amounts of reagents. McMurry coupling of **2b** yielded the tetramer **4a**, while the hexamer **6a** was prepared by double Wittig–Horner olefination of **2c** with **2e**. Vilsmeier bisformylation of **4a** and twofold Wittig–Horner olefination of the resulting dialdehyde (**4b**) gave the octamer **8a**. Repetition of this procedure yielded the dodecamer **12a** and hexadecamer **16a** (Table 1), which are the longest ever reported nTVs (70 and 94 sp^2 carbon atoms). Optimization of the geometry of **16a** by the MM+ method (Hyperchem 5.0) gave a chain length of 95 Å, in good agreement with the value estimated from the X-ray structure of the tetramer.[13]

Table 2 lists the main cyclic voltammetry (CV) data for nTVs. As expected, chain extension leads to a negative shift of the redox potentials and to an increase in the number of accessible redox states. Whereas the CV of **2a** shows a first anodic peak indicative of an irreversible process (the subsequent polymerization),[14] that of **4a** exhibits two well-defined reversible one-electron oxidation waves corresponding to the successive generation of the cation radical and dication ($E_{pa}1$ and $E_{pa}2$). Chain extension produces a decrease in the difference $E_{pa}2 - E_{pa}1$, indicative of a reduction of Coulombic repulsion between positive charges in the dication. Thus, for **6a** the two oxidation peaks are almost merged into a single wave, and a third peak corresponding to the generation

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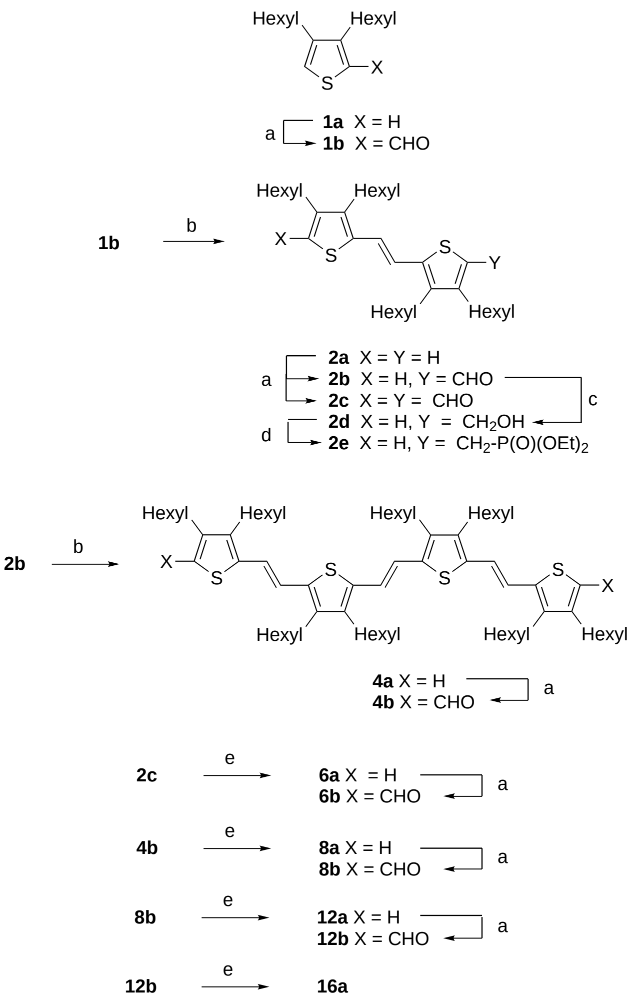

Scheme 1. a) $POCl_3$, DMF/1,2-dichloroethane, reflux; b) $TiCl_4$, Zn, THF, reflux; c) $NaBH_4$, CH_2Cl_2/methanol, room temperature; d) PBr_3, toluene/benzene, −10°C, then NaH, $HPO(OEt)_2$, THF, −10°C, then reflux; e) *t*BuOK, THF, 3 equiv **2e**, room temperature.

Table 1. Selected spectroscopic data for **4a**, **6a**, **8a**, **12a** and **16a**.

4a: Yield 86%, m.p. 76°C (decomp.), ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.99$ (s, 4H, outer C*H*=C*H*), 6.98 (s, 2H, central C*H*=C*H*), 6.76 (s, 2H, thioph.), 2.64–2.56 (m, 12H), 2.49 (t, 4H, $^3J = 7.7$ Hz), 1.63 (q, 4H, $^3J = 7.7$ Hz), 1.56–1.51 (m, 12H), 1.41–1.35 (m, 48H), 0.93–0.90 (m, 24H, CH_3). ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta = 143.41$, 141.48, 141.42, 139.99, 137.11, 134.99, 119.84, 119.37, 119.23, 117.90, 31.73, 31.58, 31.22, 31.18, 30.92, 29.63, 29.50, 29.36, 29.27, 29.02, 27.01, 26.88, 22.60, 14.14–14.07. MS(FAB): m/z (%) = 1081 (100) [M^+](calcd for $C_{70}H_{112}S_4$) = 1080.76. C,H,S analysis (calcd): C 77.40 (77.71), H 10.69 (10.43); S 11.21 (11.85).

6a: Yield 84%, m.p. 134°C (decomp.), ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.00 (s 10H), 6.77 (s, 2H), 2.65–2.57 (m, 20H), 2.50 (t, 4H, $^3J = 7.7$ Hz), 1.63 (q, 4H, $^3J = 7.7$ Hz), 1.56–1.52 (m, 20H), 1.43–1.34 (m, 72H), 0.95–0.91 (m, 36H). MS(FAB): m/z (%) = 1634 (100) [$M+H^+$] (calcd for $C_{106}H_{168}S_6$) = 1633.14.

8a: Yield 64%, m.p. 171°C (decomp.), ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 6.99 (s, 14H), 6.76 (s, 2H), 2.61 (s, 28H) 2.50 (t, 4H, $^3J = 7.6$ Hz), 1.65–1.37 (m, 128H), 0.94–0.92 (m, 48H). MS(FAB): m/z(%) = 2186 (100) [$M+H^+$] (calcd for $C_{142}H_{224}S_8$) = 2185.53. C,H,S analysis (calcd): C 77.69 (77.96), H 10.25 (10.32), S 11.77 (11.72).

12a: Yield 55%, m.p. 224°C (decomp.), ^{1}H NMR (270 MHz, $CDCl_3$): $\delta =$ 7.03 (s, 22H), 6.79 (s, 2H), 2.64 (s, 44H), 2.52 (t, 4H, $^3J = 7.6$ Hz), 1.66–1.29 (m, 192H) 1.00–0.92 (m, 72H). MS(MALDI-TOF): m/z(%) = 3295.37 (100) [M^+] (calcd for $C_{214}H_{336}S_{12}$) = 3293.74. C,H,S analysis (calcd): C 77.79 (78.04), H 10.30(10.28), S 11.64 (11.68).

16a: Yield 30%, m.p. 250°C (decomp.), ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.00 (s, 30H), 6.77 (s, 2H), 2.62 (s, 60H), 2.50 (t, 4H, $^3J = 7.4$ Hz), 1.64–1.38 (m, 256H), 0.95 (s, 96H). MS(MALDI-TOF): m/z (%) = 4402.4 (100) [M^+] (calcd for $C_{286}H_{448}S_{16}$) = 4399.66. C,H,S analysis (calcd): C 77.58 (78.08), H 10.19 (10.26), S 11.42 (11.66).

Table 2. Cyclic voltammetry data for nTVs.[a]

<table>
<tr><th>Compd</th><th>$E_{pa}1$ [V]</th><th>$E_{pa}2$ [V]</th><th>$E_{pa}3$ [V]</th><th>$E_{pa}4$ [V]</th><th>$E_{pa}5$ [V]</th><th>$E_{pa}6$ [V]</th></tr>
<tr><td>**2a**</td><td>0.96</td><td>1.30</td><td></td><td></td><td></td><td></td></tr>
<tr><td>**4a**</td><td>0.59</td><td>0.79</td><td></td><td></td><td></td><td></td></tr>
<tr><td>**6a**</td><td>0.50</td><td>0.56</td><td>1.10</td><td></td><td></td><td></td></tr>
<tr><td>**8a**</td><td colspan="2">0.46</td><td>0.80</td><td>0.92</td><td></td><td></td></tr>
<tr><td>**12a**</td><td colspan="2">0.42</td><td colspan="2">0.59</td><td>0.97</td><td></td></tr>
<tr><td>**16a**</td><td colspan="2">0.40</td><td colspan="2">0.47</td><td>0.70</td><td>0.99</td></tr>
</table>

[a] 10^{-4} M substrate in 2×10^{-1} M Bu_4NPF_6/CH_2Cl_2; Pt electrodes; reference electrode: saturated calomel electrode (SCE); scan rate 100 mV s^{-1}.

of the trication radical appears at 1.10 V ($E_{pa}3$) (Figure 1). Coalescence of the two peaks occurs for **8a**, and the dication is formed directly through a two-electron transfer (as confirmed by the 30 mV difference between $E_{pa}1$ and the potential of the corresponding cathodic peak). This two-electron wave is followed by two one-electron peaks assigned to the formation of the trication radical and tetracation ($E_{pa}3$ and $E_{pa}4$). Further chain extension to **12a** leads to the coalescence of $E_{pa}3$ and $E_{pa}4$ and a new peak corresponding to the pentacation radical at 0.97 V ($E_{pa}5$). For **16a**, the CV shows two very close two-electron waves, a negative shift of $E_{pa}5$ to 0.70 V, and formation of the hexacation at 0.99 V ($E_{pa}6$). This general behavior is reminiscent of that reported by Heinze et al. for the reduction of oligo(phenylenevinylene)s.[15]

These results are summarized by the diagram in Figure 2 in which the potential of formation of the various cationic states are plotted against the number of carbons in the conjugated chain (n). The two first convergence points at $n = 46$ and $n = 70$ correspond to the first and second bielectronic transfers $E_{pa}1$ and $E_{pa}2$ (**8a**) and $E_{pa}3$ and $E_{pa}4$ (**12a**). Extrapolation of this series of lines suggests a common convergence limit beyond $n = 120–130$. This hypothetical convergence point should correspond to the single-step multi-electron oxidation of the whole conjugated chain through a process ressembling the p-doping of the parent polythienylenevinylene (PTV).[16b]

The main optical data listed in Table 3 show that chain extension leads to an increase of the molecular extinction coefficient (ε), to a red shift of λ_{max}, and to a narrowing of the HOMO–LUMO gap as reflected by the long-wavelength absorption edge (λ_{edge}).[17] Comparison of the optical data for **16a** with those for hexadecamers with the same n value and similar or even larger dimensions such as hexadeca-1,4-phenylenethynylene (128 Å, $\lambda_{max} = 376$ nm)[4] and hexadecathiophenethynylene (100 Å, $\lambda_{max} = 442$ nm, $\varepsilon = 210000$)[5] clearly shows that **16a** exhibits the largest effective conjugation.

Although the band gap of solution-processed films of the octamer derived from 3-octylthiophene (1.70 eV)[11] is already slightly smaller than that of PTV (1.70–1.80 eV),[16] the optical data for **12a** and **16a** suggests that they should exhibit

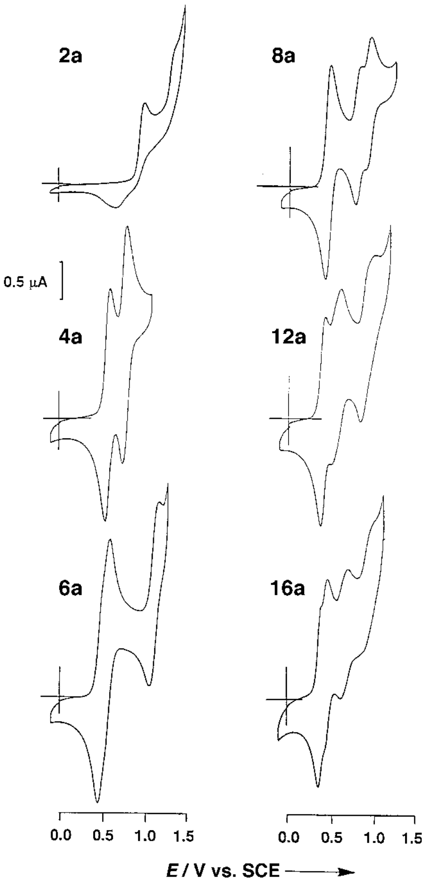

Figure 1. Cyclic voltammograms of *n*TVs. For experimental conditions see footnote [a] of Table 2.

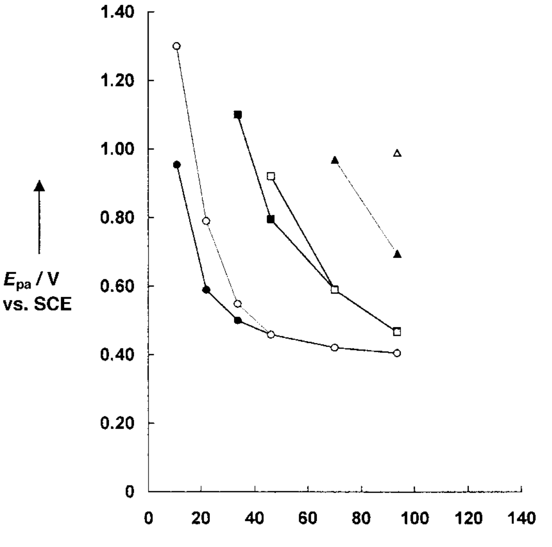

Figure 2. Anodic peak potential of the various oxidation steps for *n*TVs plotted against the number *n* of carbon atoms in the conjugated system. ●: radical cation; ○: dication; ■: radical trication; □: tetracation; ▲: radical pentacation; △: hexacation.

Table 3. UV/Vis absorption data for *n*TVs in CH_2Cl_2.

Compd	λ_{max} [nm]	λ_{edge} [nm]	ε_{max} [$L\,mol^{-1}\,cm^{-1}$]
2a	360	399	18000
4a	489	552	69500
6a	548	624	109000
8a	574	657	156000
12a	595	679	206000
16a	601	685	319000

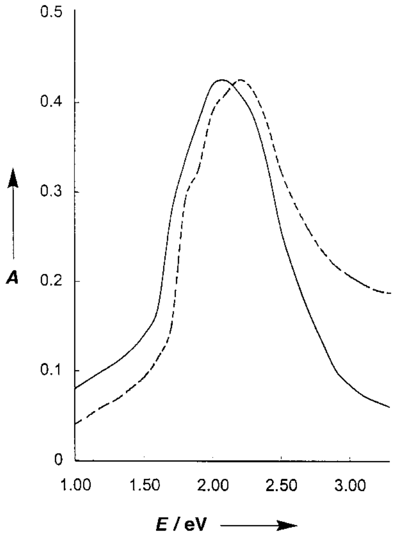

Figure 3. UV/Vis absorption spectra of films of **12a** (dashed line) and **16a** (solid line) cast on glass from a CH_2Cl_2 solution.

even smaller band gaps. This is confirmed by the solid-state optical spectra of solution-cast films of **12a** and **16a** (Figure 3). Whereas the persistence of the vibronic fine structure is consistent with a well-ordered material, the low-energy absorption edge leads to estimated band gaps of 1.65 and 1.55 eV for **12a** and **16a**, respectively. The 0.10 eV red shift of the absorption edge between **12a** and **16a** seems to indicate that in the solid state, saturation of the effective conjugation has not yet been reached for **16a.** This suggests possible further band gap reduction for longer oligomers.

As already discussed, all series of π-conjugated oligomers investigated so far exhibit saturation of effective conjugation for a certain chain length, which depends on the structure.[1, 3–6] The *n* value of the limit of the HOMO–LUMO gap and the band gap thus represents a measure of the relative efficiency of a given oligomeric system for use as molecular wires. Since nTVs exhibit the highest increase of effective conjugation per incremental carbon and the smallest gap among known π-conjugated oligomers, they are at present the most efficient extended molecular wires.

The trends in electrochemical and optical data on extension of the chain length and the indication that the saturation limit has not been reached yet provide a strong inducement to pursue chain extension: the synthesis of the higher oligomers up to the 20- to 25-mers is an urgent and exciting goal.

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[17] In several works including our previous communication[11] the gap was determined from the very onset of absorption (see R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *J. Org. Chem.* **1993**, *58*, 904; T. A. Chen, R. Rieke, *Synth. Met.* **1993**, *60*, 175). Since this procedure leads to rather large uncertainties, extrapolation of the absorption edge to zero was used here, although this procedure leads to larger values.

Deprotonated 2,3:5,6-Dibenzo-7-aza bicyclo[2.2.1]hepta-2,5-diene as a Nitrido Nitrogen Source by Anthracene Elimination: Synthesis of an Iodide(nitride)chromium(VI) Complex**

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Nitrides constitute an important class of compounds in both solid-state [1, 2] and solution chemistries.[3] A common synthon for the six valence electron N^- ion, which is isoelectronic to an oxygen atom, is the ubiquitous azide ion.[3] Typifying the formation of a nitride from an azide is the classic synthesis of $[Mo(N)(Cl)_3(bpy)]$.[4] Generation of the nitrido functionality from an azide requires a source of two electrons. Therefore, successful syntheses are typically encountered when a d^n ($n \geq 2$) metal center is employed, and the nitride product has a d^{n-2} configuration. Oxidation of the metal center occurs concomitant with dinitrogen expulsion. However, azide is not always optimal for nitride introduction due to a) the explosive nature of many of its compounds, b) the low solubility in nonpolar solvents of salts such as sodium azide, or c) the lack of steric protection which can lead to multiple or unselective substitutions.

In connection with recent investigations of chromium(VI) organometallic chemistry [5, 6] we required the iodide–nitride complex $[Cr(I)(N)(NRAr_F)_2]$ ($R = C(CD_3)_2CH_3$, $Ar_F = 2,5\text{-}C_6H_3FMe$). Attempts to synthesize the compound from the corresponding azide were unsuccessful. Although the corresponding nitrosyl derivative $[Cr(I)(NO)\text{-}(NRAr_F)_2]$ has been prepared,[7] attempts to deoxygenate it with vanadium(III) [5] have been unsuccessful, a circumstance attributable to the presence of a reactive iodide functionality. Here we describe the successful synthesis of $[Cr(I)(N)(NRAr_F)_2]$ by the reaction of d^2-$[Cr(I)_2(NRAr_F)_2]$ with $[Li(dbabh)(OEt_2)]$, where Hdbabh is 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene).[8] This chemistry shows that Hdbabh can be considered an organic analogue of hydrazoic acid in the context of transition metal nitride chemistry.

The amine Hdbabh was prepared by the literature method,[8] and treated with *n*-butyllithium to form $[Li(dbabh)(OEt_2)]$. The chromium(IV) precursor $[Cr(I)_2(NRAr_F)_2]$ was obtained in 82% yield as a black solid following treatment of $[Cr(NRAr_F)_3]$ [5] with iodine. Treatment of $[Cr(I)_2(NRAr_F)_2]$ with of $[Li(dbabh)(OEt_2)]$ in ether elicited a color change to redbrown and ultimately produced diamagnetic [Cr(I)(N)-

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